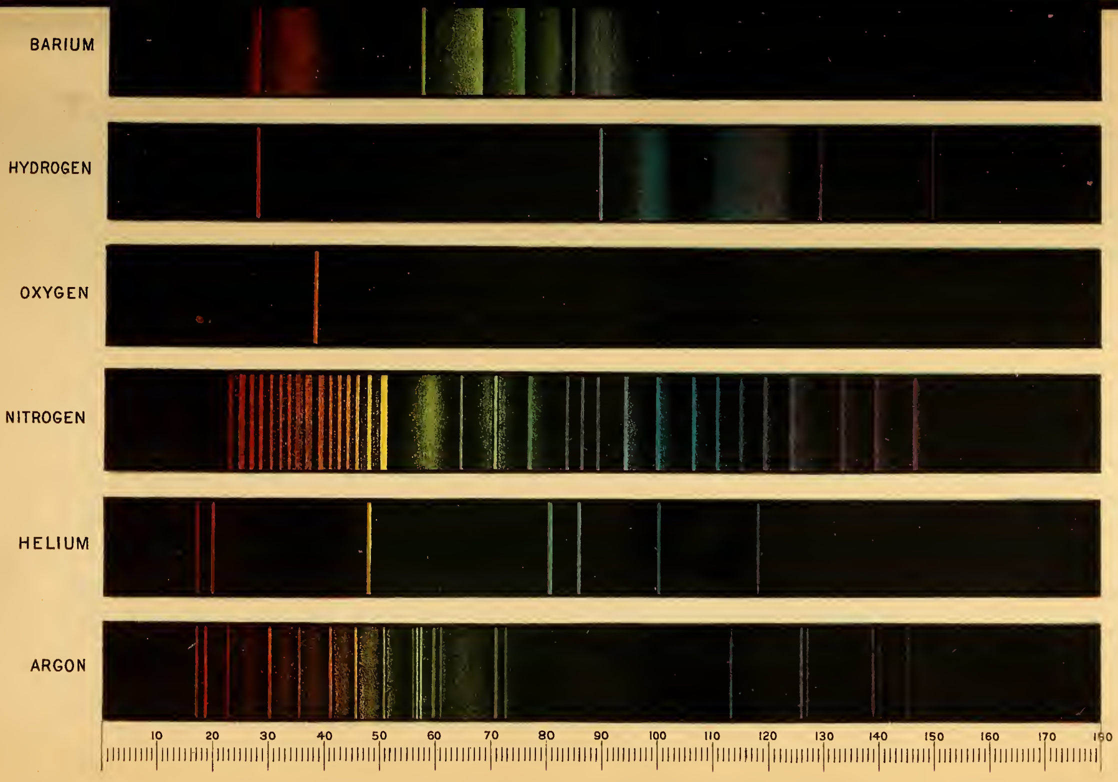
ELEMENTS OF MODERN CHEMISTRY.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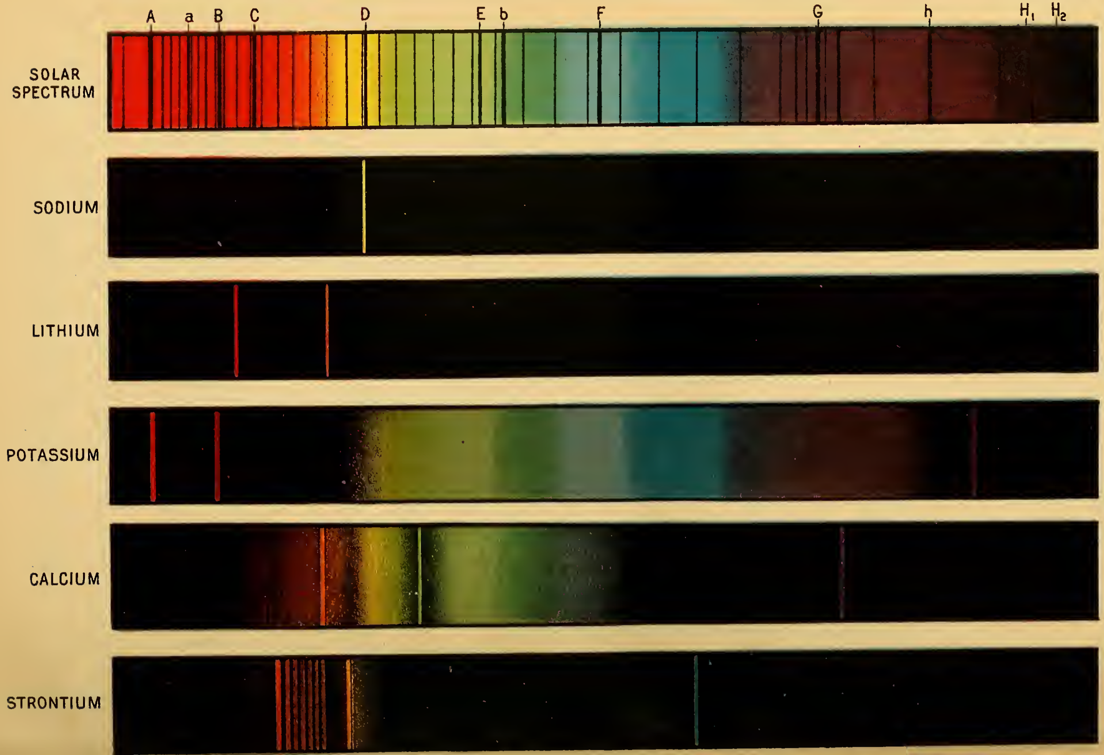

ELEMENTS

OF

MODERN CHEMISTRY.

BY CHARLES ADOLPHE WURTZ.

SIXTH AMERICAN EDITION.

REVISED AND ENLARGED BY
WM. H. GREENE, M.D.,
AND
HARRY F. KELLER, PH.D. (STRASBURG).

WITH A PORTRAIT OF THE AUTHOR AND NUMEROUS ILLUSTRATIONS.

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BIOGRAPHICAL SKETCH.

Charles Adolphe Wurtz, the most illustrious French chemist of the latter half of the nineteenth century, was born at Strasburg, November 26, 1817, and died at Paris, May 12, 1884.

Early in life his tastes led him to scientific studies, and he became a student of medicine under the Faculty of Medicine of Strasburg, in which he was appointed Director of Chemistry in 1839. After acquiring the degree of Doctor of Medicine, he continued his chemical studies under the direction of that foremost of chemical teachers, Liebig, at Giessen: here he became intimately associated with such men as Strecker, Will, Fresenius, Hofmann, and Hermann Kopp, many of whom were destined later to make world-wide reputations in the same field with himself.

In 1844 he removed to Paris, entering the laboratory of the celebrated Dumas, to whom he became assistant the following year. Besides this position, he filled that of Director of Chemistry in the Ecole Centrale des Arts et Manufactures from 1845 to 1850, and in 1847 was chosen Professor agregé at the Paris Ecole de Médecine, in which he became Professor of Chemistry in 1853, retaining this post until his death. In 1866 he was chosen Dean of the Faculty, at that time troubled by political dissensions which his tact and judgment were well adapted to calm. He took advantage of his administrative position to strengthen and improve the scientific lines of the curriculum, and when he resigned the deanship, in 1874, he had succeeded in establishing a Chair of Organic Chemistry in the Sorbonne and a laboratory of Biological Chemistry in the Medical School.

In 1858, Wurtz founded the Société Chimique de Paris, to which he presented many of his papers. In 1867 he was made a member of the Academy of Sciences (Institute de France), and was chosen president of the same in 1880.

He was a brilliant and lucid teacher, an eloquent speaker, and he possessed in a remarkable degree the faculty of inspiring his audiences with his own enthusiasm.

Wurtz's chemical work was accomplished with very modest experimental means, and his aim was always rather to simplify than to complicate. His main researches were undertaken with the object of developing the atomic theory, then just beginning to be understood, and while these works covered an extensive field, they are, as A. W. Hofmann has well expressed it, " linked together like the pearls of a necklace." His results led him to support enthusiastically the theory of which he became the greatest if not the first champion in France.

The best known of Wurtz's writings are his " Atomic Theory," published in the International Scientific Series, his " Elementary Lessons," and his " Dictionnaire de Chimie," published with the collaboration of a number of eminent French chemists. He also wrote a Medical and Biological Chemistry in three volumes.

Among the more important of his chemical researches were those on the constitution of the acids of phosphorus, on the cyanuric ethers, compound ammonias, ureas, amides, and glycerol; in the course of these he discovered the glycols, oxide of ethylene, aldol and paraldol, and hydride of copper, as well as the correct explanation of certain interesting cases of anomalous vapor density.

AUTHOR'S PREFACE

TO THE

FIRST AMERICAN EDITION.

This book is translated from the fourth French edition by my pupil and friend, M. Greene, whose perfect familiarity with the French language and thorough competence, at the same time, in chemistry I have had occasion to appreciate. The translation is, then, a faithful, or even improved, representation of the original work, in which he will certainly have detected and corrected some faults.

The French editions succeed each other rapidly, showing that this little book responds to an educational need.

It has been the endeavor to keep it up with the current of the latest discoveries, and in it to condense a considerable number of exact and well-selected facts, without banishing the theory which binds them together. Thus, the origin and foundation of the atomic theory have been given, as far as possible, in historical order. The notions concerning atomicity, so important for the appreciation of the structure of combinations and for the interpretation of chemical reactions, are presented in an elementary form.

The reader will remark that the history of the metalloids is relatively more developed than the remainder of the book. Indeed, this is the fundamental part of chemistry, and a familiar knowledge of it is indispensable to the fruitful study of the metals and of organic chemistry. It is also the most attractive portion for beginners, for it is the most easily understood.

Immediately on entering the immense domain of organic chemistry, we find the facts overwhelmingly numerous and complicated. Among all these facts a severe and careful choice has been made, the historical importance and the theoretical and practical interest of the compounds described being borne in mind. In this respect many additions have been made to the third French edition. Thus, the question of isomerism, upon which the theory of atomicity has thrown so much light, has been treated in a more thorough manner. The chapter on the aromatic compounds has been considerably augmented.

The author hopes that these "Elementary Lessons" will be well received by the new public to whom they are presented, and that they will contribute to render attractive and diffuse the knowledge of the science to which he has devoted his life.

ADOLPHE WURTZ.

PARIS, November 20, 1878.

The progress of the science has made necessary many changes in the fifth edition of this little book, which has so far retained about the form and scope given to it fifteen years ago. It has been deemed advisable to complete the organic portion, and a large number of additions and corrections have been made. Whole chapters have been added to the history of the cyanogen compounds, the hydrocarbons, the acids, and the aromatic compounds. Among these will be particularly noticed the articles on isomerism, the azoic and diazoic compounds, and the pyridic bases, subjects which have acquired great importance during the last few years.

PARIS, 15th September, 1883.

PREFACE TO NEW EDITION.

THE considerations which guided the American editors in the preparation of the fifth edition, have been followed also in the revising of the book for this new edition. Besides making numerous corrections and additions which were rendered necessary by the rapid advance of the science, the editor has endeavored to eliminate terms and symbols which are no longer generally current, or which betray the French origin of the work. A new chart showing the spectra of the principal gaseous elements, as well as those of metals, is substituted for that found in the former editions.

H. F. K.

PHILADELPHIA, September 15, 1900.

PREFACE.

SIXTEEN years ago this translation of Wurtz's "Leçons élémentaires de Chimie Moderne" was first presented to the public by one of the present editors. The hearty favor with which the book was received by American and English chemists, and the fact that it has now undergone the fifth revision, are sufficient indications of its usefulness.

In the preparation of the present edition, the aim has been to preserve as nearly as possible the original plan and character of the work, but at the same time to make such changes as will entitle it to continue to rank as a truly modern text-book. In order that this might be accomplished with the least possible enlargement, some matters of minor importance in an elementary treatise have been omitted, and the new matter which has been introduced will, it is believed, be found to include the latest developments of the science.

A number of the original illustrations have been replaced by more modern designs, but in not a few instances it has been deemed desirable to retain cuts, which, while they do not represent the newest forms of apparatus, are yet of great historical value in illustrating the development of chemical experimentation.

To meet numerous requests, mention has been made of many matters that are of special interest to the student of medical chemistry.

W. H. G.
H. F. K.

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ELEMENTS OF MODERN CHEMISTRY.

INTRODUCTION.

THE material objects surrounding us present striking and infinite differences. Sulphur is readily distinguished from charcoal, rock-crystal from flint, iron from copper, water from spirit of wine, and wood from ivory. It is known to all that these bodies differ not only in form, density, and structure, but also in their proper substance. They differ, too, in the changes through which they pass under the same conditions. When subjected to the action of heat they receive very differently the impression of that force. They become heated more or less quickly, and transmit the heat with greater or less rapidity throughout their own substance. A short bar of iron cannot be grasped in the hand by one extremity if the other be heated to redness; under the same conditions a cylinder of charcoal may be handled with impunity. Communicate sufficient heat to water and it is converted into steam; remove heat from it, and if the cooling be sufficient, it is frozen into ice. Spirit of wine requires less heat to become vaporized, and extreme cold to congeal it. If a magnet be placed among iron filings, they attach themselves in tufts around the two poles; on the contrary, copper filings are indifferent to the magnetic attraction.

Rock-crystal is transparent to light; flint is opaque. These two bodies are unalterable by fire. They may be heated to redness in a furnace, but after the temperature has abated they will be found with their original characters unchanged. It is very different with the coal which we burn in our grates. This body disappears during the combustion, and leaves only a quantity of ashes. But it has not been destroyed, and its substance is found in entirety in a certain gas produced by the combustion. Like charcoal, sulphur is combustible, and is converted by burning into a gas, the suffocating odor of which is well known.

Neither sulphur nor charcoal undergo any alteration when exposed to damp air; it is not the same with iron. In a moist atmosphere this metal experiences a striking and lasting change. Its surface becomes covered with rust and is no longer iron.

In the forests, the leaves which fall and remain upon the moist soil are slowly consumed and disappear in the course of seasons.

All of these changes, these phenomena, take place daily before our eyes, and are familiar to all of us. On comparison, striking differences are discovered between them: some are but passing, and do not affect the proper nature of the body. They are the results of forces which act at sensible distances, and which leave the body in its primitive state as soon as their action has ceased. A piece of soft iron is attracted by the magnet before contact is established, and when under the magnetic influence, is capable of attracting other soft iron in its turn: the action of the magnet has made the iron itself magnetic, but it immediately loses this property when the magnet is withdrawn; and further, this momentary change in property has brought about no alteration in the intimate nature of the iron. It is found after the experiment in precisely the same condition as before.

In the same manner, rock-crystal undergoes no change in its specific identity by the passage of a ray of light. Withdraw from the vapor of water the heat which has been communicated to it, and the liquid water is recovered with all its properties. Restore to the ice the heat which was abstracted in its formation, and water is regenerated as before. This is characteristic of the changes produced by *physical forces.* Under the influence of such forces, bodies experience modifications more or less profound, more or less lasting, but which never affect their specific nature.

But the iron which rusts undergoes a complete and lasting change in its properties and in its substance. The rust is no longer iron, and vainly would it be sought to isolate the metal by mechanical means, or to discover its presence by the aid of the most powerful microscopes. The metal has disappeared as such; it has undergone a complete transformation; it has become another body. It has attracted one of the elements of the air, oxygen, and has, moreover, fixed to itself the moisture of the atmosphere. These latter bodies, which differ from iron in substance, have intimately united with the metal itself, and the result of this union, of this *combination* as it is called, is a new body, rust or hydrated oxide of iron. In this case the alteration is profound, the change is lasting; the specific nature of the body is affected. This is characteristic of *chemical action.*

In the same manner, when the charcoal and the sulphur are burned in the air, they attract oxygen and combine with it, forming two new bodies that are called carbonic and sulphurous acids.

These phenomena may be rendered more clear by simple and well-known experiments.

Experiment 1.—A globe (Fig. 1) is filled with oxygen, a gas which constitutes one of the elements of the atmosphere, and which is eminently fitted to support combustion; into it is plunged a morsel of charcoal lighted at one end; immediately the coal glows with a brilliant light, the combination takes place actively, and the charcoal is rapidly consumed. But presently the light becomes paler, the combustion ceases, and the charcoal is extinguished. The oxygen is now nearly or quite consumed, and the globe is filled with another gas which is no longer oxygen, although it contains that oxygen. It contains also the matter of the charcoal which has disappeared, and these two bodies have combined to form a new body, which is carbonic acid. This latter will not support combustion, but, on the contrary, it extinguishes burning bodies. It is then a body having entirely new properties, and is formed by a chemical action.

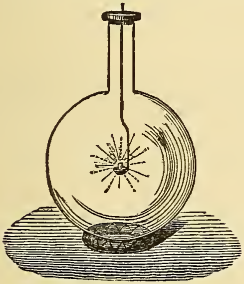


FIG. 1.

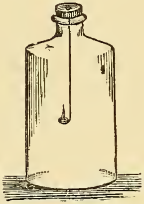


FIG. 2.

Experiment 2.—Into another jar filled with oxygen (Fig. 2) is plunged a spoon containing ignited sulphur. The combustion takes place with a beautiful blue flame, and in burning in the oxygen with so much energy, the sulphur unites with the gas and forms with it a new body, which is called anhydrous sulphurous acid. It is a suffocating gas, which extinguishes flame. It reddens, and afterwards bleaches, a solution of blue litmus poured into the jar. These are special properties which do not belong to the oxygen at first contained in the jar. They characterize a new body, the result of the combination of the sulphur with the oxygen, and formed by chemical action.

Carbon, sulphur, and oxygen are *simple bodies* or *elements.* They are so called because from neither of them can more than one kind of matter be obtained. But when the charcoal in burning unites with the oxygen, the carbonic acid which results from the union contains two kinds of matter,—carbon and oxygen; and these two elements are united in such an intimate manner that the body which contains both does not resemble either carbon or oxygen: it is endowed with new properties which do not in any manner recall those of the elements which constitute it. In fact, it is a new substance, a *compound body* formed by the combination of the matter of the charcoal with the matter of the oxygen.

Considering the preceding facts, we may give to chemistry the following definition: chemistry studies those intimate actions of bodies upon each other which modify their natures and cause a complete and lasting change in their properties.

Iron may be reduced to a fine powder. This may be mixed with sulphur itself reduced to powder, and if the mixture be sufficiently intimate, it will present neither the lemon-yellow color of sulphur nor the gray-black of finely-divided iron. Nevertheless, a homogeneous substance cannot be formed in this manner. If the powder be examined under the microscope, the particles of iron may be recognized disseminated among those of the sulphur, but the two are not merged together. By the aid of a magnet the iron may be separated. On the other hand, if the mass be thrown into water, the particles of iron will sink first to the bottom, while the lighter particles of sulphur remain in suspension. Thus, after having triturated the sulphur and iron together, not only can each substance be recognized in the mass, but they can be again separated by mechanical means. Here there has been no chemical action, but simply a *mixture.* If, however, this mixture be heated, the sulphur will first be seen to melt, and afterwards the whole mass will blacken and enter into fusion if the temperature be sufficiently elevated. After cooling, it is perfectly homogeneous, and neither iron nor sulphur can be recognized. Both have disappeared as such, and in their place is found a substance having new properties; it is the sulphide of iron.

They have disappeared, but their substance is not lost; and it may be proved by experiment that the weight of the sulphide of iron produced is exactly equal to the sum of the weights of the iron and the sulphur. The ponderable matter of the iron is then added to the ponderable matter of the sulphur, and has formed with it a union so intimate that there results a new body, the smallest particles of which are perfectly similar to each other and to the entire mass. This example and a thousand others that might be given prove that when bodies combine there is neither loss nor creation of matter. The result of the combination, that is, the compound body, contains the whole of the substance and nothing more than the substance of the combining bodies. This is an essential characteristic of chemical combination.

The force which determines chemical combination is called *affinity*. It is important that this force be distinguished from another which is often opposed to it, and which is *cohesion*.

In order to reduce to powder a solid substance, such as pyrites or sulphide of iron, it is necessary to overcome the resistance opposed by the particles of the mass to their separation. This resistance is due to a special force, which brings and maintains in relation to each other the homogeneous particles of the sulphide of iron, as indeed of all solid bodies. This is cohesion. The particles which are bound together by this force are not only those minute particles which are visible to the naked eye or under the microscope, and of which the most impalpable powder of a solid body is composed. Such particles still present a magnitude that can be measured; they must be considered as little masses, so to speak, indivisible by the mechanical means at our command, but formed in reality of particles still smaller. These smallest particles of a solid body which are bound by cohesion are called *molecules*. They are not in immediate contact with each other. In a perfectly compact and homogeneous mass, such as sulphide of iron, the molecules do not touch each other. Between them exist spaces of considerable magnitude, compared to the real volume of the molecule. This idea must not be confused with that of porosity, which is caused by those accidental spaces which form visible pores in solid bodies. The intermolecular spaces are those which separate the molecules of a homogeneous and compact solid body, and physicists have further been led to believe that even in solid bodies the molecules are not perfectly immobile, but that they execute vibratory movements in the spaces which separate them, at the same time maintaining their own relative positions.

If a solid body be heated, a part of the heat is employed in raising the temperature, another part serves to increase the distances which separate the molecules: the body expands in becoming heated. But, as the distances between the molecules increase by the action of the heat and the effect of the expansion, the molecular attraction necessarily becomes more feeble. Cohesion is thus somewhat diminished, and if the heat be further increased, it may be so much diminished that the molecules, which have thus far been maintained in definite relations, can move and glide freely over each other; the solid body then enters into fusion: it becomes a liquid. The liquid state is produced by a diminution of cohesion, and is characterized by a greater mobility of the molecules.

But if the liquid body be still further heated, at a certain point the additional heat may produce such a separation of the molecules that, already freed from all mutual attraction, they become completely independent of each other. This is characteristic of the gaseous state.

It may be stated, then, that cohesion is considerable in solid bodies, but slightly energetic in liquids, and null in gases, and we have just seen that heat, by causing the changes of state of a body, can overcome and even practically abolish this physical force.

Chemical force or affinity is at the same time more intimate and more powerful. It modifies the molecules themselves. It brings heterogeneous substances into intimate relations, and thus produces new molecules. A consideration of the examples already cited may indicate more clearly the meaning of this important proposition.

We have brought together sulphur and iron, and by their reciprocal action and the aid of heat there has been formed a new body,—sulphide of iron. We know that the smallest mass of sulphur we can obtain is composed of a collection of perfectly homogeneous molecules, aggregated by cohesion. In each of them but one kind of matter can be found. It is the same with iron: the particles of this metal are perfectly homogeneous. Sulphur and iron are simple bodies or elements.

Let us now consider the sulphide of iron which results from their combination. This body also is formed of a collection of molecules, bound together by cohesion and perfectly similar to each other, but not homogeneous, for in each molecule we distinguish two kinds of matter,—sulphur and iron.

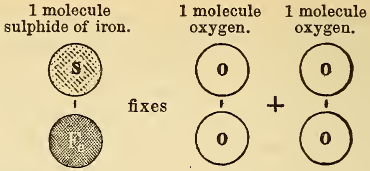
It cannot be admitted that these two substances are confounded in the molecule, or that the effect of the combination of sulphur with iron is an interpenetration of the two bodies so intimate that they both disappear in what might be called a homogeneous mixture. On the contrary, it is supposed that the combination results from the juxtaposition of two infinitely small masses, each of which possesses a real magnitude and a constant weight.

These little masses that no force, chemical or physical, can divide further, constitute the *atoms*. In each molecule of sulphide of iron there exist two of these masses,—one of sulphur and one of iron; and the atom of sulphur and the atom of iron are united, but not merged together, by chemical force. And when sulphur combines with iron it is because the atoms of the sulphur arrange themselves in juxtaposition with those of the iron, and it is affinity which brings about the action.

When these atoms again separate, the sulphide of iron is said to *decompose*. When it attracts the atoms of another body, it is said to combine with that body.

If sulphide of iron remain for some time exposed to moist air, its surface becomes covered with an efflorescence formed of a saline matter. In this case it has attracted one of the elements of the air, oxygen, with which it has combined to form green vitriol or sulphate of iron.

As we shall see later on, we have reason to believe that the molecules of oxygen gas are each formed of two atoms, but these atoms are of the same kind; the molecules of sulphide of iron, on the contrary, are each formed of two unlike atoms, —one of sulphur and one of iron. These attract four atoms of oxygen, which constitute two molecules of that gas, which group themselves around the atom of sulphur and the atom of iron, forming with them one single molecule, more complex than the original molecule of sulphide of iron, for it contains in addition four atoms of oxygen.



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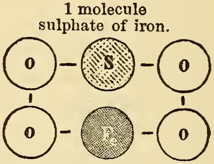


It is seen from what precedes that the words molecule and atom are far from being synonyms. The chemical molecule constitutes a whole of which the atoms form the parts, and these atoms are held together by affinity. In the preceding figure, this exchange of affinities between the atoms is indicated by lines of union.

Chemical molecules have been well compared to edifices: the atoms constitute the materials, and it is readily conceived that such molecular edifices differ from each other according to the nature, number, and arrangement of the atoms, that is, the materials composing them.

An edifice may be enlarged by the addition of new parts: it may be reduced in size or it may be entirely demolished. In the same manner a chemical molecule may be increased by the annexation of new atoms, or diminished by the separation of some of those which it already contains. In the first case there is combination, in the second, decomposition.

We may still further consider these phenomena of combination and decomposition.

Since the combination of two bodies results from the reciprocal action of their atoms, and has for effect a change in the nature of the molecules, it is evident that it can only take place when these atoms, and consequently the molecules, are brought into intimate relations; or more precisely, when the molecules of one of the bodies enter within the sphere of action of the molecules of the other body. And this sphere of action is very limited, for the affinity or elective attraction of the atoms is only exercised at infinitely small distances, In consequence affinity is often retarded by cohesion, which maintains the relations between the molecules of a solid body. These two forces are frequently in opposition, and that the first may attain the supremacy it is necessary that the other shall yield. To make manifest or to increase the affinity between two bodies, it is then necessary to diminish their cohesion. On this condition the molecules can enter within the spheres of their reciprocal attraction, and the atoms of one body can attract those of the other.

It has been seen from one of the experiments already cited that in order to combine iron with sulphur it is necessary to elevate the temperature. Now, the heat, by fusing the sulphur, diminishes its cohesion, and, giving its molecules freedom of motion, puts them into more intimate contact with those of the iron. Chemical action then commences.

Instead of heating the sulphur and iron to bring about chemical action, it would be sufficient to moisten the mixture with water. By the intervention of this liquid the particles of sulphur and of iron are, as it were, cemented together and thus brought into more intimate relations. For a stronger reason can chemical action between two solids be facilitated by dissolving them both in water and mixing the solutions. Dissolved, they themselves assume the liquid state and lose, in great part, their cohesion. The ancients understood the influence of the liquid state upon reactions, and stated it with exaggeration: *Corpora non agunt nisi soluta.*

Although the liquid state facilitates chemical reactions, it does not follow that it always determines them. Frequently liquids and even gases, after being mixed, must be heated before they will react upon each other.

Experiment.—In a glass tube (Fig. 3) two gases, oxygen and hydrogen, are mixed in the proportion of one volume of the first to two of the second. Although the mixture is perfectly homogeneous and very intimate, and although the cohesion of the gaseous molecules is null, no action takes place. But as soon as the mixture is heated by approaching a lighted taper to the mouth of the tube, combination takes place energetically. An explosion occurs and the two gases unite, forming water. In this case the heat has determined combination by increasing the intensity of the movements which animate the molecules of each gas, and so bringing the molecules of the one within the sphere of attraction of those of the other.

The electric spark produces the same effect, and it probably acts by the heat which it communicates to the mixture.

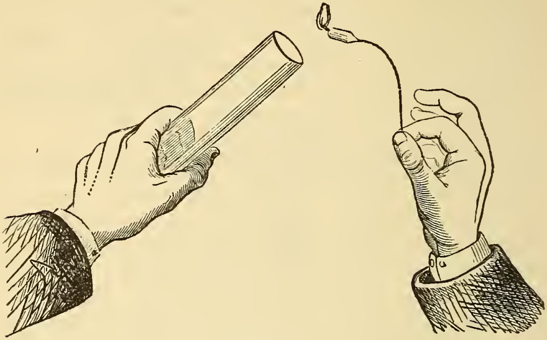


FIG. 3.

More rarely combination is brought about by the influence of light.

If a small bottle be filled with a mixture of equal volumes of hydrogen and chlorine gases, and then thrown into the air so that it may be struck by the direct rays of the sun, the combination of the two gases takes place instantly and with explosion.

Such are some of the conditions which favor or determine chemical combination. Let us now study the circumstances which accompany these phenomena.

Experiment.—If sulphur be strongly heated in a small glass flask until it begins to boil, and some copper turnings be then thrown into the flask, a brilliant incandescence takes place immediately. It is produced by the combination of the two bodies. Charcoal, sulphur, and phosphorus produce a brilliant light when they are burned in oxygen. Their combination with the gas takes place with evolution of light and heat.

When any combustible body whatsoever is burned in the air, the heat and light are developed by the combination of the body with oxygen, one of the elements of the air. In general, all chemical combinations give rise to the production of heat, more or less intense; in many cases it is accompanied by light; sometimes it is scarcely perceptible.

While heat acts as the determining cause of a great number of combinations, and while it is the result of such combination, it may play still another rôle in chemical reactions. In place of favoring combination, it may act in the opposite manner, separating atoms which are united by chemical attraction.

Mercury retains indefinitely its brilliant surface when exposed to the air at ordinary temperatures, but at a temperature near its boiling-point it slowly attracts the oxygen of the air, and becomes covered with an orange-red powder, which is oxide of mercury. In this case heat has assisted the formation of a compound.

If, however, this red powder be heated in a small retort to a temperature near redness, it is again resolved into mercury, which appears in drops in the neck of the retort, and into oxygen which may be collected.

In this case an intense heat breaks up the compound which is formed at a temperature less elevated; it occasions a *decomposition.*

Heat acts thus in a great number of cases. A body is said to decompose when the elements composing it are separated from each other.

The electric spark may occasion such separation when it is passed through compound gases. If a series of electric discharges be passed through ammonia gas, the latter is *decomposed*, that is, resolved into its two elements,—nitrogen and hydrogen.

In like manner, the current of the voltaic pile decomposes a great number of chemical compounds, the elements of which separate and appear, each at its appropriate pole of the battery. The decomposing action exerted by the electric current upon chemical compounds was discovered about the commencement of the present century by Nicholson and Carlisle. These physicists were the first to decompose water by this agent.

Lastly, light may decompose certain bodies, among which are a great number of the compounds of silver. The art of photography is founded upon the decomposing action of light upon certain of these combinations.

There is another class of decompositions which it is important to consider with attention. They are occasioned by the intervention of more powerful affinities than those which maintain united the elements of a compound body.

If copper be heated in the air, it attracts oxygen and is converted into a black powder, a compound of oxygen and copper, which is called oxide of copper. The affinity which unites the two bodies is considerable; it cannot be overcome by the action of heat alone; at any ordinary temperature to which the oxide so formed may be exposed, the atoms of copper still remain intimately associated with those of the oxygen. But if this oxide be mixed with powdered charcoal and then heated, a moment arrives when the affinity of the charcoal for the oxygen is superior to that of the copper. The atoms of oxygen then abandon the copper and combine with the charcoal, thus forming a new compound, carbonic acid, which is disengaged in the form of gas. Here there is at the same time decomposition and combination. The molecules of oxide of copper are decomposed; those of carbonic acid are formed.

Nothing is created in combinations; nothing is lost in decompositions. In the preceding experiment only copper remains; the charcoal and oxygen have disappeared, but their substance is not lost. All of the matter of the charcoal is found combined with all of the matter of the oxygen in the product of their combination, the carbonic acid, in such a manner that the weight of the latter added to the weight of the copper remaining, exactly represents the weight of the oxide of copper and charcoal.

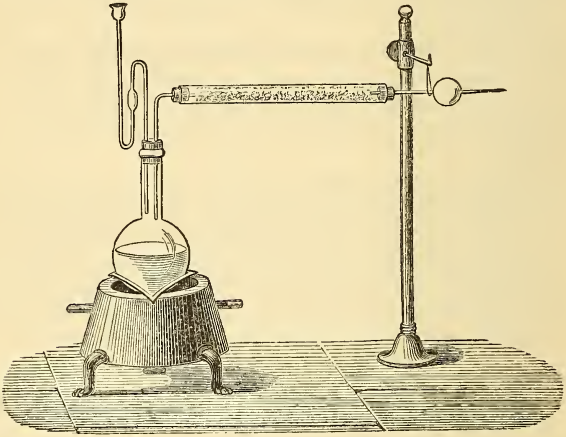


Fig. 4.

Experiment.—Some oxide of mercury, of which we have seen the decomposition by heat, may be placed in a tube through which is passed a current of hydrochloric acid gas, a gas composed of chlorine and hydrogen (Fig. 4). An energetic reaction takes place. The orange-red powder is converted into a white crystalline substance, and much heat is produced. At the same time a small quantity of liquid condenses in the bulb. This is water, and the white powder formed is mercuric chloride, or corrosive sublimate, a compound of mercury and chlorine. The hydrochloric acid has converted the mercuric oxide into mercuric chloride. The mercury, at first combined with oxygen, is now combined with chlorine. But what has become of the oxygen? It has combined with the hydrogen of the hydrochloric acid, forming water. We have brought into presence of each other two compound bodies:

Mercuric oxide,
Hydrochloric acid,

and from their reciprocal action two new compounds result:

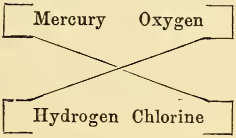
Mercuric chloride,
Water or oxide of hydrogen.

This reaction has then occasioned an interchange of elements. The mercury of the mercuric oxide has combined with the chlorine of the hydrochloric acid, and the oxygen has left the mercury and combined with the hydrogen, which was abandoned by the chlorine. The reaction has been as easy as energetic, thanks to the intervention of two affinities, for the affinity of chlorine for mercury has been aided by that of hydrogen for oxygen. Two molecules are decomposed, and two new molecules are formed by an exchange which may be represented in the following manner:

BEFORE THE REACTION.

Mercury + Oxygen = Mercuric oxide.
Hydrogen + Chlorine = Hydrochloric acid.

DURING THE REACTION.



AFTER THE REACTION.

Mercury + Chlorine = Mercuric chloride.
Hydrogen + Oxygen = Water.

Such reactions, characterized by an interchange of elements, are called *double decompositions.* They are the more usual reactions in chemistry.

The examples cited have been demonstrated by experiments easy to comprehend and to repeat, and are sufficient to give an idea of chemical phenomena. We have seen how, on the contact of two heterogeneous bodies, this elective attraction, which is called affinity and which sets in motion the smallest particles of bodies, comes into play to produce either combination or decomposition; we have seen how this force modifies the chemical molecules either by interposing other molecules, or under the influence of physical forces, such as heat and electricity. The study of all these phenomena constitutes chemistry, the science of molecular changes; a science grand in purpose and in magnitude, since it penetrates to the very nature of the bodies surrounding us; a science unlimited in its applications, since through it we learn to know and control the powerful forces which are at work in the most intimate structure of matter.

If we trace the acquired facts to the most obvious and most certain conclusion, we must admit the existence of a number of bodies, each of which, when submitted to the various tests consisting in the application of physical and chemical forces, furnishes but one and the same substance, and it is impossible to obtain anything else than this substance from the body. We maintain, then, until proved to the contrary, that each of these bodies contains but a single kind of matter, to which the name simple body or element is applied. The chemical forces reside, as has been seen, in the most remote particles, in the atoms of these bodies. In uniting together, the elements form compound bodies, and it has already been stated that such combinations result from the juxtaposition of the atoms which attract each other. The idea of atoms was originally an hypothesis, but in its development it has been found to be supported by so many important facts, and moreover to weave them together in the most natural manner, that it has attained the dignity of a theory. Chemists have universally adopted it, and it has rendered immense service to the science. Let us proceed, now, to a consideration of the facts upon which it is based.

LAW OF DEFINITE PROPORTIONS.

The proportions by weight according to which bodies combine are invariable for each combination—These proportions are equivalent among themselves—Experiments demonstrating this fact.

Experiment.—A test-glass (Fig. 5) contains a liquid which is universally known as sulphuric acid. Although largely diluted with water, that is, mixed with a large quantity of that liquid, it still manifests its presence by energetic properties. It has a very sour and corrosive taste,—a quality of an acid. If a few drops of blue litmus solution be added to it the blue color instantly changes to bright red. Another glass contains a solution of caustic potash or potassium hydrate. This substance possesses a strong, lye-like, alkaline taste, very easy to distinguish from that of the acid. The color of the blue litmus is not affected by this liquid, but if a few drops of the litmus solution, previously reddened by an acid, be added, the blue color is immediately restored. This caustic substance has properties which are different from those of acids, and which are called basic or alkaline properties. Potassium hydrate is an alkali or powerful base.


Fig. 5.

If now the alkaline liquid, which has a blue color, be poured drop by drop into the reddened acid, and the mixture be stirred with a glass rod, a moment arrives when the red color of the acid liquid changes to blue. Exactly at this moment we have a solution which has no action upon litmus; it will not redden the blue solution, neither will it restore the blue color to the red. This may be demonstrated by dipping into it first a red and then a blue litmus-paper. Furthermore, this liquid possesses neither the acid taste of the oil of vitriol nor the alkaline taste of the caustic potash, but its taste is salty.

By their mixture and reciprocal action the sulphuric acid and the potash have lost the energetic properties which they manifested before mixing. They are exactly saturated; they are *neutralized.* That is, the liquid which now contains both, or more properly the product of their reaction, is neither acid nor alkaline; it is neutral, and its neutrality is manifested both by its indifference to vegetable colors and by its taste. There is no excess, neither of sulphuric acid nor of potash, but the two bodies have reacted exactly upon each other and both have disappeared, and from their reciprocal action two new bodies result,—a salt called potassium sulphate, and water.

Whenever sulphuric acid is thus saturated by potash, there arrives a moment when the whole of the acid is precisely neutralized by the alkali, and when the two bodies are converted, without residue of either one or the other, into potassium sulphate and water; and it is always easy to recognize the instant at which this effect is produced by the action of the liquid upon vegetable colors, such as solution of litmus, or syrup of violets. The latter is reddened by an acid, changed to green by an alkali, and assumes its natural violet tint when the neutral point is reached. Now, it has been found that this last effect is only produced when the acid and the alkali are mixed in certain proportions, which remain invariable, whatever may be the quantities which are mixed. In other words, it has been found that the quantities of sulphuric acid and potash which reciprocally neutralize each other and form potassium sulphate, maintain a constant ratio to each other. It may be easily proved that when the state of neutrality has been once attained, it is immediately passed and disturbed by the least excess of either acid or base that may be added to the liquid. This is made evident by the immediate change in the color of the liquid to either red or green.

Thus, in order to form sulphate of potassium with a given quantity of sulphuric acid, it is necessary to add an invariable quantity of potash; and if the quantity of sulphuric acid be increased by a third, or in any proportion whatever, it is necessary to increase by a third, or in the same proportion, the quantity of potash.

Experiments of this kind have been made with other acids and other bases, and have introduced into the science the fundamental notion that these bodies react upon each other in definite proportions to form salts, and that consequently the composition of the latter bodies is perfectly fixed. A given quantity of any acid whatever, invariably saturates a fixed quantity of the same base. This, then, is the first point.

It may be added that similar researches made towards the close of the last century have led to a not less important result, namely, the respective quantities of several acids which saturate a given weight of one base are exactly proportional to the quantities of the same acids which saturate a given weight of another base. The law which governs the composition of salts was discovered towards the close of the last century by a German chemist, Richter. We cannot now expose it in detail; such development will be better placed and better understood in that part of this work which treats of the formation of salts. For the present it is sufficient to state that the law mentioned is a consequence of the law of definite proportions, and that the latter law is universal. It applies not only to the reaction of acids upon bases, but is true for all chemical combinations. It is generally known as Dalton's first law, and may be thus expressed: *the relative weights according to which bodies combine are invariable for each combination.*

There is one feature of the laws which control the composition by weight of bodies that it is important to comprehend well.

It may be best illustrated by experiment:

100 gr. of mercury are put into the presence of chlorine gas, a body possessing very powerful affinities. In this manner mercuric chloride or corrosive sublimate is formed, and it is found that 35.5 gr. of chlorine are necessary to convert 100 gr. of mercury into this compound. These figures—100 and 35.5—express the invariable ratio in which these elements are combined in corrosive sublimate. Here we have the definite proportions.

Now let the 135.5 gr. of corrosive sublimate be dissolved in water, and a plate of copper be placed in the solution; this metal will displace the mercury, and combining with the 35.5 gr. of chlorine will form with it cupric chloride, which will remain in solution, coloring the liquid green. The 100 gr. of mercury are then precipitated, and it will be found that 31.75 gr. of copper have entered the solution and actually combined with 35.5 gr. of chlorine.

Into this solution of cupric chloride a plate of zinc is now plunged; all of the copper is precipitated in its turn, and 33 gr. of zinc enter into combination with the 35.5 gr. of chlorine, forming zinc chloride.

The 35.5 gr. of chlorine have now been combined successively with

100 gr. of mercury,
31.75 gr. of copper,
33 gr. of zinc.

These numbers, which express the respective quantities of mercury, copper, and zinc which combine with the same quantity of chlorine, may be called the equivalents of these metals. In fact, these quantities are equivalent to each other in relation to the same quantity of chlorine, the experiment having shown us that in order to displace 100 gr. of mercury combined with 35.5 gr. of chlorine it is necessary to employ 31.75 gr. of copper or 33 gr. of zinc.

To continue, 100 gr. of mercury are combined with oxygen, and it is found that this quantity of the metal requires 8 gr. of oxygen to form the red powder called mercuric oxide.

But how much oxygen is necessary to form cupric oxide with 31.75 gr. of copper? Remarkable as it seems, exactly 8 gr. are required, and 8 gr. are also requisite to form oxide of zinc with 33 gr. of zinc.

100 gr. of mercury,
31.75 gr. of copper,
33 gr. of zinc,

which are equivalent compared to 35.5 gr. of chlorine, are then also equivalent in relation to 8 gr. of oxygen.

Chlorine itself may be oxidized, and there exists a gaseous compound of chlorine and oxygen which contains precisely 8 gr. of oxygen for 35.5 gr. of chlorine.

Thus, there are required

$$\left.\begin{array}{l}\text{35.5 gr. of chlorine to form chlorides with . .}\\ \text{8 gr. of oxygen to oxidize . . . .}\end{array}\right\}\begin{array}{l}\text{100 gr. of mercury,}\\ \text{31.75 gr. of copper,}\\ \text{33 gr. of zinc,}\end{array}$$

and also

8 gr. of oxygen to oxidize 35.5 gr. of chlorine.

In general, if

A, B, C, combine with D,
A, B, C, combine also with E,
and further, D combines with E,

the letters A, B, C, D, E, representing the weights of the different elements which enter into combination, or the proportions according to which the bodies combine among themselves.

They are expressed by numbers that have been called combining weights or equivalents; these represent the ratio of weights or the relative weights. They are indeed relative to a unit which has served as a term of comparison, and which is the equivalent of hydrogen. That is, the quantity of hydrogen which combines with 35.5 of chlorine being 1, the equivalent quantities of oxygen, zinc, copper, and mercury will be represented by the numbers 8—33—31.75—100.

These are the facts of experiment. Let 33 gr. of zinc be treated with hydrochloric acid, the latter is immediately decomposed; its chlorine combines with the zinc, forming chloride of zinc, and its hydrogen is disengaged. In this experiment the hydrogen of the hydrochloric acid is simply displaced by the zinc. Now, 33 gr. of this metal will displace exactly 1 gr. of hydrogen.

It is seen that the numbers which have been given do not express absolute quantities, but merely the relative weights according to which the bodies combine or replace each other in compounds, these relative weights being compared to that of hydrogen, which is taken as unity.

Such is the signification of the numbers.

100	31.75	33	35.5	8	1	which represent equivalent quantities of these elements.
of mercury,	of copper,	of zinc,	of chlorine,	of oxygen,	of hydrogen.	

This being admitted, in order to determine the equivalent of an element it is sufficient to find the quantity of that element which combines either with 1 of hydrogen or with a quantity of another element which is equivalent to 1 of hydrogen, for instance, 8 of oxygen.

The notion of equivalent proportions can be understood from the preceding considerations; it appears as a consequence of the law of definite proportions; it comprehends certain facts relative to the laws of the composition of bodies, but it by no means represents the full scope of these laws. The following developments add important features.

MULTIPLE PROPORTIONS.

Two bodies may combine in several proportions. Thus, with oxygen, carbon forms two compounds, both of which are gaseous. The less rich in oxygen is carbon monoxide; the richer is carbon dioxide, or carbonic acid gas. Dalton was the first to perceive that for the same quantity of carbon, carbonic acid contains exactly twice as much oxygen as carbon monoxide. He made analogous observations concerning the composition of two compounds of carbon and hydrogen, the monocarbide of hydrogen or marsh gas, and the dicarbide of hydrogen or olefiant gas. From these observations he deduced the law of multiple proportions, which may be thus stated: *when two bodies, simple or compound, unite in several proportions to form several compounds, the weight of one of these bodies being considered as constant, the weights of the other vary according to a simple ratio.*

Thus, taking up one of the examples given above, carbon unites with oxygen in two proportions:

Carbon monoxide contains 16 parts of oxygen to 12 parts of carbon.

Carbon dioxide contains 32 parts of oxygen to 12 parts of carbon. The numbers 16 and 32 are in the ratio of 1 : 2.

Nitrogen forms five compounds with oxygen; if such quantities of these compounds be taken as contain the same weight of nitrogen, the weights of the oxygen will be proportional to the numbers 1, 2, 3, 4, 5.

Nitrogen monoxide	contains for	28	parts of	nitrogen	16	parts of	oxygen.
Nitrogen dioxide	"	28	"	"	32	"	"
Nitrogen trioxide	"	28	"	"	48	"	"
Nitrogen tetroxide	"	28	"	"	64	"	"
Nitrogen pentoxide	"	28	"	"	80	"	"

These numbers, 16, 32, 48, 64, 80, are multiples of the first by the numbers 1, 2, 3, 4, 5.

Five compounds of manganese and oxygen are known, and similar relations exist between the quantities of oxygen contained in these compounds.

The first	contains	55	parts of	manganese to	16	of oxygen.
The second	"	55	"	"	24	"
The third	"	55	"	"	32	"
The fourth	"	55	"	"	48	"
The fifth	"	55	"	"	56	"

The numbers 16, 24, 32, 48, 56 are in the simple proportion 1 : 1.5 : 2 : 3 : 3.5.

Such is the law of multiple proportions discovered by Dalton.

HYPOTHESIS OF ATOMS.

The brilliant researches of Dalton did not terminate with the acquisition of facts: he sought to account for them by a theoretical conception. Taking up the old idea of Leucippus and the word of Epicurus, he supposed all ponderable matter to be composed of indivisible particles which he called *atoms.* He gave a precise meaning to the vague and ancient notion by considering on one hand that the atoms of each kind of matter, of each element, possess an invariable weight, and on the other that combination between different kinds of matter results from the juxtaposition of their atoms. Such is the atomic hypothesis, the substance of which we have already indicated in treating of chemical phenomena in a general manner. It permits a simple and rational interpretation of the laws of the composition of bodies, and establishes between these laws a firm bond of theory.

Indeed, if the combination of bodies results from the juxtaposition of their atoms, the latter being considered as indivisible and possessing a constant weight for each element, it is evident that combination can only take place in definite proportions, for these proportions represent the invariable relations between the weights of the atoms which are in juxtaposition. If, on the other hand, one body may combine with another in several proportions, such combination can only take place by the juxtaposition of 1, 2, 3, 4, etc., atoms of one body with one or more atoms of the other. It evidently results that the weight of the latter body being constant, the weights of the other in these various combinations must be multiples of each other.

An hypothesis which gives such a simple and precise explanation of the facts relative to definite and multiple proportions is surely worthy of attention. It acquires still further import and becomes elevated to the rank of a theory when to these facts are added others entirely different from the first, but not less important.

GAY-LUSSAC'S LAWS.—ATOMIC THEORY.

Gases combine in simple volumetric proportions—Relations which exist between the volumes of gases and their atomic and molecular weights—Equal volumes of gases or vapors contain the same number of molecules—The molecular weights are equal to double the densities compared to hydrogen.

Among these new facts it is convenient to first notice those which were discovered by Gay-Lussac, from 1805 to 1808. They relate to the volumes of gases which combine together.

Experiment.—A straight graduated glass tube about one metre long, closed at one end and having two platinum wires soldered through the glass near the closed end, is filled with mercury and inverted over a tall glass mercury cistern (Fig. 6), in the bottom of which is a thick caoutchouc pad. This tube, which is called a eudiometer, is surrounded by a wider glass tube fitting firmly on a cork passed over the eudiometer. The cork is also perforated for the passage of a bent glass tube through which steam from a boiler can be delivered into the space between the eudiometer-tube and the mantle. The mouth of the eudiometer being about one centimetre below the level of the mercury, which completely fills the cistern, a mixture of two volumes of hydrogen with one volume of oxygen is now introduced until the level of the mercury in the tube indicates the latter to contain exactly 30 cubic centimetres. The wires of the eudiometer are now connected with the poles of an induction-coil, and steam is passed from the boiler until it no longer condenses in the space between the tubes; that is, when the temperature is 100°. The gases have been expanded by the heat, and the eudiometer must be lowered into the cistern until the level of the mercury in the tube again marks 30 cubic centimetres, when the clamps of the

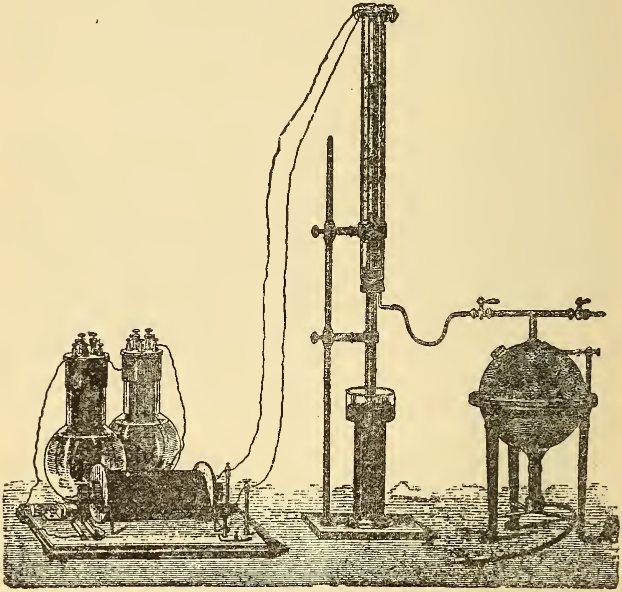


Fig. 6.

stand are so adjusted that the upper one is fixed at this mercury level. The tube is now lowered into the mercury until its lower end rests upon the caoutchouc pad; a spark from the coil is passed in the eudiometer, and this causes the oxygen and hydrogen to combine instantly, as is seen by a bright flash. Now, on raising the tube until the mercury in it stands as before, at the level of the upper clamp, it is found that the eudiometer contains only 20 cubic centimetres of gas instead of 30. The 20 cubic centimetres consist of steam formed by the union of 20 cubic centimetres of hydrogen with 10 cubic centimetres of oxygen. As the apparatus cools, the steam will condense to water, and as the latter occupies a very small volume compared with that of the steam, the mercury will rise and fill the tube.

From the facts thus established we draw the conclusion that 2 volumes of hydrogen exactly combine with 1 volume of oxygen to form 2 volumes of vapor of water.

There is thus determined a simple ratio not only between the volumes of hydrogen and oxygen which combine, but further, between the volume of vapor of water formed and the sum of the volumes of the composing gases. 3 volumes of the latter are reduced to exactly 2 by the combination.

Analogous facts have been discovered for other gases, as shown by the following examples:

2 volumes of nitrogen + 1 volume of oxygen = 2 volumes of nitrogen monoxide.
2 volumes of chlorine + 1 volume of oxygen = 2 volumes of chlorine monoxide.

In other cases the combination of two gases determines a still greater contraction, and the initial volume is reduced one-half. Thus

1 volume of nitrogen + 3 volumes of hydrogen = 2 volumes of ammonia gas.

Finally, when two gases combine in equal volumes, their combination usually takes place without contraction; in other words, the volume of the gas produced is equal to the sum of the volumes of the component gases.

From these collected facts we may draw the following general conclusions:

1. There is a simple relation between the volumes of gases which combine.

2. There is a simple relation between the sum of the volumes of the combining gases and the volume of the gas resulting from the combination.

These laws were first signalized by Gay-Lussac, whose name is attached to them. Their importance is immense; they have added a notable development to the atomic theory.

If the definite proportions by weight in which bodies combine represent, according to Dalton, the relative weights of their atoms, it is natural to conclude that the definite and simple proportions by volume in which gases combine, according to Gay-Lussac, represent the volumes occupied by the atoms. Under the same volume gases would then contain the same number of atoms. This was first proposed by Ampère, who based his conclusion on the important consideration that gases dilate and contract nearly equally when submitted to the same variations of temperature and pressure. Within certain limits the proposition is true; it applies to a large number of simple gases. But if equal volumes of these gases, measured, let it be well understood, under the same conditions of temperature and pressure, contain the same number of atoms, it is evident that the weights of these equal volumes should represent the weights of the atoms. In other words, the atomic weights of the simple gases should be proportional to their densities.

The densities of gases and vapors represent the weights of these gases or vapors compared to the weight of an equal volume of air. To determine the density, a certain volume of the given gas is weighed, and this weight is divided by that of an equal volume of air, under the same conditions of temperature and pressure. The air is then the unit to which are compared the densities of gaseous bodies. On comparing these densities to that of hydrogen,[1] which we take as unity, we find that the same numbers express almost exactly the densities and the atomic weights, the unit to which the densities are compared, that is, hydrogen, being the same as that to which are compared the atomic weights. The figures in the following table demonstrate this to be the case:

Elements.	Densities of Gases or Vapors, Air being Unity.	Densities, Hydrogen being Unity.	Atomic Weights.
Hydrogen	0.0695	1	1
Oxygen	1.1015	15.9	15.9
Nitrogen	0.9714	14	14
Sulphur (density at 1000°)	2.22	32	32
Chlorine	2.44	35.2	35.5
Bromine	5.53	79.7	80
Iodine	8.716	125.8	127

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[1] To do this it is sufficient to multiply the densities of the gases compared to air by $\frac{1}{0.0695} = 14.388$, which is the density of the air compared to hydrogen as unity.

It is seen from this table that if the densities of gases be compared to hydrogen as unity, just as the weights of their atoms are compared to hydrogen as unity, the same figures, or very nearly the same figures, express both the densities and the atomic weights. We may add that, for all the elements taken in the gaseous state, there has been determined between the densities referred to hydrogen and the atomic weights, if not equality, at least a simple ratio. These remarkable relations were pointed out by Gay-Lussac.

Equal volumes of the simple gases above enumerated contain the same number of atoms. Two volumes of hydrogen, then, contain twice as many atoms as one volume of oxygen; and when these gases combine in the ratio of 2 volumes of the first to 1 of the second, we must admit that each atom of oxygen combines with 2 atoms of hydrogen. We say, then, that water is composed of 2 atoms of hydrogen and 1 atom of oxygen. These three atoms so united constitute the smallest quantity of water that can exist in the free state. This is called *a molecule* of water.

But what volume does this molecule occupy? The experiment has shown us. We have seen that 2 volumes of hydrogen, in combining with 1 volume of oxygen, yield 2 volumes of vapor of water. One molecule of water in the gaseous state, then, occupies 2 volumes, if 1 atom of hydrogen occupy 1 volume, and if 1 atom of oxygen occupy 1 volume. It is seen that the volumes represent the atoms, and the relative weights of equal volumes, that is, the densities, represent the weights of the atoms.

Let us now consider another compound gas,—ammonia,—composed of hydrogen and nitrogen. A very simple experiment will show in what proportion the atoms of these elements are combined in this gas, and the volume occupied by the compound compared with the volumes of its component gases.

Experiment.—100 volumes of ammonia gas are introduced into a tube inverted upon the mercury-trough (Fig. 7), and the walls of which are pierced at the upper end by two platinum wires, between the ends of which a small space is left. To these wires are attached the extremities of the two conducting wires of a Ruhmkorff coil, and the current is passed so that a series of electric sparks traverses the ammonia between the extremities of the wires in the tube. The gas is immediately decomposed, and the level of the mercury in the tube is depressed. When the experiment has terminated it is found that the volume of the gas has been doubled. Instead of 100 volumes, there are now 200, the gas being measured under the same conditions of temperature and pressure as before. It is found, by an analytical process that will be indicated further on, that these 200 volumes of gas resulting from the decomposition of 100 volumes of ammonia are composed of 150 volumes of hydrogen and 50 volumes of nitrogen. These 150 volumes of hydrogen and 50 volumes of nitrogen are condensed by their union into 100 volumes of ammonia. In other words, 3 volumes of hydrogen and 1 volume of nitrogen are combined together in 2 volumes of ammonia. And as the volumes represent atoms, it follows that in ammonia gas 3 atoms of hydrogen are combined with 1 atom of nitrogen. But the quantity of ammonia containing 1 atom of nitrogen and 3 atoms of hydrogen is the smallest quantity of ammonia that can exist. It is a *molecule* of ammonia, and this molecule occupies 2 volumes, if 1 atom of nitrogen or 1 atom of hydrogen occupy 1 volume.

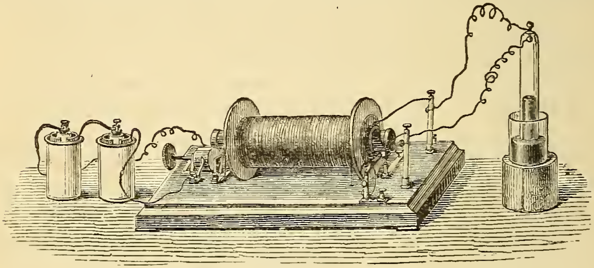

FIG. 7.

Here, then, is another compound gas,—ammonia,—of which the molecule occupies 2 volumes, like that of water. It is the same with all the gases. All of the atoms which are combined to constitute the molecule of a gas or vapor are so condensed that the molecule occupies the same volume as the molecule of hydrogen, of vapor of water, or of ammonia.

We may state, then, with the Italian chemist, Avogadro, that *equal volumes of gases contain the same number of molecules*, and that each of these molecules occupies 2 volumes, if 1 atom of hydrogen occupy 1 volume. It follows that the weight of 2 volumes of any gas, whether elementary or compound, represents the weight of its molecule, the weight of one volume of hydrogen being 1. But the weight of 2 volumes of a gas or vapor is twice its density compared to hydrogen, for the density is the weight of 1 volume compared with the weight of 1 volume of hydrogen. To find the weight of the molecule (the weight of 2 volumes) of a gas or vapor, it is then only necessary to multiply its density compared to hydrogen (the weight of 1 volume) by 2.

The densities of gases and vapors are generally referred to air as unity. To bring them to the hydrogen standard, they are multiplied by the number expressing the relation of the density of hydrogen to that of air, which is $\frac{1}{0.0695} = 14.388$. The product thus obtained expresses the density compared to hydrogen, that is, the weight of 1 volume. To find the weight of 2 volumes, or the molecular weight, it is then only necessary to multiply the densities compared to air by twice the ratio of the density of the air compared to hydrogen, that is, by the constant factor,—

$$2 \times \frac{1}{0.0695} = \frac{2}{0.0695} = 28.776.$$

It is seen that if the atomic weights of certain gases can be deduced from a comparison of their densities, this same physical notion may also serve for the determination of the molecular weights of compound gases.

The numbers which represent double the densities of gases or vapors compared to hydrogen, express also the molecular weights of these gases or vapors, that is, the sum of the weights of all the atoms in the molecule, the weight of one atom of hydrogen being 1.

Considering the examples already given, we may deduce the molecular weights of water and of ammonia from the densities of steam and ammonia gas.

The density of vapor of water, determined by Gay-Lussac, is 0.6235. To find the molecular weight of water, it is sufficient to multiply this figure by 28.776. The product, 17.9, expresses the weight of a molecule of water, which is indeed composed of

2 atoms of hydrogen	= 2
1 atom of oxygen	= 15.9
1 molecule of water	= 17.9

Sir Humphry Davy found for the density of ammonia the number 0.5901. This being multiplied by 28.776, the product, 16.98, should represent the weight of one molecule of ammonia. Ammonia contains

3 atoms of hydrogen	3
1 atom of nitrogen	14
1 molecule of ammonia	17

The discovery of the laws which govern the combination of gases by volume has seconded in the most efficacious manner the progress of the atomic theory.

In the first place, it has established a marked distinction between the old idea of equivalents and the modern one of atoms. The equivalents represented merely the ponderable proportions according to which bodies combine; the atomic weights represent the relative weights of the volumes of gases which combine. The equivalent of hydrogen—unity—expressed merely that hydrogen was the unit to which were referred the weights of other bodies with which it entered into combination. The atomic weight of hydrogen is the weight of one volume of hydrogen, taken as unity, and to this unit are referred the atomic weights of other bodies.

In the second place, the discovery of Gay-Lussac has shown how the atomic weights of simple bodies and the molecular weights of compound bodies can be deduced from the densities of gases and vapors.

However, this resource would be insufficient in very many cases. It only applies to gaseous bodies, or such as can be converted into vapor without decomposition. Now, there are many substances with which this is impossible, and serious difficulties would be encountered in the determination of the atomic weights of certain elements were it not for another physical law, discovered by two French physicists, Dulong and Petit. It denotes the relations which exist between the specific heats and the atomic weights.

LAW OF SPECIFIC HEATS.

It is known that in order to raise the temperatures of different bodies through the same number of thermometric degrees very different amounts of heat are required. Thus, one kilogramme of water requires 30 times more heat than one kilogramme of mercury to raise its temperature one degree, and if the quantity of heat required to raise the temperature of one kilogramme of water one degree be represented by 1, the quantity required to raise the same weight of mercury one degree will be represented by $0.0333 = \frac{1}{30}$. This fraction expresses the specific heat of mercury between 0 and 100°.

The specific heat of a solid or liquid body is then the amount of heat required to raise the temperature of a certain weight of the body one degree, the amount required to raise the temperature of an equal weight of water one degree being taken as unity.

In 1820, Dulong and Petit discovered the remarkable fact that if the figures which express the atomic weights of the elements, liquid or solid, be multiplied by those which express their specific heats, the product obtained is sensibly constant; in other words, the specific heats of the elements are inversely as their atomic weights. It follows that if such quantities of the elements be taken as represent their atomic weights, the amount of heat required to raise the temperature of each one degree will be sensibly the same. The law discovered by Dulong and Petit may then be expressed,—*the atoms of the solid elements possess sensibly the same specific heats.*

This law permits the deduction of the atomic weights from the specific heats. Indeed, it is evident that if the product of the specific heats by the atomic weights be a constant, that may be called the *atomic heat*, dividing this product by the specific heat should give the atomic weight. The product which represents the atomic heat is approximately 6.4, as may be seen from the following table:

NAMES OF THE SOLID ELEMENTS.	Specific Heats.	Atomic Weights.	Products of the Specific Heats by the Atomic Weights. Atomic Heats.
Sulphur, between 0 and 100° . .	0.2026	32	6.483
Selenium	0.0762	79.5	6.058
Tellurium	0.0474	127	6.023
Bromine, between —78 and —20°	0.0843	80	6.744
Iodine, between 0 and 100° . .	0.0541	127	6.873
Phosphorus, between + 1 and 30°	0.1887	31	5.850
Arsenic	0.0814	75	6.105
Carbon, diamond, at 600° . . .	0.46	12	5.52
Boron, crystallized, at 600° . .	0.5	11	5.5
Silicon, at 1000°	0.202	28	5.66
Potassium	0.1695	39.1	6.500

TABLE.—*Continued.*

NAMES OF THE SOLID ELEMENTS.	Specific Heats.	Atomic Weights.	Products of the Specific Heats by the Atomic Weights. Atomic Heats.
Sodium, between —34 and + 7°	0.2934	23	6.748
Lithium	0.9408	7	6.586
Thallium	0.03355	204	6.844
Magnesium	0.2499	24	5.998
Aluminium	0.2143	27	5.786
Manganese	0.1217	55	6.693
Iron	0.0110	56	6.116
Zinc	0.09555	65.2	6.230
Cadmium	0.05669	112	6.349
Cobalt	0.1068	59	6.301
Nickel	0.1089	59	6.424
Tungsten	0.0334	184	6.146
Molybdenum	0.0722	96	6.931
Lead	0.0314	207	6.499
Bismuth	0.0308	210	6.468
Copper	0.09515	63.5	6.042
Antimony	0.05077	120	6.092
Tin	0.05623	118	6.635
Mercury, between —77.5 and —44°	0.03247	200	6.494
Silver	0.05701	108	6.157
Gold	0.0324	197	6.383
Platinum	0.03293	195	6.421
Palladium	0.0593	106.5	6.315
Osmium	0.031	191	5.921
Rhodium	0.05803	104.4	6.058
Iridium	0.03259	193	6.291

Carbon, silicon, and boron have long been regarded as exceptions to Dulong and Petit's law. Their specific heats had been determined at comparatively low temperatures, and the products of the numbers obtained by the atomic weights fell much below 6.4. These exceptions have disappeared; the experiments of Weber have shown that the specific heats of carbon, silicon, and boron increase with the temperature, and that for the first two elements they attain limits, where they remain sensibly constant. The figures given in the preceding table for these three elements are those of Weber, and it is seen that on multiplying them by the respective atomic weights of carbon, silicon, and boron, values are obtained which approximate 6.4.

It will otherwise be remarked that there are sensible differences between the numbers expressing the atomic heats of the various solid elements, showing that Dulong and Petit's law, although true in its generality and striking in its enunciation, is not free from certain perturbations which give to it the character of an approximate law. It is the same with other physical laws, Mariotte's law, for example.

ISOMORPHISM.

While considering the atomic theory and the determination of the relative weights of the ultimate particles of bodies, we cannot pass in silence a discovery which has had a great influence upon the development of that theory. It is due to E. Mitscherlich, who, in 1819, made known the *law of isomorphism.* This law may be thus stated: there is such a relation between the atomic constitutions of compound bodies belonging to the same group and their crystalline form, that "the same number of atoms combined in the same manner produce the same crystalline form, the latter being independent of the chemical nature of the atoms, and determined solely by their number and arrangement." While this proposition is not strictly true, it has rendered important aid in the study of atomic structure of bodies. We will reconsider it when treating of the general characteristics of salts, but we may remark here that it has been of great value in the determination of certain atomic weights. Indeed, in some cases considerations of a chemical nature cannot decide between two numbers for the atomic weight of a given element. The choice is then determined by the following considerations: such a value must be attributed to the atomic weight that the isomorphous compounds formed by the element, and by another to which it is analogous, may be represented by similar atomic formula.

The methods employed for the determination of the molecular weights of such bodies as cannot be vaporized without decomposition will be described under "Organic Chemistry" (page 442).

CHEMICAL NOMENCLATURE AND NOTATION.

General Considerations.—Nearly eighty substances are known which have not been resolved into simpler forms of matter, and are consequently considered as simple bodies or *elements.* By combining together, they form an innumerable multitude of *compound bodies* containing two or more elements.

In order to distinguish these bodies from each other it is necessary to give a name to each, for each constitutes a distinct substance.

The names of the simple bodies have been chosen at will, and in some cases recall some peculiar property of the substances designated. It was formerly the same with compound bodies; there was no definite rule for their nomenclature. From this there resulted a great complication of words which embarrassed the exposition of ideas, and often for the same substance there were a number of synonyms, of which the least inconvenience was to uselessly fatigue the memory. Hence chemists have felt the necessity of a regular nomenclature, applicable to compound bodies, and capable of indicating their composition. Such is the principle of the chemical nomenclature suggested by Guyton de Morveau, and developed by Lavoisier, Berthollet, and Fourcroy. This nomenclature, with some modifications, introduced by the progress of the science, is still adopted.

Independently of this language, the rules of which will presently be detailed, chemists have adopted a written notation which expresses in concise form the atomic constitution of compounds. The name of each element is represented by a symbol, which also expresses one atom of the substance. This symbol is the initial letter of the name of the element, or the initial letter with another when the names of two elements begin with the same letter. Thus, H represents one atom of hydrogen weighing 1; O represents one atom of oxygen weighing 16. By combining these symbols together, it is easy to represent in a precise manner the atomic composition of compound bodies. From such combinations result *chemical formulas*, the use of which was introduced into the science by Berzelius.

In the following table will be seen the names of the elements now known, together with their atomic weights, and the symbols by which the atoms of the elements are represented in the notation.

The greater number of the elements possess certain physical properties which characterize them as *metals.* They are opaque, and possess a peculiar lustre, which does not disappear under the burnisher. They are good conductors of heat and electricity.

Other elements, fewer in number, do not possess these prop-

Names of the Elements.	Symbols.	Atomic Weights.	Names of the Elements.	Symbols.	Atomic Weights.
Aluminium	Al	26.9	Neodymium	Nd	142.5
Antimony (stibium)	Sb	119.5	Neon	Ne	22 (?)
Argon	A	40 (?)	Nickel	Ni	58.25
Arsenic	As	74.45	Niobium (columbium)	Nb	93.03
Barium	Ba	136.4	Nitrogen	N	13.93
Bismuth	Bi	206.5	Osmium	Os	189.6
Boron	B	10.9	Oxygen	O	15.88
Bromine	Br	79.34	Palladium	Pd	106.2
Cadmium	Cd	111.55	Phosphorus	P	30.75
Cæsium	Cs	131.9	Platinum	Pt	193.4
Calcium	Ca	39.8	Potassium (kalium)	K	38.82
Carbon	C	11.9	Praseodymium	Pr	139.4
Cerium	Ce	138.0	Radium	Ra	(?)
Chlorine	Cl	35.18	Rhodium	Rh	102.2
Chromium	Cr	51.7	Rubidium	Rb	84.75
Cobalt	Co	51.7	Ruthenium	Ru	100.9
Copper	Cu	63.1	Samarium	Sa	149.2
Erbium	Er	164.7	Scandium	Sc	43.8
Fluorine	F	18.9	Selenium	Se	78.6
Gadolinium	Gd	156 (?)	Silicon	Si	28.2
Gallium	Ga	69.5	Silver (argentum)	Ag	107.11
Germanium	Ge	71.9	Sodium (natrium)	Na	22.88
Glucinum (beryllium)	Gl	9.01	Strontium	Sr	86.95
Gold (aurum)	Au	195.7	Sulphur	S	31.83
Helium	He	4 (?)	Tantalum	Ta	181.5
Hydrogen	H	1	Tellurium	Te	126.5
Indium	In	113.1	Thallium	Tl	202.61
Iodine	I	125.89	Thorium	Th	230.8
Iridium	Ir	191.7	Thulium	Tu	169.4
Iron (ferrum)	Fe	55.6	Tin (stannum)	Sn	118.1
Krypton	Kr	80 (?)	Titanium	Ti	47.8
Lanthanum	La	137.6	Tungsten (wolframium)	W	182.6
Lead (plumbum)	Pb	205.36	Uranium	U	237.8
Lithium	Li	6.97	Vanadium	V	51
Magnesium	Mg	24.1	Xenon	X	128 (?)
Manganese	Mn	54.6	Ytterbium	Yb	171.9
Mercury (hydrargyrum)	Hg	198.5	Yttrium	Y	88.3
Metargon	Aμ	40 (?)	Zinc	Zn	64.9
Molybdenum	Mo	95.3	Zirconium	Zr	90.5

erties. They are known as the *non-metals*, or metalloids, and include

ARGON.
ARSENIC.
BORON.
BROMINE.
CARBON.
CHLORINE.
FLUORINE.
HELIUM.
HYDROGEN.
IODINE.
KRYPTON.
METARGON.
NEON.
NITROGEN.
OXYGEN.
PHOSPHORUS.
SELENIUM.
SILICON.
SULPHUR.
TELLURIUM.
XENON.

It is impossible, however, to separate the metals from the non-metals by an exact line of demarcation.

Nomenclature of Compound Bodies.—The principle of chemical nomenclature is to indicate the composition of compound bodies by their names. Among such compounds the most numerous and the most important are those containing oxygen. They are binary or ternary; that is, the oxygen in them is combined with one or two other elements.

Binary Oxygen Compounds.—We will first consider the more simple oxidized bodies, those which result from the combination of oxygen with but one other element, metallic or non-metallic. These compounds are called oxides, and differ as the element associated with the oxygen is metallic or non-metallic. In combining with non-metallic elements, oxygen generally forms compounds which are the anhydrides of acids, that is, compounds capable of uniting with water to form acids; with the metals it forms metallic oxides.

Experiments.—1. A small piece of phosphorus is placed in a capsule floating on the surface of mercury. It is ignited and the capsule covered with a bell-jar (Fig. 8). The phosphorus burns, giving off a thick smoke, which condenses in white flakes on the sides of the bell-jar. This substance results from the combination of the phosphorus with the oxygen of the air: it is *phosphorus pentoxide*, or *phosphoric anhydride.*

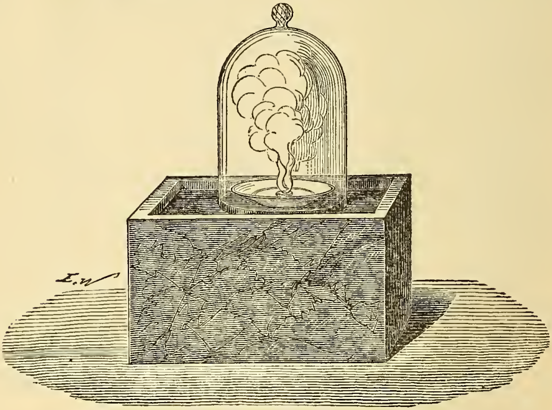

Fig. 8.

2. If lead be heated in the air and maintained for some time in a state of fusion, its brilliant surface becomes tarnished and covered with grayish particles, which are finally converted into a yellow powder. This body is formed by the combination of the lead with oxygen: it is *plumbic oxide*, or *oxide of lead.*

But, as we have seen, such combination can take place in different proportions. An atom of a body may unite with 1, 2, 3, or more atoms of oxygen, and the names of the compounds so formed should indicate the degree of oxidation.

Sulphur forms two compounds with oxygen: one contains 2 atoms of oxygen to 1 atom of sulphur; the other, 3 atoms of oxygen to 1 of sulphur. They are designated by the names sulphur*ous* oxide, or anhydride, and sulphur*ic* oxide, or anhydride.

The written notation represents them by the symbols

$$SO^2,$$
$$SO^3,$$

which express their atomic compositions. The number of atoms of any element is indicated by a small figure placed after and a little above or below the symbol of that element.

The degree of oxidation is then expressed by the termination in *ous* or *ic* of the name of the other element, which indicates the kind of oxide, *ic* denoting the superior oxide.

Mercury forms two compounds with oxygen. The first contains 2 atoms of mercury for 1 of oxygen; the second, 1 atom of mercury to 1 of oxygen. They are designated by the names and symbols as follows:

Mercurous oxide	Hg^2O
Mercuric oxide	HgO

The names monoxide, sesquioxide, dioxide, etc., as will be seen further on, are also employed.[1]

A *monoxide*	is a	combination of	1 atom	of metal	with	1 atom	of oxygen.
A *sesquioxide*	“	“	2 atoms	“	“	3 atoms	“
A *dioxide*	“	“	1 atom	“	“	2 “	“

It is easy then to understand the signification of the following names and symbols:

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[1] The prefixes *proto, bi* or *deut*, and *ter* have been, and are yet, frequently employed instead of *mono, di,* and *tri.*

Manganese monoxide	MnO
Manganese sesquioxide	Mn^2O^3
Manganese dioxide	MnO^2

The oxide most rich in oxygen is sometimes called the peroxide.

Oxygen Acids and Metallic Hydroxides.—The oxygen compounds that we have just considered may unite with the elements of water to form more complex compounds, which are ternary, that is, they contain three elements. To the two elements of the oxide is then added a third, independently of the oxygen of the water, that is, its hydrogen.

The oxygen acids usually result from the union of water with the non-metallic oxides.

Experiment. — Sulphur trioxide or sulphuric anhydride occurs in white silky tufts. It is very volatile, and if a bottle containing it be opened, its vapor comes in contact with the moist air and forms thick white fumes. If a small quantity of this substance be thrown into water, it immediately disappears and combines with that liquid. So great is the energy of the reaction that the heat disengaged gives rise to the production of steam, which, being suddenly formed and condensed in the midst of the cooler liquid mass, causes a peculiar noise, a sort of hissing. When the sulphuric oxide is dissolved in the water, the solution presents a very acid reaction. It contains sulphuric acid, the compound long known under the name of oil of vitriol.

This reaction may be represented in the abbreviated language of the notation, which expresses the atomic composition of bodies with so much precision. The formula of sulphuric anhydride or sulphur trioxide is

$$SO^3$$

that of water is

$$H^2O$$

Then if sulphuric acid result from the addition of all of the elements of water to those of sulphuric trioxide, it should contain

$$SO^3 + H^2O = H^2SO^4$$

This is a *chemical equation*, and it is seen that the two terms of the first member express the atomic composition of the reacting bodies, while the single term of the second member gives the atomic composition of the product of the reaction. Such an equation accounts for all of the atoms, and the sum of all of the atoms written in the first member must exactly balance the sum of all those written in the second.

There is a compound known as nitric anhydride, or nitrogen pentoxide. It results from the combination of nitrogen with oxygen, and its atomic composition is represented by the formula N^2O^5. In combining with water it forms nitric acid.

$$\underset{\substack{\text{Nitric anhydride.}\\\text{(1 molecule.)}}}{N^2O^5} + \underset{\text{Water.}}{H^2O} = \underset{\substack{\text{Nitric acid.}\\\text{(2 molecules.)}}}{2(HNO^3)}$$

These examples, which could be indefinitely multiplied, give an idea of the constitution of the ternary oxygen acids. The rules which have been already given for the nomenclature of the oxides apply also to the nomenclature of the acids. We have *phosphorous* acid and *phosphoric* acid. *Hypo*-phosphorous acid is an acid of phosphorus containing still less oxygen than phosphorous acid. (*Hypo*, literally, under.)

The *metallic hydrates* or *hydroxides* result from the reaction of water with metallic oxides. It is known that when quicklime is sprinkled with water it becomes heated, increases in volume, cracks into pieces, and is finally converted into a white, impalpable powder, which constitutes slaked lime,—a compound of the lime with water. Lime is the oxide of a metal called calcium. In combining with water it forms a ternary compound of calcium, hydrogen, and oxygen; this is calcium hydroxide, or, as it is commonly called, hydrate of lime.

$$\underset{\substack{\text{Calcium oxide.}\\\text{(Lime.)}}}{CaO} + \underset{\text{Water.}}{H^2O} = \underset{\text{Calcium hydroxide.}}{CaH^2O^2}$$

The metal potassium, the radical of potash, forms with oxygen a compound which contains two atoms of potassium combined with one atom of oxygen. The composition of this body is then represented by the formula K^2O.

It combines with water with great energy, and forms with it potassium hydroxide, or caustic potash.

$$\underset{\text{Potassium oxide.}}{K^2O} + \underset{\text{Water.}}{H^2O} = \underset{\substack{\text{Potassium hydroxide.}\\\text{(2 molecules.)}}}{2KOH}$$

Oxygen Salts.—The oxygen salts result from the action of the oxygen acids upon the metallic oxides or hydroxides.

Experiment.—The formation of a salt may be illustrated by a modification of one of the experiments already described.

A quantity of dilute nitric acid is slightly reddened by a solution of blue litmus or syrup of violets.[1] Some dilute solution of caustic potash is also treated with the same coloring matter; the syrup of violets will assume a green color, or blue litmus will remain unchanged.

The latter liquid, which is alkaline, is now added drop by drop to the acid, until the red color disappears, giving place to the violet color of the syrup of violets or the blue of the litmus. The liquid is now *neutral*. It contains neither free nitric acid nor free potash. Both have disappeared as such; they are reciprocally neutralized, the first having lost its acid taste, the second its extreme caustic properties. They have produced a body having a saline, cooling taste, and exerting no action upon vegetable colors. It is a neutral salt which has been formed. It is called potassium nitrate, and is the nitre or saltpetre of the ancient chemists. It is not, however, the sole product of the reaction. Water is formed at the same time, and if we would comprehend the entire phenomenon, the reaction will be expressed by the following equation:

$$\underset{\text{Nitric acid.}}{HNO^3} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium nitrate.}}{KNO^3} + \underset{\text{Water.}}{H^2O}$$

It is seen that the salt, potassium nitrate, is a ternary compound, similar in constitution to nitric acid itself. On comparing the two formulæ,

HNO^3 nitric acid,
KNO^3 potassium nitrate,

it is seen that they only differ by the K in the second occupying the place held by the H in the first. It may then be said that potassium nitrate represents in a manner nitric acid in which the hydrogen has been replaced by an equivalent quantity of potassium. This definition applies to the entire class of compounds under consideration. A salt represents an acid of which the hydrogen has been wholly or partially replaced by an equivalent quantity of metal.

The acids constitute the salts of hydrogen: they are neutralized when this hydrogen is replaced by a metal. The acid or hydrogen salt differs from the metallic salt. From a theoretic point of view, an acid is a compound of the same order as a salt, and if these bodies are separated by such great differences

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[1] An infusion of common purple cabbage may be substituted for syrup of violets.

of properties, this is due to the nature of the base. What a difference, indeed, between hydrogen gas and the metals!

We have studied the formation of a salt by the action of an acid, nitric acid, upon a metallic hydroxide, potassium hydroxide. The anhydrous oxides may also form salts by reacting with acids.

Experiment.—Yellow oxide of lead, when digested with dilute sulphuric acid, is converted into a white, insoluble powder, which is lead sulphate. This is a salt, but it is not the only product of the reaction, for water is formed at the same time.

$$\underset{\text{Sulphuric acid.}}{H^2SO^4} + \underset{\text{Lead oxide.}}{PbO} = \underset{\text{Lead sulphate.}}{PbSO^4} + \underset{\text{Water.}}{H^2O}$$

Lastly, among other modes of formation of salts, there is one which is worthy of interest, and of which an idea may be obtained from the following example.

Sulphur trioxide, or sulphuric anhydride, combines energetically with barium oxide or baryta, and from the union of all of the elements of both compounds there results a salt,—barium sulphate.

$$\underset{\text{Sulphur trioxide.}}{SO^3} + \underset{\text{Barium oxide.}}{BaO} = \underset{\text{Barium sulphate.}}{BaO,SO^3 \text{ or } BaSO^4}$$

But, whether this salt be formed under these conditions, or by the action of sulphuric acid, its composition only differs from that of the latter acid by the substitution of Ba for H^2.

H^2SO^4 sulphuric acid, hydrogen sulphate,
$BaSO^4$ barium sulphate.

The reactions which we have just studied, and which indicate the principal methods of the formation of salts, are sufficient to make clear the definition before given, that salts are derived from acids by the substitution of a metal for hydrogen. The nomenclature defines and preserves these relations. To distinguish the different salts of the same acid, the name of the metal is placed first, and this is followed by the name of the acid, which is but slightly changed,—*ic* is changed to *ate*, and *ous* to *ite*.

Thus	Sulphuric acid	gives	sulphates.
	Nitric acid	"	nitrates.
	Perchloric acid	"	perchlorates.
	Sulphurous acid	"	sulphites.
	Hyposulphurous acid	"	hyposulphites.

These generic names follow the names of the metals which enter into the composition of the salts, and which specify them, as it were. Thus, we have:

Potassium sulphate, copper sulphate, lead sulphate, etc.;
Sodium sulphite;
Potassium nitrate, barium nitrate, silver nitrate, etc.

But we know that a single metal may form several compounds with oxygen. In reacting upon the same acid these different oxides give rise to the formation of different salts.

Thus, two different sulphates of mercury are obtained, as sulphuric acid is caused to react with mercurous oxide, or with mercuric oxide.

H^2SO^4	$+$	Hg^2O	$=$	Hg^2SO^4	$+$	H^2O
Sulphuric acid.		Mercurous oxide.		Mercurous sulphate.		Water.
H^2SO^4	$+$	HgO	$=$	$HgSO^4$	$+$	H^2O
		Mercuric oxide.		Mercuric sulphate.		

It is easy to distinguish these two salts from each other by using the adjectives *mercurous* and *mercuric* before the substantive sulphate. Thus, we have chrom*ous* and chrom*ic* sulphates; ferr*ous* and ferr*ic* sulphates.

The preceding considerations will give an idea, sufficient for the time being, of the constitution and the nomenclature of salts. Their further exposition will be completed farther on.

Nomenclature of Non-Oxygenized Compounds.—The non-metallic elements other than oxygen can combine among themselves or with the metals. Such compounds are designated by the name of one of the elements followed by the abbreviated name of the other terminating in *ide*. Thus, the compounds of the metals with chlorine, bromine, iodine, sulphur, arsenic, and carbon are called chlor*ides*, brom*ides*, iod*ides*, sulph*ides*, arsen*ides*, carb*ides*. We thus have sodium chloride, potassium bromide, lead iodide, zinc arsenide, iron carbide. The termination *uret* was formerly used in place of *ide*.

But a non-metallic body, such as chlorine or sulphur, can, like oxygen, form several compounds with the same metal. In these compounds 1 atom of metal may be united with 1 or 2 atoms of sulphur, or with 1, 3, or 5 atoms of chlorine, or again with 2 or 4 atoms of chlorine. Such atomic composition is expressed by the following names and symbols:

Iron *mono*sulphide	FeS
Iron *di*sulphide	FeS^2
Phosphorus *tri*chloride	PCl^3
Phosphorus *penta*chloride	PCl^5
Tin *di*chloride	$SnCl^2$
Tin *tetra*chloride	$SnCl^4$
Antimony *tri*chloride	$SbCl^3$
Antimony *penta*chloride	$SbCl^5$

The names thus express precisely the number of atoms of the second element in combination with 1 atom of the first.

The compounds of chlorine, bromine, iodine, and several other elements with hydrogen are acids; they readily exchange their hydrogen for a metal, so forming compounds that are analogous to the oxygen salts, and which constitute the *haloid salts* of Berzelius.

Experiment.—The compound of chlorine with hydrogen is hydrochloric acid; it is a gas, and dissolves in water, forming a fuming, strongly-acid liquid. When it is carefully poured into a concentrated solution of caustic potash there appears a white precipitate, formed of little crystals and presenting the appearance of a salt. This is potassium chloride. It is formed according to the following reaction, and its formation is attended by the production of heat:

HCl	$+$	KOH	$=$	KCl	$+$	H^2O
Hydrochloric acid.		Potassium hydroxide.		Potassium chloride.		Water.

The hydrogen compounds of bromine, iodine, fluorine, sulphur, etc., possess analogous properties. They are called

Hydrobromic acid	HBr
Hydriodic acid	HI
Hydrofluoric acid	HF
Hydrosulphuric acid or sulphuretted hydrogen .	H^2S

The chlorides may combine among themselves. It is the same with the bromides, iodides, sulphides, etc. If a solution of potassium chloride be poured into a concentrated solution of platinic chloride, a yellow precipitate, constituting a compound of the two chlorides, is formed. It is the double chloride of platinum and potassium, or potassium chloroplatinate.

There exist, likewise, double sulphides formed by the union of two simple sulphides. Such compounds constitute what are called sulpho-salts.

Alloys and Amalgams.—*Alloys* are compounds or mixtures of the metals with each other. *Amalgams* are the alloys of mercury, that is, the compounds of this liquid metal with other metals.

HYDROGEN.

Density compared to air 0.0695
Atomic weight (1 volume taken as unity) $H = 1$.

This body was discovered in 1766 by Cavendish. It is one of the elements of water, hence its name, given by Lavoisier.

Experiments.—1. Into a piece of lead pipe about 4 millimetres bore, 25 millimetres long, and hammered shut at one end small pieces of sodium are pressed until the tube is full. The little tube is then inserted under the mouth of a jar filled with water and inverted in a vessel of the same liquid (Fig. 9). Bubbles of gas at once begin to rise, and by the use of several little tubes charged with sodium the jar can be soon filled with the gas (Newth). This is hydrogen, produced by the decomposition of the water; the reaction is expressed in the following equation:

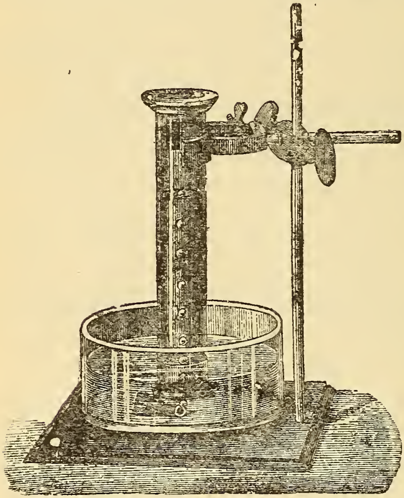

FIG. 9.

$$\underset{\text{Water.}}{2H^2O} + \underset{\text{Sodium.}}{Na^2} = \underset{\text{Sodium hydrate.}}{2NaOH} + \underset{\text{Hydrogen.}}{H^2}$$

If the jar be now inverted and a lighted taper brought to the orifice, the gas will burn with a pale flame. A piece of red litmus-paper will be at once colored blue by the sodium hydrate or caustic soda dissolved in the water in the vessel.

2. Hydrochloric acid is poured upon small pieces of zinc in a glass cylinder (Fig. 10). Rapid effervescence takes place, and if a lighted taper be brought to the mouth of the jar, the hydrogen evolved takes fire. This hydrogen is produced by the decomposition of the hydrochloric acid by the zinc, which is converted into chloride.

$$\underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Zinc chloride.}}{ZnCl^2} + \underset{\text{Hydrogen.}}{H^2}$$

Preparation.—A reaction analogous to the preceding is turned to advantage for the preparation of large quantities of hydrogen. Dilute sulphuric acid is decomposed by zinc.

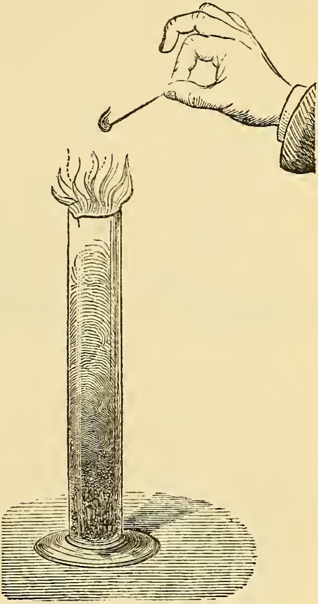

Fig. 10.

A two-necked bottle is about half filled with water, and granulated zinc, or sheet-zinc cut into small pieces, is introduced; sulphuric acid is then added in small quantities by the aid of a funnel-tube which dips under the surface of the water (Fig 11). The reaction at once commences, and hydrogen is disengaged. When the air at first contained in the bottle has been entirely expelled, the gas may be collected in jars or bottles filled with water and inverted on the pneumatic trough.

In this reaction the zinc disappears and dissolves in the liquid with evolution of heat, and it often happens, if the liquid be sufficiently concentrated, that colorless crystals of zinc sulphate are formed on cooling. This salt and hydrogen are the sole products of the reaction of pure zinc upon sulphuric acid largely diluted with water.

$$\underset{\text{Sulphuric acid.}}{H^2SO^4} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Zinc sulphate.}}{ZnSO^4} + \underset{\text{Hydrogen.}}{H^2}$$

Hydrogen may also be obtained by dissolving metals, such as zinc or aluminium, in a strong aqueous solution of potassium or sodium hydroxide.

$$2KOH + Zn = \underset{\text{Potassium zinc oxide.}}{Zn^2O^2K^2} + H^2$$

When hydrogen gas absolutely free from impurities is needed, it is best to prepare it by decomposing water acidulated with sulphuric acid by the electric current (see page 80).

Physical Properties.—Hydrogen is a colorless gas, and when pure has neither taste nor odor. It is the lightest of all known bodies, its density compared to air being 0.0695; that is, if one volume of air weigh 1, one volume of hydrogen, measured under the same conditions of temperature and pressure, weighs only 0.0695. Hydrogen is then 14.388 times lighter than air. The weight of one litre of hydrogen at 0° and under the normal pressure is 0.0899 gramme. Instead of comparing the densities of gases and vapors to that of air it is preferable to compare them to that of hydrogen taken as unity (p. 40).

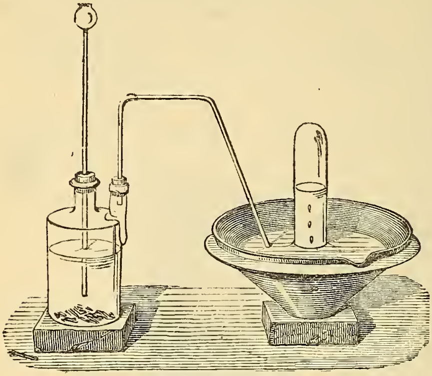

Fig. 11.

Hydrogen passes with great facility through vegetable and animal membranes, and through porous substances that are impervious to water. It cannot be kept in a glass vessel that presents the least crack, for it would pass through much more readily than air. This property is expressed by saying that hydrogen is very diffusible.

According to Magnus, it is the only gas gifted with an appreciable conductivity for heat; in this respect it is related to the metals.

Hydrogen is very slightly soluble in water, its coefficient of solubility being .0215 at 0° and .0174 at 25° (Timofejew).

Of all the known gases hydrogen is, with one exception, the most difficult to liquefy. In order that any gas may be converted into the liquid state it is necessary that its molecules be made to manifest a certain degree of cohesion, and for every gas there is a temperature above which this cannot take place. This is called the *critical temperature*, and the pressure required at this point to bring about liquefaction is known as the *critical pressure*. For hydrogen, according to Olszewski, these conditions are —234° and 20 atmospheres. By subjecting the gas to these conditions, several experimenters had observed an evanescent mist, supposed to be made up of minute droplets of the liquid. In the "dynamic state," *i.e.*, as a coherent mass, and in considerable quantities, it was quite recently obtained by Dewar. Liquid hydrogen is described as colorless and mobile. Its boiling point is about —250°, and its density rather less than 0.07.

Among the physical properties of hydrogen may be mentioned the remarkable faculty it possesses of passing through plates of iron or platinum at high temperatures (H. Sainte-Claire Deville and Troost). It is well known that it rapidly passes through thin sheets of caoutchouc. According to Graham, this property is related to that possessed by certain solid bodies, and particularly metals, such as iron, platinum, and palladium, of absorbing hydrogen gas. This chemist designated the phenomenon by the name, *occlusion* of hydrogen by the metals. Palladium especially is distinguished by the energy with which it absorbs hydrogen. It can condense in its pores nine hundred times its own volume of the gas. A palladium wire may be charged with hydrogen by arranging it in a voltameter so that it constitutes the negative pole of a small battery, the positive pole being a stout platinum wire. When the current passes, the hydrogen set at liberty at the negative pole (see page 81) is condensed in the palladium. This metal undergoes at the same time a remarkable change. Its volume augments and its density diminishes, but its metallic lustre remains, as do also, to a certain degree, its tenacity and conductivity for electricity; besides this, it becomes magnetic. There is thus formed a sort of alloy of palladium and hydrogen, containing about 20 volumes of palladium to 1 volume of hydrogen reduced to the solid state. The density of this solid hydrogen compared to that of water, according to the determinations of Troost and Hautefeuille, is 0.62. Graham insisted upon the metallic character of hydrogen thus alloyed with palladium, but the properties of liquid and solid hydrogen, as observed by Dewar, do not accord with this view.

Chemical Properties.—Hydrogen is a combustible gas, and the product of its combustion is water.

Experiments.—1. A lighted taper may be thrust into a rather wide tube filled with hydrogen (Fig. 14). The gas takes fire on contact with the flame, but the taper is extinguished in the atmosphere of hydrogen. It may be relighted by withdrawing it through the burning gas. The experiment shows at the same time that hydrogen is inflammable and that it is incapable of supporting combustion itself.

2. A gas-bottle, A (Fig. 12), is arranged for the preparation of hydrogen, and water, zinc, and sulphuric acid are introduced. The hydrogen evolved is made to traverse the tube CB, which is filled with fragments of chloride of calcium; after having been dried by this substance, which is very avid of water, the gas escapes by the tube *a*, the end of which is drawn out to a point. The jet of gas is lighted, and burns with a pale flame. A bell-jar, D, is now held over the burning jet, and the sides of the glass soon become covered with dew, the drops of which unite and run down to the edge of the jar. This is water, and it is formed by the combustion of the hydrogen; that is, by its combination with the oxygen of the air.

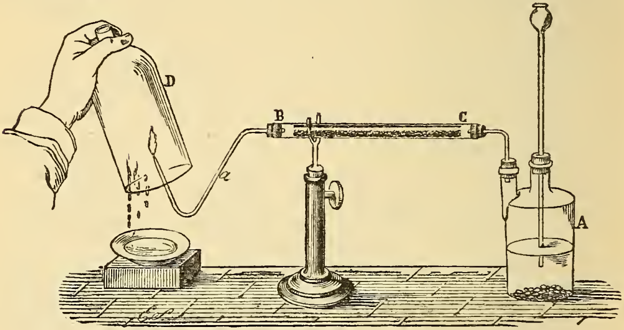

Fig. 12.

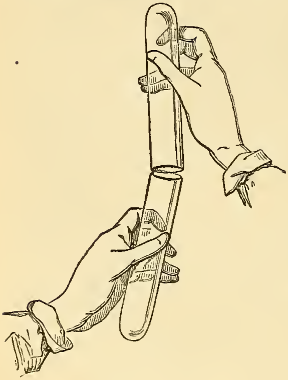

Fig. 13.

3. A jet of hydrogen may be lighted by holding in it a tuft of asbestos which has been dipped in platinum black, that is, finely-divided platinum. The condensation of the hydrogen in the pores of the finely-divided metal is so rapid that the platinum becomes heated to redness, and then ignites the gas.

4. A tube filled with hydrogen may be held in the vertical position, bottom upwards, without the gas escaping rapidly by the inferior opening. If the tube be inclined, the hydrogen overflows and escapes upwards through the air. It may then be received in a second tube held vertically above the first, which is inclined more and more (Fig. 13). The passage of the gas into the upper tube can be demonstrated by approaching to the latter a lighted taper, when the hydrogen will burn with a faint explosion.

Before igniting or collecting hydrogen escaping from a generator, it should always be ascertained that the whole of the air has been expelled, otherwise dangerous explosions may result.

5. The explosions may take place with the production of a harmonious sound, if they are made to succeed each other rapidly and at regular intervals. These conditions are realized by burning a small jet of hydrogen in a somewhat large tube (Fig. 15). The flame is drawn away from the jet by the draft in the tube, but immediately recedes as the ascending hydro-

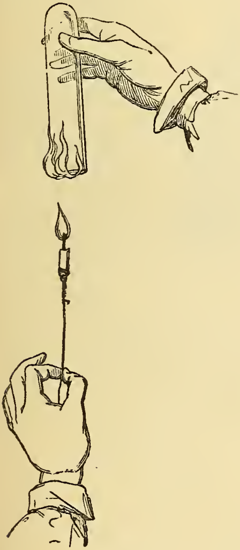

FIG. 14.

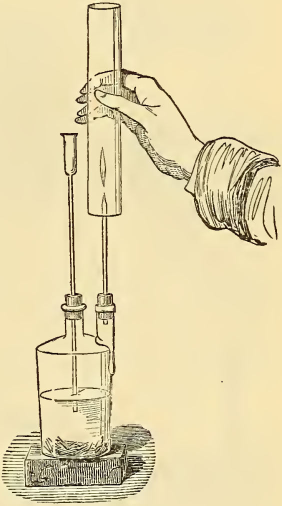

FIG. 15.

gen gas mixes with the air, at the same time producing a faint explosion, and the rapid succession of these explosions produces a musical tone.

The hydrogen condensed in palladium appears to have chemical properties more active than those of gaseous hydrogen (Graham). It combines in the dark and at ordinary temperatures with iodine and chlorine; the direct union of ordinary hydrogen with iodine is impossible, and with chlorine it takes place at the common temperature only under the influence of light. Hydrogen will not support respiration, but it is not poisonous.

OXYGEN.

Density compared to air	1.1015
Density compared to hydrogen	15.88
Atomic weight O	= 15.88

Oxygen was discovered about the year 1774, and independently, by Scheele and by Priestley. The latter obtained it by heating red precipitate or mercuric oxide.

Fig. 16.

Experiment.—A small quantity of mercuric oxide is heated in a hard glass test-tube (*a*, Fig. 16). Presently the tube becomes lined with a mirror of metallic mercury which soon separates into little drops, and if a wooden splint bearing a spark at the end be thrust into the mouth of the tube, it instantly bursts into flame, and burns with great brilliancy. This effect is due to a gas which is being disengaged, and which, to use the expression of Lavoisier, is eminently fitted to support combustion.

It is the gas to which that great chemist gave the name oxygen. It is produced by a very simple reaction. The mercuric oxide has been decomposed by heat into mercury and oxygen.

$$\underset{\text{Mercuric oxide.}}{2HgO} = \underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{O^2}$$

In the same manner a little potassium chlorate is heated in a test-tube. The salt first melts, then an effervescence takes place, and this is due to disengagement of oxygen, as is easily proved by applying the spark test.

Preparation.—Large quantities of oxygen may be prepared by a process based upon this reaction. When potassium chlorate is heated, it is converted into potassium chloride, and gives up all of its oxygen. To facilitate this decomposition a small quantity of manganese dioxide is mixed with the chlorate. The part taken by the manganese dioxide in the reaction is not thoroughly understood; it is probable that it is converted into an unstable higher oxide, continually formed and decomposed during the reaction. If the temperature be sufficiently elevated, the decomposition of the chlorate is complete, and takes place according to the following equation:

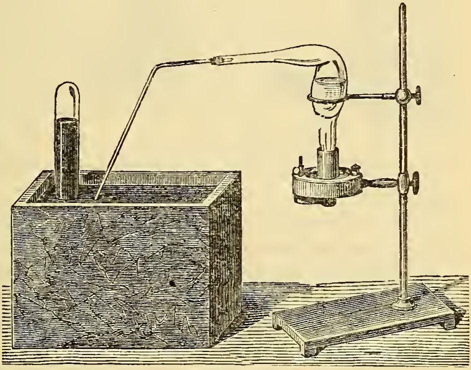
FIG. 17.

$$\underset{\text{Potassium chlorate.}}{2KClO^3} = \underset{\text{Potassium chloride.}}{2KCl} + \underset{\text{Oxygen.}}{3O^2}$$

The operation may be conducted in a glass retort, which should be about one-third filled with the mixture of chlorate and dioxide; to the beak of the retort is adapted a delivery-tube, which dips under the surface of the water or mercury in the trough (Fig. 17). The retort is then heated by an alcohol or gas lamp, and the chlorate melts and disengages its oxygen with effervescence. Towards the close of the operation, the heat is increased in order to decompose into potassium chloride and oxygen any potassium perchlorate that may have been formed by the union of a portion of the evolved oxygen with some of the chlorate.

To make larger quantities of oxygen for filling the gas-holders of laboratories, etc., a mixture of potassium chlorate and manganese dioxide is heated in a sheet-iron or copper retort (Fig. 18).

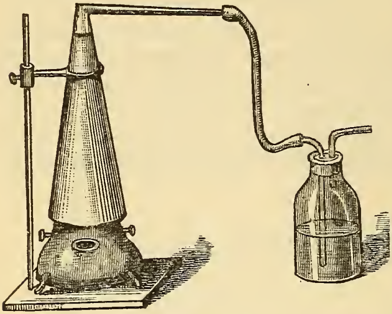

Fig. 18.

At a bright red heat manganese dioxide gives up a third of its oxygen and is converted into the red oxide of manganese.

$$\underset{\text{Manganese dioxide.}}{3MnO^2} = \underset{\text{Red oxide of manganese.}}{Mn^3O^4} + \underset{\text{Oxygen.}}{O^2}$$

Powdered potassium dichromate may be heated with twice its weight of concentrated sulphuric acid. Oxygen is disengaged.

$$\underset{\text{Potassium dichromate.}}{2K^2Cr^2O^7} + 8H^2SO^4 = \underset{\text{Potassium and chromium sulphate.}}{2K^2SO^4, Cr^2(SO^4)^3} + 8H^2O + 3O^2$$

On the large scale oxygen is manufactured by a process devised by Brin. Air is forced into a specially prepared porous barium oxide, BaO, at a temperature below redness, and barium dioxide, BaO_2 is formed. The stream of air is cut off and the barium oxide is heated to redness, the pressure in the apparatus being lowered by air-pumps. The oxygen absorbed is now disengaged, and the barium dioxide is converted into monoxide ready to absorb more oxygen.[1]

Physical Properties.—Oxygen is a colorless, odorless, tasteless gas; it is a little heavier than the air. If one volume of hydrogen weighs 1, the same volume of oxygen, measured under the same conditions of temperature and pressure, weighs 15.88. This is expressed by saying that the density of oxygen compared to that of hydrogen is 15.88. A litre of oxygen weighs 1.429 gr. at 0° and under the normal pressure.

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[1] Oxygen is now sold compressed in strong steel bottles, from which it may be conveniently drawn as required for experiment.

Oxygen, which was formerly regarded as a permanent gas, was liquefied by Cailletet, and also by Pictet, in 1877. Its critical temperature is —118°, and the critical pressure 50 atmospheres. The liquid has a bluish color, its specific gravity is 1.124, and it boils at —183°.

Oxygen is but slightly soluble in water. A litre of water dissolves 0.041 litre, or 41 cubic centimetres, at 0°; 0.032 litre at 10°; 0.028 litre at 20°. The fractions 0.041, 0.032, 0.028, represent the *coefficients of solubility* of oxygen in water at the temperatures of 0°, 10°, and 20°.

Chemical Properties.—Oxygen combines directly with most of the other elements, and the union often takes place with such energy that there results a great evolution of light and heat; it gives rise to the phenomenon of combustion.

Experiments.—A cone of charcoal of which the point is red-hot is plunged into a globe filled with oxygen (Fig. 19), and immediately combustion takes place with great brilliancy. The oxygen combines with the carbon, forming a colorless gas, which is carbonic acid gas.

In like manner, sulphur and phosphorus burn in oxygen, the first producing a colorless, irritating gas known as sulphurous acid gas, the second emitting thick fumes, which condense in white flakes of phosphoric oxide.

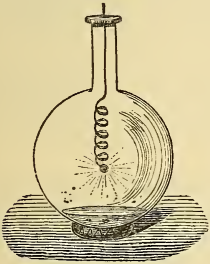

Fig. 19.

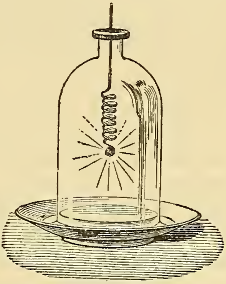

Fig. 20.

A watch-spring may be drawn out into a spiral, and a small piece of tinder attached to one end; after igniting the tinder, the spiral is rapidly plunged into a bell-jar filled with oxygen, and resting upon a plate containing a layer of water (Fig. 20). The tinder burns energetically, and heats the end of the spiral to redness; then the combustion of the iron itself commences, and goes on with extraordinary brilliancy, and a production of heat so intense that the oxide of iron formed melts and falls in incandescent drops, which fuse themselves into the surface of the plate, even after having traversed the layer of water.

In the same manner, the combustion of the metal magnesium may be effected in oxygen ; it takes place with dazzling splendor, and gives rise to the production of a white powder, which is magnesia, or magnesium oxide.

The preceding experiments are examples of *rapid combustion.* We have seen that solid substances, such as charcoal, iron, and magnesium, become incandescent in combining with oxygen : it is the phenomenon of fire. We have also seen that vapors, like those of sulphur and phosphorus, become luminous in their combination with oxygen : this is the phenomenon of flame.

But fire and flame are not necessary concomitants of the union of bodies with oxygen. It is true that such union is always accompanied by the production of heat; but often this heat is not attended by light; sometimes it is imperceptible to our senses.

Thus iron, the combination of which with oxygen at a red heat gives rise to such a brilliant combustion, may unite with this gas at ordinary temperatures under the influence of moisture. There is thus formed ferric hydrate, which constitutes rust.

This oxidation of the iron, which takes place slowly, produces a feeble disengagement of heat, which is, however, immediately dissipated. Such phenomena of oxidation are designated by the name *slow combustion.*

The term combustion would then be synonymous with oxidation did we not know, on the other hand, that all chemical combination gives rise to the production of heat. If copper be thrown into boiling sulphur, a vivid incandescence is produced, due to the union of the two bodies. Likewise antimony and arsenic, when projected in fine powder into an atmosphere of chlorine, unite with the latter body, producing a brilliant combustion. It is seen that in these cases the production of light and heat indicates an energetic combination, but not an oxidation.

Oxygen is one of the elements of the air ; it is the cause and the agent of all combustion, of all oxidation which takes place in our atmosphere ; and the oxygen fixes itself upon burning bodies in such a manner that the product of the combustion contains all of the matter of the combustible body and all of the matter of the oxygen. This is one of the fundamental truths of chemistry, and for its discovery not less than a century and a half of work was required. The glory of the discovery belongs to Lavoisier.

His researches on combustion revealed to him the true nature of the phenomena of respiration. The respiration of animals is a slow combustion; it is the source of animal heat. It gives rise to the formation of carbonic acid gas and water, products of the complete oxidation through which must pass those organic matters in the economy which no longer serve the purposes of life, and all of which contain carbon and hydrogen.

The production of carbonic acid gas by the act of respiration is easy to prove. It is only necessary to blow, by the aid of a tube, the air contained in the lungs through clear lime-water, which soon becomes milky from the formation of insoluble carbonate of lime.

An annular jet of hydrogen through which a jet of oxygen is forced constitutes what is known as the oxyhydrogen blowpipe, and is one of the most intense sources of heat known. Platinum melts before it like wax, and iron and other combustible metals burn brilliantly when introduced into its flame. The flame of the oxyhydrogen blowpipe gives but little light, but when it is projected upon a piece of lime, the latter becomes heated to dazzling incandescence, constituting the Drummond or calcium light.

OZONE, OR OXYGEN PEROXIDE.

The repeated discharges of a good electric machine develop a peculiar odor. This is due to the production of a body which was discovered by Schönbein in 1840, and which he named ozone (from ὄζω, I smell).

Experiment.—Some potassium permanganate is mixed with barium dioxide in a mortar, the mixture transferred to a flask, and moistened with sulphuric acid. The characteristic odor of ozone immediately becomes perceptible, and a moistened paper, impregnated with potassium iodide and starch and held in the neck of the flask, immediately assumes a blue color.[1] This effect is caused by the ozone evolved.

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[1] Such a paper is called ozonoscopic. It is colored blue by the combina-

This remarkable body is also formed under the following circumstances.

1. *By the passage of electric discharges through oxygen.* It is sufficient to pass a series of electric sparks through oxygen contained in a tube above a solution of iodide of potassium and starch, in order to produce the blue color caused by the ozone (Fig. 21).

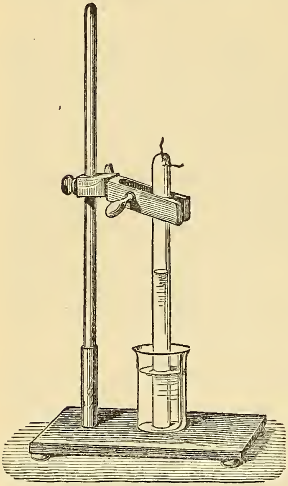

Fig. 21.

It has been noticed that the largest quantity of ozone is produced when the passage of the electricity through oxygen is effected, not by sparks, but by non-luminous or silent discharges (Andrews and Tait, von Babo). Dry and pure oxygen can be converted into ozone in this manner. But this conversion only takes place partially, the ozone formed remaining mixed with a large excess of oxygen. A contraction takes place at the moment the oxygen is transformed into ozone. These experiments prove that ozone is condensed oxygen.

An elegant and efficient apparatus for the ozonation of oxygen by electricity was devised by Berthelot and is shown in Fig. 22. *c* is a long, thin glass tube closed at the bottom, near which a bent tube, *b*, is soldered in, while a similar tube is joined to it near the top. *d* is a narrower and longer tube, closed at one end, which passes nearly to the bottom of *c*, into the mouth of which it is adapted by a bulb and ground joint. *d* is filled with dilute sulphuric acid, and the whole apparatus is placed in a jar of the same, as shown in the figure. By

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tion of the starch with the iodine set at liberty by the ozone. According to Houzeau, it is preferable to use a delicate, wine-colored litmus-paper, one-half of which is impregnated with potassium iodide. Ozone will change the color of this half to blue, for, in decomposing the potassium iodide, it forms potassium hydrate, and this restores the blue color to the litmus. Under these conditions, the other half of the paper undergoes no change in color, while it would be colored red by acid vapors, or blue by ammonia.

platinum wires the columns of sulphuric acid are made the poles of an induction coil, and oxygen is passed by one of the side tubes through the annular space in the apparatus. Under the influence of the obscure discharges the gas is rapidly ozonized.

The proportion of ozone formed is increased when the oxygen is cooled. At —23°, a mixture of oxygen and ozone, containing 17.6 per cent. of the latter, may be obtained, under normal atmospheric pressures. (Hautefeuille and Chappuis.)

2. *By the electrolysis of water.*—When acidulated water is decomposed by the battery current, the oxygen which is disengaged at the positive pole contains small quantities of ozone, and the proportion of the latter may be increased by adding a quantity of sulphuric or chromic acid to the water.

3. *During slow oxidation.*—Some sticks of cleanly-scraped phosphorus are introduced into a bottle containing enough water to just about half immerse them, and the whole is agitated from time to time. In a short time the air in the bottle will be charged with a small quantity of ozone.

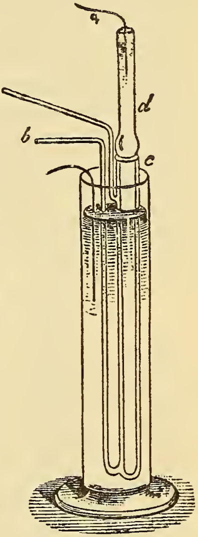


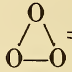
Fig. 22.

According to Schönbein, who observed these facts, ozone is produced during all slow combustions. Thus, when oil of turpentine is exposed to the air under the influence of sunlight, it is slowly oxidized, and in becoming resinified, it becomes at the same time charged with a small quantity of ozone.

Properties of Ozone.—Ozone possesses an intense and peculiar odor. Hautefeuille and Chappuis have liquefied it by allowing the strongly compressed gas to expand suddenly: the liquid is sky-blue, and the compressed gas has the same color, the tint being deeper as the temperature is lowered or the pressure increased. At a temperature of 290° it is reconverted into ordinary oxygen, the volume of which is greater than that occupied by the ozone. It is then certainly condensed oxygen. It has energetic oxidizing properties; it even oxidizes bodies which possess only feeble affinities for oxygen. In the presence of alkalies it combines with nitrogen, converting it into nitric acid, which combines with the alkali.

It oxidizes silver at ordinary temperatures, converting it into the dioxide Ag^2O^2. It instantly decomposes potassium iodide, setting free the iodine. It dissolves in about twice its volume of water, and is quite readily soluble in oil of turpentine, which it slowly oxidizes. It oxidizes and destroys most organic substances. In most of these oxidations only a third part of the oxygen contained in ozone is active; the other two-thirds become free as ordinary oxygen, the volume of which is exactly equal to that originally occupied by the ozone.

Hence it is concluded that 3 volumes of oxygen are condensed into 2 volumes by their conversion into ozone, and if ordinary oxygen be the oxide of oxygen OO, ozone will be oxygen peroxide OO^2 (Odling).

$O{=}O$ = 2 vol. oxygen.  = 2 vol. ozone.

This conclusion of Odling's concerning the nature of ozone, has been verified by the determination of the density of this body. Soret has established that when ozone diluted with oxygen is absorbed by oil of turpentine or oil of cinnamon, there is a diminution of volume sensibly double the increase of volume noticed on subjecting the same gas to the action of heat. He naturally concludes that the density of ozone is one and a half times that of oxygen, or 1.658. These figures have been confirmed by direct experiments upon the rapidity of diffusion of ozone. It has been shown by the researches of Graham that when diffusion between two gases takes place through an opening, without the interposition of a diaphragm, the rapidity of diffusion is inversely as the square roots of the densities of the gases. Soret has demonstrated that the rapidity of diffusion of ozone is notably greater than that of chlorine, and very near but somewhat less than that of carbonic acid. It follows that its density is less than that of chlorine, and a little greater than that of carbonic acid, which is 1.525; this confirms the density 1.658.

An important property of ozone is its reaction with hydrogen dioxide, yielding ordinary oxygen and water.

$$\underset{\text{Ozone.}}{OO^2} + \underset{\text{Hydrogen dioxide.}}{H^2O^2} = \underset{\text{Ordinary oxygen.}}{2(OO)} + \underset{\text{Water.}}{H^2O}$$

ATMOSPHERIC AIR.

The air is a mixture of oxygen and nitrogen. It also contains a little less than one per cent. by volume of a gas recently discovered by Lord Rayleigh and Professor Ramsay, and named by them *argon*,[1] traces of carbonic acid gas, and a variable proportion of vapor of water.

Its composition was established by Lavoisier by an experiment that has become celebrated. Having heated mercury in a limited quantity of air to a temperature near its boiling-point for several days, he observed the formation of a red powder, a combination of the mercury with oxygen. On the termination of the experiment, he found that the volume of the air had diminished about one-sixth. He carefully collected the oxide formed, introduced it into a small retort, and heated it to redness. He thus obtained a gas "eminently qualified to support combustion and respiration," and the volume of which was sensibly equal to that of the gas that had disappeared. This gas he named oxygen. He mixed it with the irrespirable residue from the first experiment, which would not support combustion, and so reconstituted atmospheric air. The composition of the latter was thus established by analysis and synthesis. This experiment was infinitely more instructive than that undertaken by Scheele at about the same time. The great Swedish chemist only absorbed the oxygen of the air by the alkaline sulphides. The nitrogen remained as residue, but the oxygen combined with the sulphide could not be again separated.

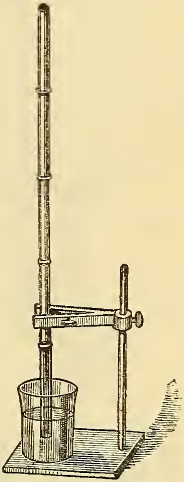


FIG. 23.

However, neither one nor the other of these methods could give the exact proportion according to which the oxygen and nitrogen are mixed in the atmosphere. This has been deduced from experiments like the following.

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[1] In the analysis of air by the methods to be presently described, the argon remains mixed with the nitrogen.

Experiments.—1. A straight glass tube closed at one end (Fig. 23) is graduated as exactly as possible into five parts of equal capacity by caoutchouc bands placed around the tube. A dry piece of phosphorus, about half a cubic centimetre in volume, is dropped into the tube, the latter is tightly corked, and the phosphorus inflamed by plunging the end of the tube into hot water. By rapidly inverting the tube and tapping the corked end on the table the ignited phosphorus is caused to fall the whole length of the tube, and in burning consumes all the oxygen of the contained air. The tube is allowed to cool, and the cork is withdrawn under colored water in a beaker. The water rises to the first band, showing that the oxygen gas removed constituted about one-fifth of the air in the tube. The gas remaining in the tube is principally nitrogen.

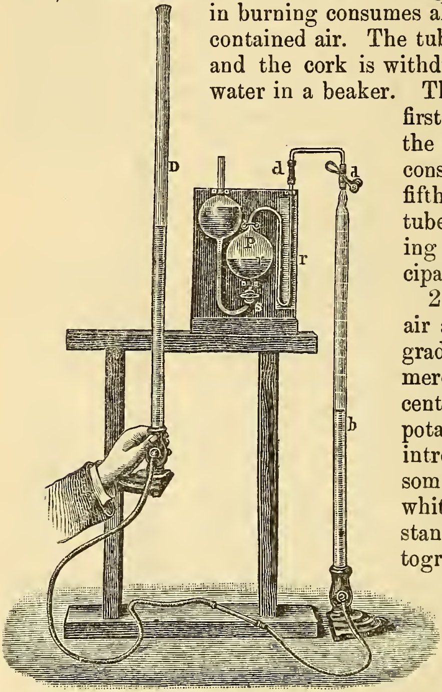

Fig. 24.

2. 100 volumes of air are measured into a graduated tube on the mercury-trough. A concentrated solution of potassium hydrate is introduced, and then some pyrogallic acid, a white, crystalline substance employed in photography. The extremity of the tube is now closed by the thumb and the contents rapidly agitated. The alkaline solution is immediately blackened by the oxidation of the pyrogallic acid. All the oxygen is absorbed, and when the tube is opened, under the surface of the mercury, the 100 volumes of air are found reduced to about 79 volumes, and the experi-

ment shows that the air contains about 21 per cent. by volume of oxygen.

3. 50 cubic centimetres of air are measured off in a Hempel gas burette (*b*, Fig. 24) and transferred to the explosion pipette, *r*, by raising reservoir-tube D. In the same manner 50 cubic centimetres of pure hydrogen are introduced. The stop-cock S and the clip *d* are now closed, and by means of the platinum electrodes P, which are fused through the walls of the pipette, a spark from an induction coil is sent through the gaseous mixture. A flash is observed and all the oxygen contained in the air combines with hydrogen to form water. The residual gas is returned to the burette and measured: it is found to have undergone a considerable contraction in volume, and one-third of this contraction represents the volume of oxygen contained in the sample of air taken, for two cubic centimetres of hydrogen disappear for each cubic centimetre of oxygen.

It is found that of the 100 cubic centimetres of gas introduced into the apparatus, 31.395 cubic centimetres have disappeared, showing that the 50 cubic centimetres of air introduced into the apparatus contained 10.465 cubic centimetres of oxygen. The remaining 39.535 cubic centimetres consist of nitrogen mixed with 1.186 per cent. of argon, and a trace of carbonic acid.

Hence 100 volumes of air contain practically 20.93 volumes of oxygen and 79.07 volumes of nitrogen.

Such is the composition of the air by volume. As nitrogen is lighter than oxygen, these volumetric relations do not express the composition of the air by weight. This was determined very exactly by Dumas and Boussingault in the following manner.

A globe, A (Fig. 25), having a capacity of 15 or 20 litres, and fitted with a brass cap and stop-cock, R″, by which it may be connected with an air-pump, is joined to a hard glass tube, BB′, having a stop-cock at each end, R and R′, and filled with metallic copper. The air is exhausted from the globe and tube, and the weight of each is then accurately determined.

The tube BB′ is placed in a combustion-furnace, and by its extremity B′ is connected with the tubes K, I, H, G, F, E, D, C. The tube with bulbs C contains a solution of caustic potash; the tubes D and E are filled with pumice-stone impregnated with caustic potash, and the tubes F and G with fragments of solid caustic potash; the bulbs H contain sulphuric acid, and the last tubes, I and K, are filled with fragments of pumice-stone saturated with sulphuric acid. The potash serves to remove from the air the small quantity of carbonic acid gas which it contains, and the sulphuric acid absorbs the moisture.

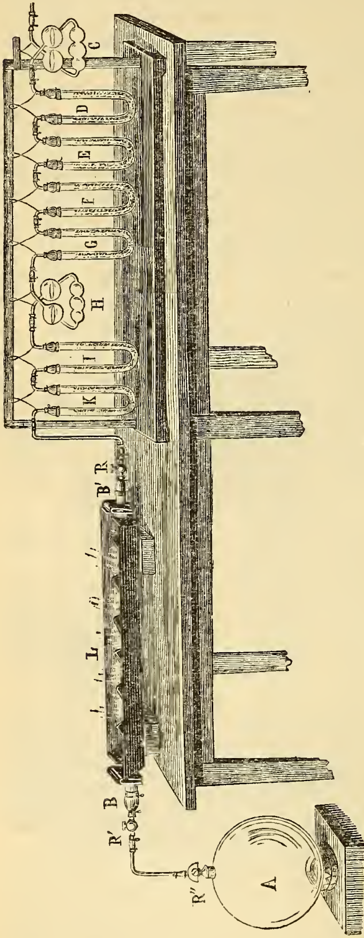

Fig. 25.

The tube filled with copper is now heated to redness, its stop-cocks being open, and the stop-cock of the globe is gradually opened. Air immediately enters, but it is first obliged to traverse the series of tubes, where it is deprived of its carbonic acid gas and vapor of water, and also the tube filled with incandescent copper, which absorbs the oxygen. It is then pure nitrogen which enters the globe. The experiment has terminated when the tension of the gas in the globe is equal to the exterior pressure, that is, when no more air enters. The stop-cock R″ is now closed. The tube and globe are allowed to cool, and are weighed separately.

The increase in weight of the globe gives the weight of the nitrogen which has entered.

The increase in weight of the tube, which was first weighed exhausted of air, gives the weight of the oxygen which has combined with the copper, plus the weight of the nitrogen remaining in the tube at the close of the experiment. The weight of this nitrogen is determined by exhausting the tube and weighing a third time. The difference between the second and third weighings indicates the weight of the nitrogen remaining in the tube at the end of the experiment, and this weight added to that of the nitrogen contained in the globe constitutes the total weight of nitrogen in the air analyzed.

The weight of the oxygen is given by the difference between the third and first weighings of the tube.

By this method Dumas and Boussingault found that 100 parts of air contain by weight

Oxygen	23.13
Nitrogen	76.87

These two gases are simply mixed in the air; they do not exist there in a state of combination; and the proportions of the mixture are universally the same with very slight variations. At the summits of the highest mountains, at the centres of the continents, and over the vast expanse of the seas, the air has been shown to be nearly equally rich in oxygen. From a comparison of a great number of analyses, Regnault has established that as a rule the percentage of oxygen only varies from 20.9 to 21.0; air which has been collected on the open sea and close to the surface of the water, has been found to contain a somewhat smaller amount (20.6), a circumstance which may be attributed to the dissolving action of the water.

Nitrogen and oxygen are by far the most abundant constituents of the atmosphere; among the substances which are contained in small proportion must be mentioned particularly the new element argon, carbonic acid gas, and vapor of water.

Argon, A = 40?—When the nitrogen obtained from air is absorbed by heated magnesium there remains a small unabsorbable residue, which, when fully purified from all known elements, appears to be entirely inert; hence the name argon (*ἄργον*, idle, inactive). This new element was discovered by Rayleigh and Ramsay in 1894, and constitutes about 0.94 per cent. of air. It is colorless, has a density of about 20 compared to hydrogen, and has about the same solubility in water as oxygen. Its critical temperature is —121°, and the critical pressure 50.6 atmospheres. The experiments thus far made show that it is incapable of combining or reacting with other substances, and chemical activity is not excited in it even by the electric spark.

Carbonic Acid Gas and Vapor of Water.—If lime-water be poured into a flat dish and exposed to the air, in a few hours its surface will be found covered with a white pellicle formed of little crystals of calcium carbonate.

This experiment demonstrates the presence of carbonic acid gas in the atmosphere. The watery vapor may be condensed by exposing to the air a glass vessel containing a mixture of ice and salt. The sides of the vessel soon become covered with a layer of frost, resulting from the solidification of the water which has been condensed from the air by the cool surface of the glass.

The exact quantities of carbonic acid gas and vapor of water contained in the air may be determined by drawing the latter through tubes containing sulphuric acid and caustic potash. The aspiration is obtained by means of a bottle or a tin vessel, V (Fig. 26), filled with water. On opening the stop-cock *r*, the water runs out, and air is drawn in through the tubes F and E, filled with fragments of pumice-stone wetted with sulphuric acid, then through D and C, containing pumice-stone

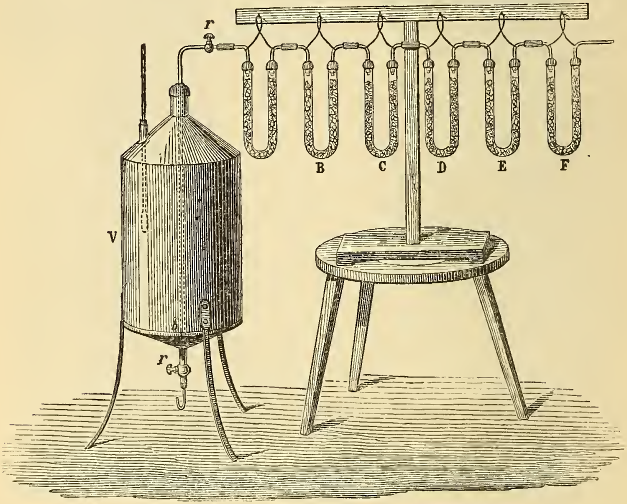

Fig. 26.

impregnated with caustic potash, and finally B, which is like the first two. These tubes increase in weight from the absorption of vapor of water in the first two, and carbonic acid in the others. The difference in weight of the tubes F and E before and after the experiment gives the proportion of condensed water; the difference of D, C, and B gives the proportion of carbonic acid gas. The volume of air is equal to that of the water which has run out of the aspirator.

The quantity of carbonic acid gas contained in the air varies from 0.029 to 0.033 per cent. It is increased in inhabited places. It is greater at night than during the day, a circumstance that must be attributed to the influence of vegetation. It is diminished after a rain, and is found in its minimum proportion above the surface of large lakes.

The sources of this carbonic acid gas are various. In certain regions fissures in the earth disengage large volumes; volcanoes emit immense quantities; certain spring waters are supersaturated, and disengage it in abundance when they reach the surface of the earth. But the greater portion is produced by the phenomena of combustion which take place on the earth's surface; and among these phenomena must be included respiration, which is a slow combustion.

Experiment.—If by the aid of a glass tube air from the lungs be blown through lime-water, the latter becomes clouded, by the formation of calcium carbonate. The carbonic acid gas thus fixed by the lime comes from the respiration, which is an abundant source of that gas.

Does carbonic acid gas accumulate indefinitely in the atmosphere? No. Rejected and excreted by animals, it serves for the respiration of plants. The green parts of vegetables possess the power of decomposing this gas under the influence of the sun's light. The carbon is fixed, and serves for the nutrition of the plant; the oxygen is rejected, if not wholly, at least in great part.

Besides the constituents that have been enumerated, the air contains other matters in very minute proportions. These include:

1. Traces of ammonia, or rather of ammonium compounds. These substances are dissolved by rain-water, and play an important part in vegetable physiology.

2. A small quantity of nitric acid in the form of ammonium nitrate. It is supposed that nitric acid is formed in the air by the direct union of the nitrogen and oxygen under the influence of atmospheric electricity. In addition to this nitric acid, the air con-

tains nitrous acid, also in the form of an ammonium salt, NH^4NO^2, and it is mainly from these compounds that most plants derive the nitrogen they require for their growth.

3. A very minute and variable proportion of a substance which has the power of liberating iodine from potassium iodide, and which is generally believed to be ozone.

4. Exceedingly small amounts of four gaseous elements, the existence of which has only recently been made known by the researches of Ramsay and Travers. These new constituents of the air closely resemble argon: they appear devoid of chemical energy, and their molecules consist of single atoms. All four are, however, distinctly characterized by their spectra (see page 316), and they differ from one another also in their physical constants, such as density and boiling point. *Krypton*, Kr, has a density approaching 40, and is found in what remains when a large quantity of liquid air is evaporated to a small bulk. The other three are "Companions of Argon," being contained in different fractions of the gas given off when liquefied crude argon is made to boil. Of these, *neon*, Ne, is the lightest (density about 11) and most volatile, while *metargon*, $A\mu$, and *xenon*, X, are specifically heavier (approximate densities 20 and 64), and less volatile than even argon.

5. Solid particles suspended in the air and carried to a distance by the winds. In perfectly calm air these corpuscles are deposited, forming a dust of which the composition is very variable. It contains various microscopic vegetable and animal germs (Pasteur).

WATER.

Vapor density compared to air	0.621
Vapor density compared to hydrogen[1]	8.94
Molecular weight H^2O	= 17.88[2]

Water is the product of the combination of hydrogen and oxygen; its composition was established by Lavoisier in 1783. The combination takes place exactly in the ratio of 2 volumes of hydrogen to 1 volume of oxygen, as demonstrated by the following experiments:

1. *Analysis of Water by Electrolysis.*—Water acidulated

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[1] The density of vapor of water compared to that of hydrogen is 8.94; that is, if the weight of 1 volume of hydrogen be represented by 1, the weight of 1 volume of vapor of water will be 8.94; in other words, vapor of water is nearly nine times more dense than hydrogen under the same conditions of temperature and pressure.

[2] The weight of the molecule, or the molecular weight, expresses the weight of 2 volumes of vapor, if the weight of 1 volume of hydrogen be represented by 1.

with sulphuric acid is poured into the bulb of a Hofmann's electrolysis apparatus (Fig. 27) until it rises in the tubes to the level of the stop-cocks, which are open. The latter are then closed, and by means of platinum wires fused through the glass and connected with two platinum plates, one in each limb of the tube, a current from a galvanic battery is passed through the liquid in the bend of the tube. Water is decomposed and bubbles of gas arise in each tube, collect together, and force the liquid up into the bulb. It soon appears that the gas disengaged at the negative pole is sensibly double in volume that disengaged at the positive. The first is hydrogen, and the second oxygen, and the proportion in which these gases are set free would be exactly that of 2 to 1, were it not that a small quantity of oxygen remains dissolved in the acid liquid, or, under certain conditions, combines with a portion of the water surrounding the negative pole to form hydrogen dioxide, as will be mentioned farther on.

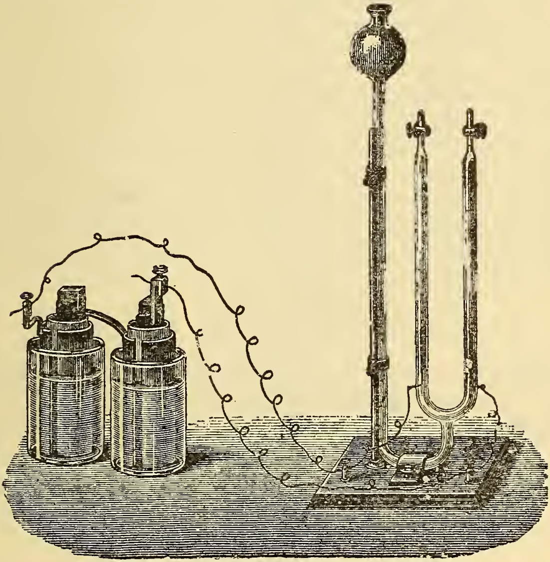

FIG. 27.

2. *Eudiometric Synthesis.*—The composition of water can be established by *synthesis*, that is, by the combination of the two elements, hydrogen and oxygen. The experiment, which is made in an eudiometer, has already been described (page 38). It demonstrates that the two gases combine in the exact ratio of 2 volumes of the first to 1 of the second, and that these 3 volumes of gas are condensed into 2 volumes of vapor of water.

These experiments establish the volumetric composition of water; its composition by weight can be deduced from them, the densities of hydrogen and oxygen being known; for the weighable matter of 2 volumes of hydrogen being added to the weighable matter of 1 volume of oxygen, it is only necessary to add twice the weight of 1 volume of hydrogen to the weight of 1 volume of oxygen in order to determine the weight of 2 volumes of vapor of water. That is to say, the ratio by weight in which hydrogen combines with oxygen to form water is that of double the density of hydrogen (the weight of 2 volumes of H) to the density of oxygen (the weight of 1 volume of O). This ratio is

$$\frac{2 \times 0.0695}{1.1015} = \frac{0.1390}{1.1015} = \frac{1}{7.94}$$

It may be deduced in a more simple manner by a comparison of the densities of hydrogen and oxygen. If 1 volume of hydrogen weighs 1, 1 volume of oxygen weighs 15.88; the weight of 2 volumes of hydrogen will then be 2, and it will be seen that the two gases unite, by weight, in the ratio of

$$\frac{2}{15.88} = \frac{1}{7.94}$$

17.88 grammes of water then contain 15.88 grammes of oxygen and 2 grammes of hydrogen. This composition of water by weight has also been ascertained by various other methods, of which that employed by Dumas has become classic, and will now be described.

3. *Synthesis of Water by the Gravimetric Method.*—In order to determine the composition of water by synthesis it is sufficient to combine an indeterminate quantity of hydrogen with a precisely determined weight of oxygen, and to weigh exactly the water formed. By subtracting from this latter weight that

of the oxygen contained in the water, the weight of the hydrogen which has combined with that oxygen is obtained.

In order to thus combine hydrogen with oxygen, it is convenient to make the former gas react upon an oxidized body which will readily yield its oxygen to the combustible gas. Cupric oxide, or black oxide of copper, CuO, first suggested by Gay-Lussac, and employed for this purpose by Berzelius and Dulong, fulfils these conditions. Although undecomposable by heat alone, it is readily reduced by hydrogen when heated in an atmosphere of that gas. Dumas employed the apparatus represented in Fig. 28.

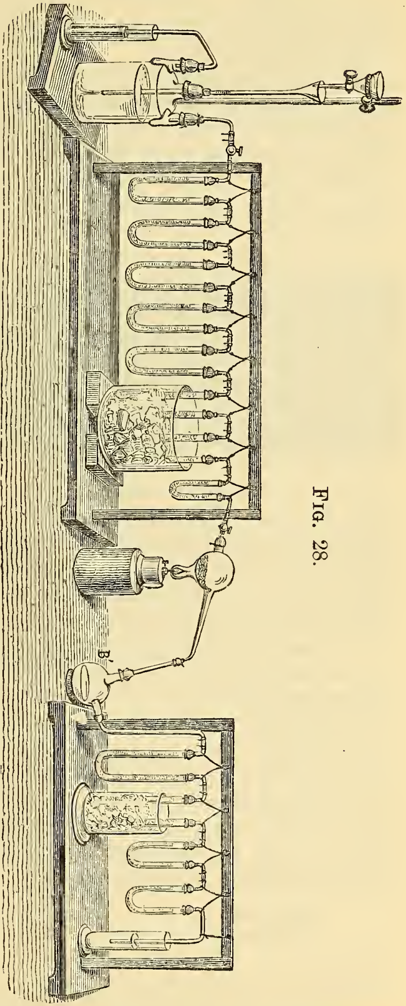

FIG. 28.

Hydrogen is prepared by the action of dilute sulphuric acid upon zinc, and is purified by being conducted through a series of U tubes, the first containing fragments of glass wet with a solution of lead acetate, the second, fragments of glass wet with a solution of silver sulphate, and the third, pumice-stone, impregnated with caustic potassa. The lead acetate retains hydrogen sulphide; the silver sulphate absorbs hydrogen arsenide, and the potassa absorbs any traces of carbides of hydrogen.

The hydrogen thus purified is dried by passage through another series of U tubes, the first containing calcium chloride, and the others pumice-stone saturated with sulphuric acid. The latter tubes are cooled by being surrounded with ice. The gas is lastly passed through a smaller tube containing phosphoric oxide. The weight of this tube must remain constant during the whole of the experiment. It is called the *control-tube.*

The pure and dry hydrogen now passes through a hard glass bulb, which contains pure cupric oxide. The weight of this bulb, together with the oxide which it contains, is determined with care. The receiver B′, as well as the U tubes which terminate the apparatus, are also accurately weighed.

When the whole of the air contained in the apparatus has been expelled by the hydrogen, the bulb is heated and the cupric oxide is reduced. Water is formed and is in great part condensed in the liquid state in the receiver, but a portion of the vapor remains uncondensed and is carried off by the excess of hydrogen. This vapor is retained in the second series of U tubes, which contain calcium chloride and pumice-stone saturated with sulphuric acid. When the reduction has almost terminated, the bulb is allowed to cool, the current of hydrogen being continued; this gas is finally displaced by a current of air, and the weighings are then made.

The weight of the bulb has decreased by that of all of the oxygen which has been taken from the oxide of copper by the hydrogen, and which now exists in the water formed.

The weight of the receiver and the condensing apparatus connected with it is increased by the weight of all the water formed.

By subtracting the weight of the oxygen from that of the water we find the weight of the hydrogen.

By the aid of this rigorous method it is found that 100 parts by weight of water contain[1]

Hydrogen	11.18
Oxygen	88.82
	100.00

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[1] The figures given are slightly different from those obtained by Dumas. They represent the mean results of more recent investigations by Rayleigh, Scott, Morley, and others. By uniting oxygen and hydrogen directly, and weighing the gases before they combine, as well as the water produced, Morley has achieved completeness in this gravimetric synthesis.

These numbers are in the exact ratio of

Hydrogen	1
Oxygen	7.94

Physical Properties.—Pure water has neither taste nor odor. It is limpid and colorless. It occurs in three states in nature; during the colds of winter it is solid, assuming the different forms of ice, snow, frost, and hail. The temperature at which ice melts is one of the standard points in the thermometric scale. To this temperature corresponds the 0 of the centigrade scale, which is adopted in this work.

Snow consists of aggregations of minute hexagonal crystals like those shown in Fig. 29.

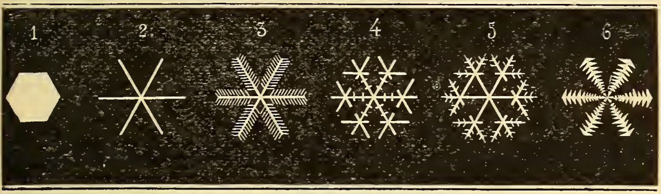


Fig. 29.

At the moment of freezing, water expands, and its density is then less than that which it possesses in the liquid state. The density of ice is 0.93. Water contracts in volume from 0 to + 4°, and presents its maximum density at the latter temperature. Its density at this point is chosen as the unit of comparison for the densities of solid and liquid bodies.

Water and even ice are continually emitting invisible vapors which mix with the air, and are, as it were, dissolved in it. This vaporization increases as the temperature is raised.

The air is said to be saturated with vapor at any given temperature when it refuses to take up any more vapor at that temperature. Under these conditions, if the temperature be lowered, a portion of the vapor is condensed in fine drops, which remain suspended in the air in the form of mist or visible vapor. The point at which the moisture of the air is condensed is called the *dew-point.*

Water begins to boil when its vapor acquires sufficient tension to overcome the atmospheric pressure. This is the boiling-point, and under a pressure of 0.760 metre corresponds to 100° of the centigrade scale.

Chemical Properties.—Water is partially decomposed by the highest temperatures at our command. On pouring melted platinum into an iron mortar containing water, Grove observed a disengagement of bubbles composed of an explosive mixture of oxygen and hydrogen. According to H. Sainte-Claire Deville, vapor of water undergoes a partial decomposition, which he calls *dissociation*, when exposed to a temperature between 1100 and 1200°. In order to collect the gases resulting from this decomposition it is necessary to separate them before they have reached a part of the apparatus where a less elevated temperature would permit their recombination. For this purpose Deville directed a current of steam through a porous clay tube, *a* (Fig. 30), surrounded by a tube of glazed porcelain, *b*, which was heated to whiteness in a powerful furnace. A current of carbonic acid gas was passed through the annular space between the two tubes, by means of the tube *c*. The vapor of water was decomposed by the heat into hydrogen and oxygen; but these two gases separated from each other: the hydrogen, being the more diffusible, passed in great part through the porous tube, while the oxygen was delivered by the interior tube, together with a small quantity of carbonic acid gas, which entered by diffusion. The gases evolved by the two tubes were collected in a small jar filled with a solution of caustic potash by which the carbonic acid gas was absorbed, and there remained an explosive mixture of hydrogen and oxygen.

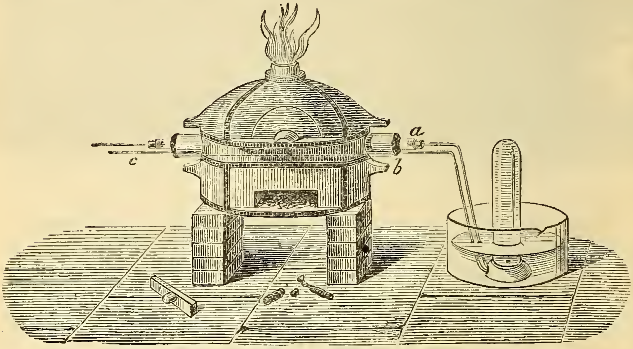


Fig. 30.

Water is decomposed by an electric current, as already seen.

It is likewise decomposed by many of the elements, metallic and non-metallic, which combine with one or the other of its component elements. Thus, chlorine decomposes it at a red heat, uniting with the hydrogen to form hydrochloric acid, and setting free the oxygen; also under the influence of light at ordinary temperatures. A number of the metals decompose water, liberating the hydrogen.

Iron decomposes it at a red heat, taking up the oxygen and setting free the hydrogen; potassium and sodium, as we have seen in the case of the latter metal, produce the same effect at ordinary temperatures.

Many compound bodies seize upon the elements of water, and are decomposed by it. Such are the chlorides of phosphorus and antimony. In these reactions, which will be studied farther on, the hydrogen of the decomposed water unites with the chlorine, the oxygen with the other element.

We have already noticed the action of water upon the non-metallic and metallic oxides. It combines with many of these compounds, forming *hydroxides*, which are either acid or basic. Certain of these reactions are worthy of reconsideration. It is especially important to fully appreciate the part played by the water which enters into them.

When potassium oxide becomes hydrated to form caustic potash, the reaction takes place by a double decomposition, which may be expressed by the following equation:

$$(1)\quad \underset{\text{Potassium oxide.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}O} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} = \underset{\text{Potassium hydroxide.}}{\left.\begin{matrix}K\\H\end{matrix}\right\}O} + \underset{\text{Potassium hydroxide.}}{\left.\begin{matrix}H\\K\end{matrix}\right\}O}$$

It will be seen that both the potassium oxide and the water are converted into potassium hydroxide by the exchange of an atom of potassium for an atom of hydrogen. Potassium hydroxide is, as it were, derived from water by the substitution of an atom of potassium for an atom of hydrogen. This substitution takes place directly when water is decomposed by potassium.

$$(2)\qquad 2H^2O + K^2 = 2KOH + H^2$$

The potassium hydroxide in its turn may lose the remaining atom of hydrogen; if it be heated with potassium, this hydrogen is displaced, and potassium oxide is formed.

$$(3)\quad \underset{\text{Potassium hydroxide.}}{2KOH} + \underset{\text{Potassium.}}{K^2} = \underset{\text{Potassium oxide.}}{2K^2O} + \underset{\text{Hydrogen.}}{H^2}$$

It will be seen from what precedes that, starting with water, we may form potassium hydroxide (2), potassium oxide (3), and this again may be converted into potassium hydroxide (1). The three compounds are then closely related. Each contains 1 atom of oxygen combined with 2 atoms of another body, hydrogen or potassium, and the relation is clearly expressed in the following formulæ:

$$\begin{array}{ccc} \left.\begin{matrix}H\\H\end{matrix}\right\}O & \left.\begin{matrix}K\\H\end{matrix}\right\}O & \left.\begin{matrix}K\\K\end{matrix}\right\}O \\ \text{Water.} & \text{Potassium hydroxide.} & \text{Potassium oxide.} \end{array}$$

If hypochlorous oxide, Cl^2O, be poured into water, it is instantly dissolved and converted into hypochlorous acid. The reaction is expressed in the following equation:

$$\begin{array}{ccccccc} \left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O & + & \left.\begin{matrix}H\\H\end{matrix}\right\}O & = & \left.\begin{matrix}H\\Cl\end{matrix}\right\}O & + & \left.\begin{matrix}Cl\\H\end{matrix}\right\}O \\ \text{Hypochlorous oxide.} & & \text{Water.} & & \text{Hypochlorous acid.} & & \text{Hypochlorous acid.} \end{array}$$

Both the hypochlorous oxide and the water are converted into hypochlorous acid by the exchange of an atom of hydrogen for an atom of chlorine, so that the hypochlorous acid may be said to represent water in which 1 atom of chlorine is substituted for an atom of hydrogen.

Thus, by their atomic constitution both potassium hydroxide and hypochlorous acid are closely related to water. But on comparing them together they are found to differ widely in their properties, both from each other and from water itself. How could it be otherwise with bodies containing elements as unlike as potassium and chlorine? Indeed, the distance which separates potassium hydroxide and hypochlorous acid is not greater than that which separates potassium and chlorine. Thus, a difference of elements may imply a marked difference of properties between bodies which otherwise present a similar constitution, and which may be said to belong to the *same type.*

Water is one of these types. Its constitution serves as a sort of model for that of a multitude of compounds. It will be sufficient to reconsider the examples already cited, and we may say that water, potassium hydroxide, potassium oxide, hypochlorous acid, and hypochlorous oxide belong to the *water type.*

$$\begin{array}{ccccc} & & \text{TYPE.} & & \\ \left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O & \left.\begin{matrix}Cl\\H\end{matrix}\right\}O & \left.\begin{matrix}H\\H\end{matrix}\right\}O & \left.\begin{matrix}K\\H\end{matrix}\right\}O & \left.\begin{matrix}K\\K\end{matrix}\right\}O \\ \text{Hypochlorous} & \text{Hypochlorous} & \text{Water.} & \text{Potassium} & \text{Potassium} \\ \text{oxide.} & \text{acid.} & & \text{hydroxide.} & \text{oxide.} \end{array}$$

The preceding considerations give but a limited idea, but one sufficient for the present, of the rôle played by water in chemical phenomena. This rôle is one of great importance, for water takes part in an immense number of reactions, either by its decomposition, its formation, or its combination.

Water presents still another mode of action. It dissolves very many bodies, and this solvent action is exerted upon gases, liquids, and solids.

Solvent Properties of Water.—When a gas dissolves in water, it changes its state, it becomes itself liquid, and in liquefying it evolves heat. In the same manner a solid body becomes liquid by the act of solution, but in order to become liquid it must absorb heat. Consequently, the solution of a gas in water takes place with a production of heat; that of a solid body takes place with a lowering of temperature, or, to use a common expression, a production of cold.

But sometimes this physical phenomenon of the solution of a solid body in water, that is, its liquefaction and diffusion in the liquid, is complicated by a chemical action.

Experiment.—If water be poured upon dried and powdered calcium chloride, the salt is instantly dissolved with a production of heat. This heat is the evidence of a chemical combination, and the water has indeed combined with the calcium chloride; if now the solution be sufficiently evaporated, it will deposit fine transparent crystals of hydrated calcium chloride. The water contained in these crystals, and which is necessary for their formation, is what is called *water of crystallization*. It is contained in definite proportions, and is retained in the crystals by affinity. For this reason the combination of water with calcium chloride is accompanied by a production of heat.

If these crystals of calcium chloride be dissolved in water, they disappear, and the temperature of the liquid is depressed. The physical phenomenon of the solution of a solid body in water can thus be separated from the chemical phenomenon of its combination with that liquid.

Natural State of Water.—Water is not met with in a pure state in nature. Whether it has rested upon or has flowed over the surface of the soil, whether it has fallen in the form of rain, mist, or dew, or whether it has just issued from its subterranean passages, it always contains various matters in solution.

It takes up the gases from the atmosphere, and also certain bodies which it there finds suspended or in vapor. On the surface or in the bosom of the earth it dissolves the soluble substances which it encounters. Hence the composition of natural water presents great variations, according to the origin of the water and the localities where it has collected, or the soils through which it has travelled. In general, *meteoric waters*, that is, those which result from the condensation of the aqueous vapor diffused through the atmosphere, are more pure than those which have collected upon the earth's surface. The latter present in their physical and chemical properties, in their composition, and in their action upon the animal economy, such differences that they are classified in several groups.

Soft or *potable* waters are distinguished from *hard* waters. The first are such as hold only small quantities of foreign matters in solution, and are essentially fit for domestic use. The second are too highly charged with saline matters, and principally the salts of calcium, to be fit for such purposes. Good potable water should be cool, limpid, without odor, should have a faint but agreeable taste, which should be neither insipid, saline, nor sweet, and should cook and soften vegetables and dissolve soap. The purest water is not necessarily the best. Thus distilled water, rain-water, and that coming from the melting of ice and snow, although more pure, are less salubrious than good spring or river water.

Good potable water should be aerated, that is, it should hold in solution the gases contained in the atmosphere: oxygen, nitrogen, and carbonic acid. Rain-water takes from the atmosphere a proportion of oxygen, and especially of carbonic acid gas, much greater than that in which these gases are contained in the air. This must be so, for Dalton has shown that the solvent action of water upon a gaseous mixture is measured for each gas by the product of its coefficient of solubility and the figure expressing the proportion of that gas in the mixture. These gases are driven out of water by boiling.

The following figures give the proportions of the atmospheric gases expelled by boiling from a litre of water from the Seine, the same quantity from the Delaware, and also the proportions contained in a litre of rain-water:

	Water of the Seine in January.	Water of the Delaware in July.	Rain-Water in Jan.	
Carbonic acid gas . .	22.6 c. c.	1.6 c. c.	0.5 c. c.	1.77
Nitrogen	21.4	12.2	15.1	64.47
Oxygen	10.1	5.3	7.4	33.76
	54.1	19.1	23.0	100.00

It is seen that at the same season the running water contains a larger amount of all of the gases than rain-water, and a notably larger proportion of carbonic acid.

Solid Matters dissolved in Water.—Soft waters generally contain a small proportion of fixed matters, among which are certain salts of calcium and magnesium, certain alkaline salts, silica, and organic matters.

The calcium salts are the carbonate and sulphate, and sometimes traces of the chloride, nitrate, and phosphate.

Calcium carbonate, or carbonate of lime, is almost insoluble in pure water, but dissolves readily in water charged with carbonic acid gas; in such solutions it exists as dicarbonate. When water thus charged with calcium dicarbonate is boiled, that salt is decomposed, carbonic acid gas is disengaged, and neutral calcium carbonate is precipitated. When the proportion of calcium dicarbonate contained in spring-water is large, it may happen that as the water loses carbonic acid gas the calcium carbonate is deposited at ordinary temperatures. This effect is favored by the tumultuous movements to which spring-water is subjected either in flowing over an inclined bed or in conducting-pipes. The carbonate then forms a crystalline deposit, which incrusts the interior walls of the pipes and, in general, whatever objects may be plunged into such waters, which for this reason are called *incrusting* or *petrifying waters.*

The presence of small quantities of calcium dicarbonate in drinking-water may be considered as a good condition, from a hygienic stand-point, for the system needs calcareous salts for the development and nutrition of the bony structures.

Calcium sulphate, or sulphate of lime, exists in solution in many waters, especially in spring and well waters. When the proportion does not exceed fifteen or twenty centigrammes per litre, such water may be used without inconvenience for domestic purposes. Water largely charged with calcium sulphate is called selenitous water; it does not become clouded on ebullition. Like all other strongly calcareous water, it does not dissolve soap without first forming a flocculent precipitate. Salts of barium produce with such water an abundant white precipitate of barium sulphate, which is insoluble in nitric acid. Such water is unfit for economic purposes. In general, the proportion of calcareous salts in potable water should not exceed five or six decigrammes per litre; water containing more than this is difficult to digest, and is called hard water. Potable water should not contain more than mere traces of organic matter. If the organic matter be due to sewage, the water yields ammonia when boiled with an alkaline solution of potassium permanganate: more than 0.10 per million of such ammonia indicates an unwholesome water.

Mineral or Medicinal Waters.—These are waters that by virtue of their temperature or chemical constituents exercise a special action upon the animal economy, and consequently have a therapeutic value.

They are cold or warm. They are called warm when their temperature at the moment of emergence is above 20°. Their temperatures vary greatly, and may rise to the boiling-point of water. The temperature of the Grand Geyser in Iceland is even above 100° in the depths of the tube from which it issues. According to their constituents, mineral waters are classified as follows:

Acidulous or gaseous waters, characterized by the presence of free carbonic acid.

Alkaline waters, characterized by the presence of sodium dicarbonate, or of an alkaline silicate.

Chalybeate waters, holding a salt of iron in solution.

Saline waters, or those containing certain neutral salts.

Sulphur waters, characterized by the presence of hydrogen sulphide or other soluble sulphide.

On arriving at the surface of the earth, certain of these mineral waters undergo a change in chemical constitution. Such are the sulphur waters which absorb oxygen, as will be noticed presently. Those containing free carbonic acid lose a part of their gas, and it often happens that some of the carbonates held in solution by an excess of carbonic acid become insoluble, and are deposited after the escape of that excess. This is the principal cause of the deposits which form in the basins and conducting-pipes of many mineral waters. These deposits vary greatly in composition; sometimes they are flocculent or pulverulent, and collect in the form of mud; sometimes they form hard concretions or scales. Calcium and magnesium carbonates, ferric hydrate, alumina, and silica are the most ordinary constituents of such deposits. Besides these, arsenic, various metallic oxides, and materials which it would be difficult to detect in the water itself, are sometimes concentrated, as it were, in these deposits. Thus, arsenic is detected much more readily in the ochrey deposits around a ferruginous spring than in the water of the spring itself.

ACIDULOUS OR GASEOUS WATERS.—Free carbonic acid is the characteristic and predominant element of these waters; it is dissolved in the depths of the earth under a pressure much greater than that of the atmosphere; hence a certain portion of the gas is disengaged as soon as the water emerges from the soil, giving rise to a greater or less effervescence. Gaseous waters are cold; their taste is piquant at the moment of emergence, but often becomes saline or even alkaline after the disengagement of the greater part of the carbonic acid gas. Natural gaseous waters never consist of a solution of carbonic acid in pure water; they always contain a small quantity of saline matters, principally traces of sodic, calcic, and magnesic carbonates, and even traces of chlorides and sulphates. Such is the composition of the celebrated Seltzer water and of Soultzmatt water. The water of certain of the Saratoga springs approximates in composition to Seltzer water.

ALKALINE WATERS.—These waters possess an alkaline reaction, either immediately on their emergence or after the loss of their free carbonic acid. This reaction may be due to an alkaline silicate, but is generally referable to an alkaline carbonate. Sodium acid carbonate, $NaHCO^3$, commonly called bicarbonate of soda, exists in nearly all waters of this class, together with an excess of carbonic acid. Vichy water contains about 5 grammes of this salt per litre.

CHALYBEATE WATERS.—Nearly all waters contain traces of iron in solution; chalybeate waters are such as contain sufficient of that metal to give them an astringent taste and special therapeutic properties. The iron may exist in three conditions:

1. As ferrous carbonate held in solution by carbonic acid.
2. As ferrous crenate. Berzelius gave the names crenic and apocrenic acids to two bodies which are related to peculiar acids existing in the soil or humus, and which are known as ulmic, humic, and geic acids. Ferrous crenate is soluble in water; its constitution is not known.
3. As ferrous sulphate.

Consequently, chalybeate waters may be carbonated, crenated, and sulphated.

The ferrous salts are never contained in these waters in large proportions. Many ferruginous waters of undoubted efficacy do not contain more than 4 or 5 centigrammes per litre. When exposed to the air they lose the greater part of their carbonic acid, and ferrous carbonate is deposited, but this loses its carbonic acid and is converted into brown ferric hydrate. Such is the manner of formation and the nature of the ochrey deposits always noticeable around ferruginous springs.

Chalybeate waters are widely diffused. Those of Spa, Belgium, and Pyrmont (carbonated), Bussang in the Vosges, and Forges (crenated), and Passy, at Paris, are well known. Celebrated springs of this class exist at Bedford, Pennsylvania, Manitou, Colorado, and indeed in many localities in the United States.

SALINE WATERS.—This class includes a great number of waters charged with various neutral salts, among which are the chlorides, bromides, and iodides. The salts of sodium, magnesium, and calcium are those more usually met with in these waters. According to the predominating or peculiarly active principle present, they are classified as chlorinated, sulphated, and bromo-iodated waters. The Saratoga springs yield an acidulo-saline water.

Chlorinated Saline Waters.—The chlorides generally found in mineral waters are those of sodium, magnesium, and calcium; the former is much the more abundant, and constitutes one of the most common constituents of mineral waters. It communicates to them a pure salty taste, free from bitterness. A great number of saline springs serve for the extraction of sodium chloride. After the evaporation of the water and the deposition of the salt, a mother-liquor remains in which various less abundant salts are concentrated, principally the alkaline bromides and iodides.

Sea-water is a chlorinated water. It is well known that it contains a notable proportion of sodium chloride (2.5 to 2.7 per cent.). The common salt is accompanied by the chlorides of magnesium and potassium, and by a considerable quantity of magnesium sulphate (0.6 to 0.7 per cent.).

The Dead Sea and the Great Salt Lake of Utah are the most concentrated natural saline waters. The water of the latter contains 20 per cent. of sodium chloride.

Sulphated Saline Waters.—These are characterized by sodium, magnesium, or calcium sulphate. The springs of Carlsbad, in Bohemia, contain a large proportion of sodium sulphate, together with sodium bicarbonate and sodium chloride.

The purgative waters of Epsom, England, contain magnesium sulphate. The waters of Hunyadi, Friedrichshall, and Seidlitz contain magnesium sulphate and sodium sulphate. Their taste is bitter. The Avon Spring, New York, is of this class.

Bromo-iodated Waters.—Many mineral waters contain small quantities of bromides and iodides, independently of the chlorides which generally exist in much larger proportions. The water of the Dead Sea, so rich in magnesium and sodium chlorides, contain 0.43 per cent. of magnesium bromide. The Iodine Spring at Saratoga contains a notable proportion of alkaline iodides.

SULPHUR WATERS.—By this name are designated those waters containing a soluble sulphide or sulphuretted hydrogen. They are either *natural sulphur waters* or *accidental sulphur waters.* The first contain sodium sulphide; they are generally warm, and contain but little solid matter. They all disengage nitrogen on their emergence from the soil. They contain a nitrogenized organic matter (baregine), and sometimes deposit a gelatinous precipitate (glairine).

Celebrated springs exist in the Pyrenees, at Bagnères-de-Luchon, and at Aix la Chapelle. The sulphur springs of Sharon and Avon, in New York, and the Red and White Sulphur Springs of Virginia are well known.

Accidental sulphur waters are those which are formed upon the spot by the reduction of sulphates, and particularly calcium sulphate, contained in the waters. This reduction is accomplished by the action of organic matters which impregnate the soil, and of which the combustible elements, carbon and hydrogen, remove the oxygen of the sulphates. It is thus that the sulphur water of Enghien is formed at the gates of Paris.

HYDROGEN DIOXIDE.

H^2O^2

This remarkable compound was discovered by Thenard in 1818. It is formed by the action of barium dioxide upon dilute hydrochloric acid. Barium dioxide, powdered and made into a fine paste with water, is introduced by small portions into cold and dilute hydrochloric acid. It dissolves without disengagement of gas, yielding barium chloride and hydrogen dioxide.

$$\underset{\text{Barium dioxide.}}{BaO^2} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Barium chloride.}}{BaCl^2} + \underset{\text{Hydrogen dioxide.}}{H^2O^2}$$

The barium chloride is converted into insoluble sulphate by the cautious addition of dilute sulphuric acid, and hydrochloric acid is regenerated, so that an additional quantity of barium dioxide may be added; this operation is several times repeated.

$$\underset{}{BaCl^2} + \underset{\text{Sulphuric acid.}}{H^2SO^4} = \underset{\text{Barium sulphate.}}{BaSO^4} + 2HCl$$

The barium chloride finally remaining in solution is exactly precipitated by a solution of silver sulphate, and the hydrogen dioxide solution poured off and evaporated in vacuo. For use in medicine and the arts dilute hydrogen peroxide is manufactured in considerable quantities by the reaction of hydrated barium dioxide with cold dilute phosphoric or sulphuric acids.

Pure hydrogen dioxide is a syrupy, colorless, odorless liquid, having a density of 1.499. It is very unstable, and readily gives up half of its oxygen, being converted into water. This decomposition takes place with a brisk effervescence when the dioxide is heated towards 100°; it is also produced by contact with a great number of bodies, some of which are themselves unaltered, some oxidized, and others even reduced. Hence hydrogen dioxide enters into three classes of reactions.

1. If a solution of hydrogen dioxide be poured into a test-tube containing manganese dioxide, the hydrogen dioxide is reduced with effervescence into water and oxygen. The manganese dioxide remains unchanged. Finely divided platinum, gold, silver, and carbon act in the same manner.

2. Hydrogen dioxide energetically oxidizes arsenic and selenium to arsenic and selenic acids, and lead sulphide to lead sulphate.

$$\underset{\text{Lead sulphide.}}{PbS} + 4H^2O^2 = \underset{\text{Lead sulphate.}}{PbSO^4} + 4H^2O$$

3. Potassium permanganate, $KMnO^4$, is a salt very rich in oxygen; it dissolves in water, forming a solution having an intense purple color. If hydrogen dioxide be added to it, it is immediately reduced and decolorized. The oxygen from the decomposition of the hydrogen dioxide is in this case added to that from the reduction of the permanganate, and both are disengaged in the free state.

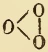
If hydrogen dioxide be added to a solution of potassium dichromate, the latter assumes a deep blue color, but this rapidly disappears, giving place to a green tint. At the same time an evolution of oxygen takes place. In this case the reaction is complex: a portion of the hydrogen dioxide oxidizes the chromic acid for an instant into blue perchromic acid, but the latter is instantly reduced, with disengagement of oxygen, by another portion of the hydrogen dioxide, which at the same time loses half of its oxygen.

The oxygen gas liberated comes then at the same time from the perchromic acid and the hydrogen dioxide, both of which are supersaturated with oxygen, and which mutually reduce each other. The perchromic acid formed may be removed from the action of the excess of hydrogen dioxide by immediately agitating the liquid with ether: the latter dissolves the acid and assumes a dark-blue color.

These experiments of reduction are of great interest, and permit of but one explanation. The fact of the reciprocal reduction of two bodies each supersaturated with oxygen can only be explained by admitting that the oxygen of one body possesses an affinity for that of the other, and that the oxygen which is set free is formed by the union of two atoms, one from the hydrogen dioxide, the other from the perchromic or permanganic acid. These two atoms unite to form a molecule of oxygen OO. This would represent oxygen in the free state, and occupy two volumes. It would be a true combination, and we here encounter for the first time the important notion that the atoms of certain elements are not isolated when in the free state, but combined in pairs, each pair being held together by chemical force. Free oxygen would then be oxygen oxide, a combination of two atoms of oxygen, both together forming a molecule, and occupying two volumes like the molecule of water.

1 molecule of water	$H{-}O{-}H = 2$ volumes.
1 molecule of oxygen . . .	$O{=}O = 2$ volumes.

While the molecular structure of free oxygen or oxygen oxide corresponds in a measure to that of hydrogen oxide or water, there exists a peroxide of oxygen which corresponds in a measure to hydrogen peroxide; it is ozone.

Hydrogen dioxide	$H{-}O{-}O{-}H$
Oxygen dioxide (ozone)	

SULPHUR.

Vapor density compared to air	2.22
Vapor density compared to hydrogen	32.
Atomic weight S	= 31.83

Sulphur has been known from the greatest antiquity. It exists in combination in a large number of sulphides, among which are those of iron and copper (pyrites), of lead (galena), zinc (blende), mercury, etc. In certain volcanic countries it is found on the surface of the earth in the native state. Sicily and Iceland contain large deposits in the neighborhood of extinct volcanoes (solfatares). In order to separate it from the earthy matters which accompany it, the ore is piled symmetrically in hemispherical kilns about 10 metres in diameter built on the side of a hill (Fig. 31); air-channels are left through the mass, and the whole is covered with a layer of earth or burnt-out ore. The sulphur is then ignited at the bottom, and the heat produced by the combustion of a portion of the sulphur causes that remaining in the mass to melt. The liquid sulphur runs out at the bottom of the kiln, and solidifies in masses or is cast into moulds.

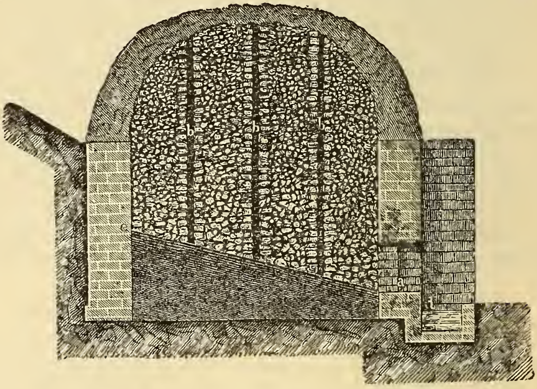


FIG. 31.

Crude sulphur is thus obtained. It is purified by distillation from the foreign matters which it retains. This refining process is conducted in an apparatus represented in Fig. 32.

A horizontal cast-iron cylinder, A, receives the melted sulphur from the vessel C, which is heated by the waste gases from the furnace, and which serves as a reservoir. The sulphur vapor enters a large masonry chamber, B, the floor of which is slightly inclined in order that the condensed liquid sulphur may flow towards a tap, H, which can be opened as is necessary. A damper, R, that can be regulated by an articulated wire, permits the closing and opening of the mouth of the cylinder. The vault of the chamber is provided with a safety-valve, K, which allows of the escape of the expanded air.

At the commencement of the operation, when the walls of the chamber are cold, the sulphur condenses in the form of a fine powder, which is known as *flowers of sulphur*. But when the walls of the chamber become heated above the melting-point of sulphur, the vapor condenses into a liquid, and on opening the tap at H, it is drawn off into a vessel, E, from which it is distributed into slightly conical or cylindrical moulds, where it solidifies. Roll sulphur is thus obtained.

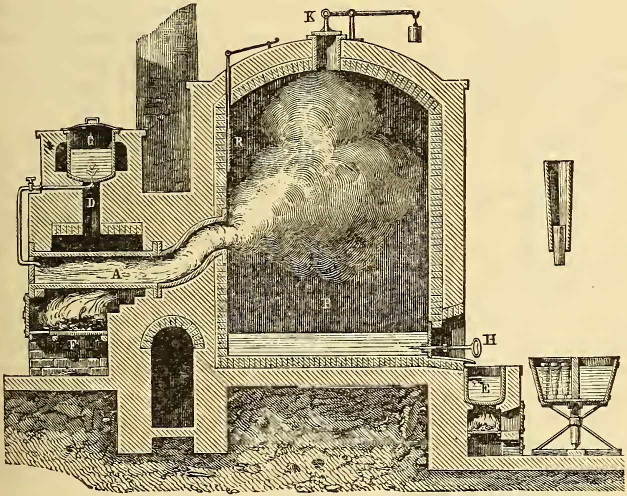


Fig. 32.

Physical Properties.—Sulphur is a lemon-yellow solid. It is tasteless, odorless, and brittle; it is a non-conductor of heat and electricity. A stick of sulphur pressed in the hand or plunged into warm water produces a crackling sound, and finally breaks into pieces; this is due to the unequal expansion from the circumference to the centre of the non-conducting mass of sulphur, the crystalline particles of which are but slightly held together by cohesion.

The density of sulphur is about 2.03. At 111.5° it melts into a brownish-yellow, transparent liquid. If this liquid be allowed to cool slowly until a crust forms upon the surface, and the crust be pierced and the part still remaining liquid be decanted, after removing the crust the vessel is found lined with long, transparent, flexible needles of a brownish-yellow color. These crystals are monoclinic prisms having a density of 1.98. This is not the only crystalline form assumed by sulphur. If a solution of sulphur in carbon disulphide be allowed to evaporate spontaneously, orthorhombic pyramids are deposited having a density of 2.05. This form is also that of native sulphur.

Sulphur crystallizes, then, in two distinct crystalline systems. It is *dimorphous.* It is a curious fact that the prisms formed by way of fusion do not long retain their transparency and their flexibility. At ordinary temperatures, they soon become opaque and brittle, owing to their transformation into microscopic orthorhombic octahedra.

Conversely, the transparent octahedral crystals become opaque when maintained for some time at a temperature of 111°; they are then transformed into a multitude of little crystals of prismatic sulphur. The two crystalline modifications of sulphur are thus transformed into each other by varying the conditions.

Sulphur melted in a sealed tube will remain liquid for a long time at temperatures below its ordinary point of solidification; it is then said to be in a state of superfusion. When it finally solidifies, it crystallizes in voluminous octahedra having the form of crystallized native sulphur.

There are other and amorphous modifications of sulphur.

Experiment.—If sulphur be melted in a flask, and the temperature be gradually raised above its point of fusion, it assumes a thick consistence and a dark color. At 220° it has a brown-red color and is very thick. Above 260° it again becomes fluid; if while in this state it be poured into cold water, it is converted into a soft, transparent, brownish-yellow, and elastic mass. It has become *amorphous*, and is now *soft sulphur*. When abandoned to itself for several days, it hardens, becomes opaque, and reassumes the properties of ordinary sulphur. This change takes place immediately if the soft sulphur be heated to 90 or 95°; is then accompanied by a sensible disengagement of heat (Regnault).

There are two modifications of soft sulphur. If it be treated with carbon disulphide, a part of it is dissolved, and a residue remains. The soluble part constitutes soluble soft sulphur; the residue is insoluble soft sulphur (Ch. Sainte-Claire Deville). In recently-sublimed flowers of sulphur the sulphur exists in the amorphous condition.

Sulphur boils at 448°; its vapor is yellowish brown. The density of the vapor at 470° is nearly 8, but it gradually diminishes when the temperature is raised, until it becomes constant at about 1000°. Between 1000° and 1700° it is 2.22 compared to air, or 32 compared to hydrogen. Hence the molecular weight of sulphur is $2 \times 32 = 64$. This corresponds to the formula S^2.

At temperatures below 1000° sulphur does not appear to assume the true gaseous condition: its molecules then consist of more than two atoms. It was formerly believed that just above the boiling-point the sulphur molecules consist of six atoms, the vapor density being approximately 96. This value, however, does not remain constant. In solutions the molecular weight of sulphur has been found to correspond to the formula S^8.

Sulphur is insoluble in water, but very slightly soluble in alcohol, a little more soluble in ether and benzene. Its best solvent is carbon disulphide.

Chemical Properties.—Sulphur possesses energetic affinities. It combines directly with a great number of the other elements. It is well known that it is combustible, burning with a blue flame. Its combustion in air or oxygen produces sulphur dioxide.

Sulphur combines directly with chlorine, bromine, iodine, phosphorus, arsenic, and carbon, and with very many of the metals. Iron and copper burn in the vapor of sulphur. The sulphides thus formed generally possess the atomic constitution of the corresponding oxides. Thus, the compound of sulphur and carbon, carbon disulphide, is analogous to carbonic acid gas. This analogy is maintained between a great number of oxygen and sulphur compounds, as will be seen by the following examples:

H^2O water.
H^2S hydrogen sulphide.
KOH potassium hydroxide.
KSH potassium sulphydrate.
CO^2 carbon dioxide.
CS^2 carbon disulphide.

K^2O potassium monoxide.
K^2S potassium monosulphide.
BaO barium monoxide.
BaS barium monosulphide.
K^2CO^3 potassium carbonate.
K^2CS^3 potassium sulphocarbonate.

SULPHYDRIC ACID, OR HYDROGEN SULPHIDE.

Density compared to air	1.192
Density compared to hydrogen	17.
Molecular weight H^2S	$=33.83$

This gas, known also as sulphuretted hydrogen, was discovered by Meyer and Rouelle, and studied by Scheele, in 1777, and by Berthollet.

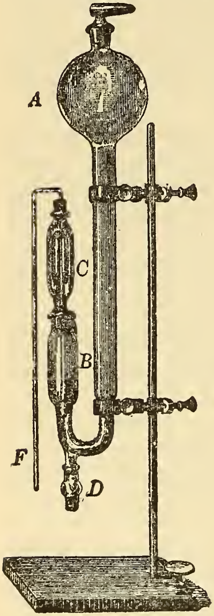


FIG. 33.

Preparation.—Hydrogen sulphide is usually prepared in the laboratory by the reaction of dilute sulphuric acid and ferrous sulphide, as indicated in the following equation:

$$\underset{\text{Ferrous sulphide.}}{FeS} + \underset{\text{Sulphuric acid.}}{H^2SO^4} = \underset{\text{Ferrous sulphate.}}{FeSO^4} + H^2S$$

The apparatus used for the preparation of hydrogen may be employed. As hydrogen sulphide is very largely used as a reagent, many forms of self-regulating apparatus have been devised by which the gas may be obtained as required. One of the most convenient of these is due to Norblad, and is represented in Fig. 33. Ferrous sulphide is introduced into the bulb *B*, to which another bulb, *C*, is adapted by a well ground joint. The only passage from *B* to *C* is by means of a groove in one side of this joint in *B* and a small hole in *C* which may be brought opposite the groove. The hole opens into a tube which rises in *C* and is then directed downward, so that gas coming from *B* must pass through a little water contained in the bulb *C* and be thus washed. Dilute sulphuric acid is poured into the reservoir *A*, the stop-cock *D* being closed. As soon as the liquid comes in contact with the ferrous sulphide, hydrogen sulphide is disengaged and passes out by the delivery-tube *F*. On closing the passage from *B* to *C* by rotating *C* so that the opening in the ground joint is not opposite the groove in *B*, the accumulation of gas forces the acid liquid back into the reservoir *A*, and the reaction ceases as soon as the acid is no longer in contact with the ferrous sulphide. The stop-cock *D* serves to draw off the liquid when the acid becomes exhausted.

A much purer hydrogen sulphide may be prepared by heating antimony trisulphide with hydrochloric acid. The reaction takes place according to the following equation, the antimony trichloride remaining in solution:

$$\underset{\text{Antimony trisulphide.}}{Sb^2S^3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Antimony trichloride.}}{2SbCl^3} + 3H^2S$$

It has been recently recommended to employ aluminium sulphide, Al^2S^3, when the gas is wanted perfectly pure. The reaction which takes place is exactly analogous to the preceding.

Hydrogen sulphide may be collected over warm water or by dry downward displacement.

Physical Properties.—Hydrogen sulphide is a colorless gas. It has a penetrating odor of putrid eggs. Under a pressure of 17 atmospheres, it condenses to a transparent, strongly refracting liquid, having a density of about 0.91. At —85.5° this liquid solidifies to a white crystalline mass (Faraday). Hydrogen sulphide is soluble in water. At 0°, one volume of water dissolves 4.37 volumes; at 10°, 3.58 volumes; and at 20°, 2.90 volumes.

Composition.—2 volumes of hydrogen sulphide contain 2 volumes of hydrogen and 1 volume of sulphur vapor.

If a given volume of this gas be introduced into a bent tube over mercury (Fig. 44), and a morsel of tin be then introduced and heated for about twenty minutes, the hydrogen sulphide is decomposed; the sulphur combines with the tin, and the hydrogen is set free. After cooling, the latter gas occupies a volume exactly equal to that of the hydrogen sulphide at first contained.

The density of hydrogen sulphide . . . . = 17
hence its molecular weight . . . . = 34
subtracting from this the weight of one molecule of hydrogen . . . . = 2
we obtain the weight of one atom of sulphur . . . = 32

It is hence concluded that one molecule of hydrogen sulphide contains one atom of sulphur to two atoms of hydrogen.

It is also seen that hydrogen sulphide has exactly the same chemical constitution as vapor of water.

$H^2O = 2$ volumes or one molecule of vapor of water.

$H^2S = 2$ volumes or one molecule of hydrogen sulphide.

The analogy between sulphur and oxygen is here manifested in a striking manner. One atom of each of these elements requires two atoms of hydrogen. This is expressed by saying that both oxygen and sulphur are *diatomic* elements.

Chemical Properties.—Hydrogen sulphide is combustible, burning with a bluish flame. The products of its complete combustion are water and sulphur dioxide. When mixed with one and a half times its volume of oxygen, it explodes on the application of a flame or the passage of an electric spark.

$$\underset{\text{Two volumes.}}{2H^2S} + \underset{\text{Three volumes.}}{3O^2} = \underset{\text{Two volumes.}}{2SO^2} + \underset{\text{Two volumes.}}{2H^2O}$$

When the supply of oxygen is insufficient, the combustion is incomplete and sulphur is deposited.

In the presence of water, oxidation takes place slowly at ordinary temperatures, occasioning a deposit of sulphur. In contact with porous matters and oxygen the oxidation goes further, sulphuric acid being formed.

Hydrogen sulphide has a feeble acid reaction; it changes blue litmus to a wine-red color. When it reacts with potassium hydrate, water and potassium sulphydrate are formed.

$$\underset{\text{Hydrogen sulphide.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}S} + \underset{\text{Potassium hydrate.}}{\left.\begin{matrix}K\\H\end{matrix}\right\}O} = \underset{\text{Potassium sulphydrate.}}{\left.\begin{matrix}K\\H\end{matrix}\right\}S} + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Chlorine, bromine, and iodine decompose hydrogen sulphide, combining with its hydrogen. When these bodies are dry, the action is energetic, and the sulphur combines with the excess of the element employed. If water be present, the sulphur is set at liberty.

Bodies rich in oxygen readily decompose hydrogen sulphide.

Experiments.—1. If a few drops of the strongest nitric acid be poured into a jar filled with hydrogen sulphide, the gas is instantly inflamed. The nitric acid gives up oxygen, water is formed, sulphur is set free, and abundant red fumes appear at the same time.

2. If four volumes of hydrogen sulphide be mixed with two volumes of sulphur dioxide over the mercury-trough, a deposit of sulphur is at once formed.

$$\underset{\substack{\text{Hydrogen sulphide.}\\\text{(4 volumes.)}}}{2H^2S} + \underset{\substack{\text{Sulphur dioxide.}\\\text{(2 volumes.)}}}{SO^2} = \underset{\text{Water.}}{2H^2O} + \underset{\text{Sulphur.}}{3S}$$

Hydrogen sulphide decomposes a great number of metallic solutions, forming insoluble sulphides, which are precipitated. The color, solubility in acids and alkalies, and other characteristics of the precipitates thus formed render hydrogen sulphide an almost indispensable reagent in analysis.

Experiments.—1. If hydrogen sulphide be passed into a solution of blue vitriol or cupric sulphate, a brownish black precipitate of cupric sulphide is formed. The reaction is expressed by the following equation:

$$\underset{\text{Cupric sulphate.}}{CuSO^4} + H^2S = \underset{\text{Cupric sulphide.}}{CuS} + \underset{\text{Sulphuric acid.}}{H^2SO^4}$$

2. By an analogous reaction, a solution of plumbic acetate, or a paper impregnated with that salt, is at once blackened by the presence of hydrogen sulphide.

In the same manner hydrogen sulphide throws down white zinc sulphide from alkaline solutions of zinc salts, the precipitate being redissolved by acids. In acid solutions of antimony it forms an orange precipitate of antimony trisulphide insoluble in ammonia, while arsenic is precipitated as yellow arsenic trisulphide, soluble in ammonia, from acid solutions of arsenic.

Hydrogen sulphide acts as a poison when inhaled in large quantities or for any length of time.

HYDROGEN PERSULPHIDE.

H^2S^5 (probably).

This compound is prepared by pouring, drop by drop, a solution of calcium disulphide into dilute hydrochloric acid.

$$\underset{\text{Calcium disulphide.}}{4CaS^2} + \underset{\text{Hydrochloric acid.}}{8HCl} = \underset{\text{Calcium chloride.}}{4CaCl^2} + 3H^2S + \underset{\text{Hydrogen persulphide.}}{H^2S^5}$$

Hydrogen persulphide is formed and collects at the bottom of the vessel in the form of a yellowish oil, having a disagreeable, irritating odor.

Under a pressure of five millimetres it may be distilled at about 60°, and is then colorless. When perfectly dry it is stable if kept in the dark, but in the light, or if moisture be present, it soon decomposes into hydrogen sulphide and sulphur. This decomposition is also brought about by presence of the bodies that react with either hydrogen sulphide or sulphur.

OXYGEN ACIDS OF SULPHUR.

1. Sulphur forms four compounds with oxygen:

Sulphur sesquioxide	S^2O^3
Sulphur dioxide	SO^2
Sulphur trioxide	SO^3
Persulphuric oxide	S^2O^7

2. By combining with a molecule of water, the last three are converted into the corresponding acids.

$SO^2 + H^2O = H^2SO^3$ sulphurous acid.
$SO^3 + H^2O = H^2SO^4$ sulphuric acid.
$S^2O^7 + H^2O = 2HSO^4$ persulphuric acid.

3. There are two other important acids of sulphur, thiosulphuric and hyposulphuric acids. The former may be considered as sulphuric acid in which 1 atom of oxygen is replaced by an atom of sulphur.

H^2SO^4 sulphuric acid.

$H^2(SO^3)S$ thiosulphuric (formerly called hyposulphurous) acid.

Hyposulphuric acid may be considered as resulting from the addition of sulphurous oxide to sulphuric acid.

$$SO^2 + H^2SO^4 = H^2S^2O^6 \text{ hyposulphuric acid.}$$

4. These are not the only known sulphur acids.

Hyposulphuric acid, which is called also dithionic acid, is the first of a series of acids, each of which contains 2 atoms of hydrogen and 6 atoms of oxygen, the number of sulphur atoms regularly increasing. This series is called the *thionic* series. The following is the nomenclature and composition of the acids:

$H^2S^2O^6$ dithionic or hyposulphuric acid.
$H^2S^3O^6$ trithionic acid.
$H^2S^4O^6$ tetrathionic acid.
$H^2S^5O^6$ pentathionic acid.

5. Schützenberger made known a new sulphur acid, which he named hydrosulphurous acid, and which is formed by the action of zinc upon sulphurous acid, as will be described farther on. The composition of this acid, which is properly named hyposulphurous, is represented by the formula

$$H^2SO^2 \text{ or } H^2S^2O^4$$

There is an interesting relation between this acid and sulphurous and sulphuric acids.

H^2SO^2 hyposulphurous acid.
H^2SO^3 sulphurous acid.
H^2SO^4 sulphuric acid.

Sulphur sesquioxide, S^2O^3, appears to be a green solid, obtained by the action of sulphur on sulphur trioxide in the cold. It is very unstable, decomposing readily into sulphur and sulphur dioxide.

SULPHUR DIOXIDE.

Density compared to air	2.234
Density compared to hydrogen	31.795
Molecular weight SO^2	= 63.59

Sulphur dioxide or sulphurous acid gas may be prepared by decomposing sulphuric acid with copper. The metal in small clippings and the acid are introduced into a flask fitted with a delivery-tube (Fig. 34); heat is applied and the gas collected over the mercury-trough. The reaction which takes place is expressed by the following equation:

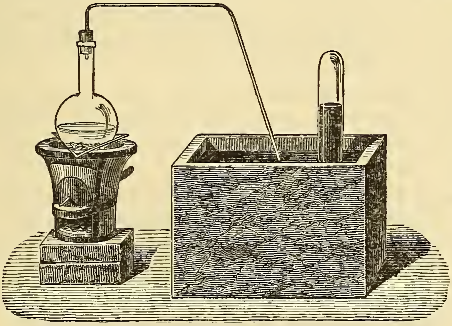


FIG. 34.

$$\underset{\text{Copper.}}{Cu} + \underset{\text{Sulphuric acid.}}{2H^2SO^4} = \underset{\text{Cupric sulphate.}}{CuSO^4} + 2H^2O + SO^2$$

A solution of sulphurous acid in water is often needed in the laboratory. It may be conveniently prepared by reducing sulphuric acid by charcoal; the products of the reaction are water, and sulphurous and carbonic acid gases.

$$\underset{\text{Sulphuric acid.}}{2H^2SO^4} + C = 2H^2O + 2SO^2 + \underset{\text{Carbon dioxide.}}{CO^2}$$

The mixed gas is passed through a series of bottles containing water, which dissolves the sulphur dioxide, but takes up only an insignificant quantity of the carbon dioxide.

Physical Properties.—Sulphur dioxide is a colorless gas having a pungent, suffocating odor. It is readily liquefied by being led into a vessel surrounded by a mixture of ice and salt. It condenses at ordinary temperatures, under a pressure of about two atmospheres. The liquid has a density of 1.45; it boils at — 8°, and produces great cold by its evaporation; on this account it is used for the manufacture of ice, and in other cases where intense cold is required. — 73° may be obtained by the evaporation of liquid sulphurous acid aided by double-acting pumps (Raoul Pictet).

Water at 0° dissolves 79.9 times its volume of sulphur dioxide, and only 39.4 volumes at 20°.

Experiments.—1. If a small quantity of mercury contained in a porcelain capsule be covered with a deep layer of liquid sulphur dioxide, and the evaporation of the latter be favored by directing a rapid current of air over its surface, the mercury is frozen into a solid button.

2. When liquid sulphurous acid is poured into not too great a quantity of water, a part of it is dissolved, but the excess absorbs heat from the mass of liquid, volatilizes suddenly, and the water is frozen.

Chemical Properties.—Sulphur dioxide is not decomposed by heat. It is incombustible, and extinguishes burning bodies.

Its most striking property is its affinity for oxygen. If a mixture of two volumes of sulphur dioxide and one volume of oxygen be passed through a tube containing slightly heated spongy platinum, the two gases combine, forming sulphur trioxide (Kuhlmann).

A solution of sulphur dioxide in water slowly absorbs oxygen, and is converted into sulphuric acid. It may be admitted that the aqueous solution contains the veritable sulphurous acid.

$$\underset{\text{Sulphurous acid.}}{H^2SO^3} + O = \underset{\text{Sulphuric acid.}}{H^2SO^4}$$

Sulphurous acid reduces a great number of oxidized bodies. At ordinary temperatures it takes the oxygen from iodic acid, setting free the iodine; but the latter disappears on the addition of an excess of sulphurous acid, sulphuric and hydriodic acids being formed.

$$H^2SO^3 + H^2O + I^2 = H^2SO^4 + 2HI$$

It decolorizes the purple solution of potassium permanganate, forming manganese sulphate and potassium sulphate. It converts arsenic acid into arsenious acid. It combines directly with lead dioxide, forming lead sulphate.

$$\underset{\text{Lead dioxide.}}{PbO^2} + SO^2 = \underset{\text{Lead sulphate.}}{PbSO^4}$$

Chlorine will unite directly with sulphur dioxide. If a mixture of equal volumes of chlorine and sulphur dioxide be exposed to sunlight, the two gases combine, forming a liquid having a suffocating odor. It is *sulphuryl chloride.* Its density is 1.66, and its boiling-point is 77°. It may be regarded as sulphur trioxide in which one atom of oxygen is replaced by two atoms of chlorine.

$SO^3 = (SO^2)''O$ sulphuryl oxide or sulphuric oxide.
$SO^2Cl^2 = (SO^2)''Cl^2$ sulphuryl chloride.

In these reactions in which the sulphur dioxide combines directly with either one atom of oxygen or two atoms of chlorine, it plays the part of an element; it is a *compound radical*, and this radical is *diatomic*, because it unites with two atoms of the *monatomic* element chlorine, or with one atom of the diatomic element oxygen, which is equivalent to two atoms of chlorine.

In the formulæ given, the diatomicity is expressed by the accents $''$.

Sulphurous acid bleaches various vegetable and animal matters. A bouquet of violets or a rose is bleached in a few minutes by a solution of sulphur dioxide. This property renders sulphur dioxide a valuable bleaching agent. It is extensively employed also as a disinfectant, and for arresting or retarding processes of putrefaction and fermentation.

HYPOSULPHUROUS (HYDROSULPHUROUS) ACID.

H^2SO^2

While sulphurous acid reduces a number of bodies, it is in its turn reduced by the action of zinc upon its aqueous solution. A yellow liquid is thus obtained which energetically bleaches indigo and litmus solutions (Schönbein). Schützenberger has shown that the liquid gifted with these properties contains the zinc salt of a new acid, which is properly named *hyposulphurous.* This acid is formed by the combination of hydrogen with sulphur dioxide. The reaction is expressed by the following equations:

$$\underset{\text{Sulphurous acid.}}{H^2SO^3} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Zinc sulphite.}}{ZnSO^3} + H^2$$

$$\underset{\text{Sulphur dioxide.}}{SO^2} + H^2 = \underset{\text{Hyposulphurous acid.}}{H^2SO^2}$$

When this liquid is treated with very dilute sulphuric acid, it gives a liquor of a dark orange-yellow color, having energetic bleaching powers. It then contains hyposulphurous acid. It soon becomes clouded and deposits sulphur. This acid is not stable, but its acid sodium salt is more so; the latter has the composition $NaHSO^2$. It readily absorbs oxygen from the air, being converted into sodium acid sulphite.

$$NaHSO^2 + O = NaHSO^3$$

This oxidation is also brought about by the presence of certain metallic salts, such as those of copper, mercury, and lead. In this case the metal is reduced and precipitated, and the hyposulphite is decomposed, yielding sulphur dioxide.

$$\underset{\text{Sodium hyposulphite.}}{NaHSO^2} + \underset{\text{Cupric sulphate.}}{CuSO^4} = \underset{\text{Sodium acid sulphate.}}{NaHSO^4} + SO^2 + Cu$$

Sodium acid hyposulphite may be obtained by the electrolysis of a solution of sodium acid sulphite. In this case the hydrogen, which would otherwise be disengaged at the negative pole, accomplishes the reduction.

$$NaHSO^3 + H^2 = NaHSO^2 + H^2O$$

SULPHUR TRIOXIDE, OR SULPHURIC OXIDE.

(SULPHURIC ANHYDRIDE.)

Vapor density compared to hydrogen	39.735
Molecular weight SO^3	=79.47

Sulphur trioxide is formed by the union of oxygen with sulphur dioxide in the presence of finely-divided platinum.

It has long been prepared by gently heating fuming sulphuric acid in a retort; vapors are given off which, when condensed in a receiver surrounded by a freezing mixture, solidify into a white mass, having a fibrous appearance and a silky lustre. According to Weber, the silk-like solid is an impure trioxide containing small quantities of $3SO^3.H^2SO^4$. It is purified by repeated meltings at a moderate temperature, decanting the liquid from the still solid portion until all melts at the same temperature.

Thus prepared, sulphur trioxide is a mobile liquid which boils at 46.2°, and upon slow cooling solidifies in long prisms which melt at 14.8°. At ordinary temperatures it produces white fumes in the air by condensing the atmospheric moisture. Its most striking property is its affinity for water; when thrown into that liquid, it becomes hydrated with such energy that a portion of the water is suddenly vaporized, and a hissing noise is produced similar to that heard on plunging a red-hot iron into water.

SULPHURIC ACID.

Molecular weight $\begin{matrix}HO\\HO\end{matrix}\!>\!SO^2$ . . . . = 97.35

This acid, which has been known for centuries, was formerly obtained by the distillation of ferrous sulphate. Now that enormous quantities of it are annually consumed in the manufacture of many important products, it is universally obtained by what is known as the *lead chamber process*. This consists in conducting into leaden chambers a mixture of sulphur dioxide, oxides of nitrogen, and steam: oxidation takes place, and the sulphur dioxide is converted into sulphuric acid.

$$SO^2 + \underset{\text{Nitrogen peroxide.}}{NO^2} + H^2O = H^2SO^4 + \underset{\text{Nitric oxide.}}{NO}$$

The nitric oxide resulting from this reaction then combines with the oxygen of the air contained in the chamber, and is reconverted into nitrogen peroxide.

$$2NO + O^2 = 2NO^2$$

The latter again reacts with the sulphur dioxide and steam which continually arrive in the chamber, and more sulphuric acid results. It is a continuous operation, which theoretically leaves no residue, and permits of the conversion of an indefinite amount of sulphur dioxide into sulphuric acid.

It is really the oxygen of the air, continually absorbed and given up by the nitric oxide, which effects the oxidation of the sulphur dioxide; the nitrogen peroxide is the direct agent, and the nitric oxide is intermediate, for it is the vehicle for the transfer of the oxygen.*

The reactions may be well exhibited by the aid of the apparatus shown in Fig. 35, in which sulphur dioxide from the flask B and nitric oxide prepared by the action of nitric acid on copper in the generating bottle C are conducted into a large globe, A, containing a little water. The cork of the globe is also provided with two bent tubes, through one of which air or oxygen may be blown in, while the other serves as an exit for the gases. The color of the gases in the globe indicates the phases of the reaction, the red vapors produced by the action of air on the nitric oxide being rapidly reduced to colorless NO by contact with the sulphur dioxide. During the reaction the walls of the globe become lined with long white crystals, which are a compound of sulphurous acid and nitrogen peroxide; on agitating the globe so that they come in contact with water, they are at once decomposed into sulphuric acid and red vapors. They are known as *the leaden chamber crystals.*

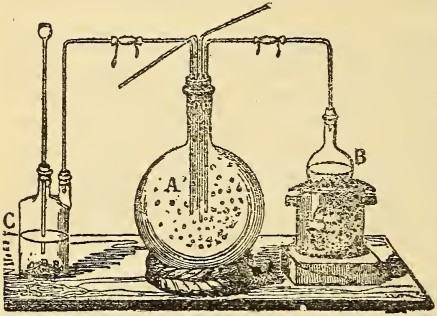


Fig. 35.

Fig. 36 represents a section of a series of leaden chambers for the manufacture of sulphuric acid.

Sulphur or pyrite is burned in furnaces, AA, and the heat generated is employed to boil the water contained in the boilers

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* According to Lunge the formation of sulphuric acid in the lead-chamber process is more correctly represented by the following equations:

$$2SO^2 + NO + NO^2 + O^2 + H^2O = 2H(NO)SO^4$$

The product, *nitrosyl sulphuric acid,* is then converted into sulphuric acid by an excess of water.

$$2H(NO)SO^4 + H^2O = 2H^2SO^4 + NO + NO^2$$

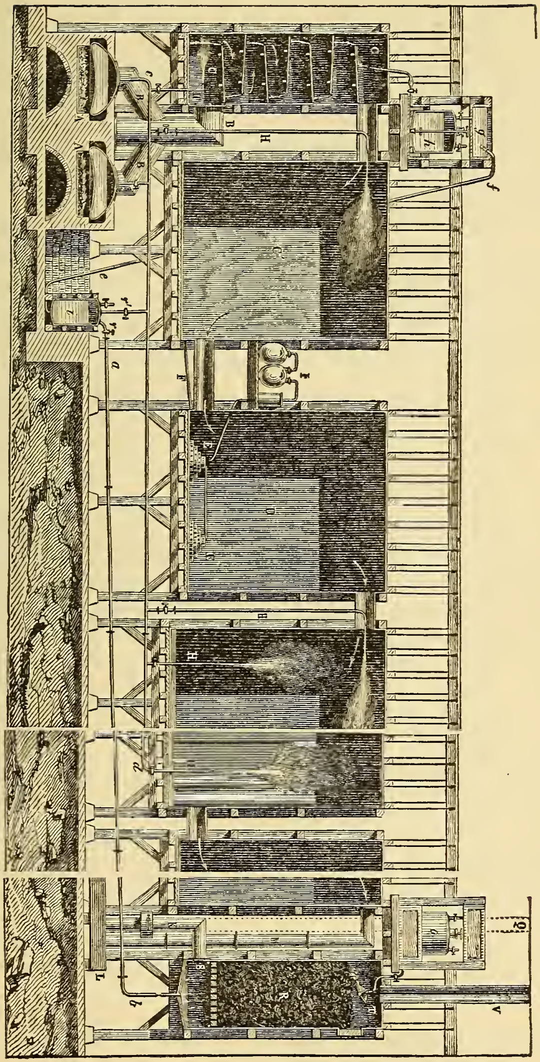


FIG. 36.

above the flame, the steam being distributed to the chambers by the pipes *c d*. The sulphurous oxide, together with a great excess of air, passes through the pipes BB into a leaden drum, C. A thin layer of sulphuric acid charged with nitrous products trickles over the inclined shelves in the drum. The gases pass first into the chamber C, then into D, where they meet with nitric acid, which falls in thin layers over a double cascade, EE, in such a manner as to present a large surface for the action of the sulphurous oxide. The sulphuric acid which is formed in this chamber is charged with nitrous products; it is therefore allowed to flow by the inclined tube F into the chamber C, where it encounters an excess of sulphurous oxide, and which is called the denitrifier. The sulphurous oxide, the excess of air, and the nitrogen peroxide pass from D into the large chamber HH, into which steam is projected by several jets. Here the larger portion of the sulphuric acid is produced, and the reaction is completed in another chamber. In the engraving the last two chambers are not fully represented. The gases from the last chamber enter a refrigerator, in which the condensation takes place; they are lastly conducted into a leaden column, R, filled with coke which is kept saturated with sulphuric acid by a thin stream from the reservoir O. This acid completely absorbs the nitric oxide, and descends by the tube *ba* into the reservoir *i*, situated near the furnace. As soon as this reservoir is full, the stop-cock *r* is closed, and *r'* is opened; the pressure of the steam then forces the acid up into the reservoir *g*, which feeds the first drum. The gas which escapes from the last column, which is known as Gay-Lussac's tower, consists of nitrogen charged with an insignificant quantity of nitrous vapors.

The acid which is drawn from the chambers is not sufficiently concentrated, having a density of only about 1.5. It is first evaporated in leaden vessels until it becomes strong enough to act upon the lead, and the concentration is then finished in large platinum retorts. The excess of water is thus driven out. The concentrated acid possesses a density of 1.842.

In many manufactories pyrites is burned instead of sulphur. Sulphurous oxide is produced, and a residue of ferric oxide remains.

Purification of Sulphuric Acid.—The sulphuric acid of commerce contains impurities. It holds in solution a small quantity of lead sulphate, formed in the evaporating basins; it is often charged with nitrous products, and sometimes with arsenic acid, when the sulphurous oxide employed in its preparation has been obtained by the combustion of arsenical pyrites. It may be freed from these impurities by distillation. The nitrous products are first disengaged, and are found in the first portions of the distillate, which must be rejected. Pure sulphuric acid then passes; the lead sulphate and arsenic acid remain in the retort with the last portions of the acid, which must not be distilled.

The operation may be conducted in a glass retort connected with a cooled receiver. The retort should be heated laterally by an annular flame so that explosive evolution of vapor may be avoided, and it is well to introduce some platinum wires with the acid, and to cover the retort with a sheet-iron hood.

Constitution of Sulphuric Acid.—Since oxygen combines directly with sulphur dioxide to form sulphuric oxide, the latter may be regarded as sulphuryl oxide, SO^2O.

Sulphuric acid is the hydrate of this oxide.

$$SO^3 + H^2O = H^2SO^4$$

The following experiment indicates the relations which exist between the elements composing this hydrate.

If sulphuryl chloride be poured into water, it disappears, sulphuric acid and hydrochloric acid being formed.

$$\begin{array}{ccccccc} SO^2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. & + & \begin{matrix}HOH\\HOH\end{matrix} & = & SO^2\left\{\begin{matrix}OH\\OH\end{matrix}\right. & + & 2HCl \\ \text{Sulphuryl chloride.} & & \text{2 molecules of water.} & & \text{Sulphuric acid.} & & \text{2 molecules hydrochloric acid.} \end{array}$$

Sulphuric acid is thus formed by the decomposition of 2 molecules of water, of which 2 atoms of hydrogen have been removed by 2 atoms of chlorine, and replaced by the group SO^2. It may then be truly said that sulphuric acid is derived from two molecules of water by the substitution of the diatomic radical $(SO^2)''$ for two monatomic atoms of hydrogen.

$$\begin{array}{ccc} \begin{matrix}H.OH\\H.OH\end{matrix} & \qquad & (SO^2)''\left\{\begin{matrix}OH\\OH\end{matrix}\right. \\ \text{2 molecules of water.} & & \text{Sulphuric acid.} \end{array}$$

If the composition of sulphuric acid be compared to that of sulphuryl chloride, from which it may be formed, it will be seen that both compounds contain the same nucleus or radical SO^2, and that instead of the two atoms of chlorine of the chloride, the acid contains two groups OH. The group OH is a residue, as it were, which represents a molecule of water minus one atom of hydrogen, and which is called hydroxyl. It is a monatomic group, and sulphuric acid is formed by the saturation of the affinity of the diatomic radical sulphuryl by two monatomic groups hydroxyl, which replace the two atoms of chlorine of sulphuryl chloride. Williamson has described an intermediate compound in which the radical sulphuryl is combined with one atom of chlorine and one OH group.

$$\underset{\text{Sulphuryl chloride.}}{SO^2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.} \qquad \underset{\text{Sulphuryl chlorohydrate.}}{SO^2\left\{\begin{matrix}Cl\\OH\end{matrix}\right.} \qquad \underset{\text{Sulphuric acid.}}{SO^2\left\{\begin{matrix}OH\\OH\end{matrix}\right.}$$

Physical Properties.—Sulphuric acid is a colorless oily liquid; its density at 12° is 1.842 (Marignac). Its boiling-point is 325°, and it solidifies at —34°. If it be crystallized several times at a low temperature, and the part remaining liquid be decanted off each time, the melting-point is gradually raised to +10.5°, where it remains stationary. According to Marignac, the acid which solidifies and fuses at +10.5° constitutes the true monohydrated acid, H^2SO^4. At a temperature about 40° it emits some fumes, and between this point and 290° it disengages a small quantity of vapor of sulphuric oxide. At 290° it begins to boil, but its boiling-point soon rises to 338°, where it remains. Such are, according to Marignac, the properties of monohydrated sulphuric acid. According to this chemist, the acid purified by simple distillation, and boiling at 325°, still contains a small amount of water.

Chemical Properties.—When exposed to a red heat, sulphuric acid decomposes into sulphur dioxide, oxygen, and water.

$$H^2SO^4 = SO^2 + O + H^2O$$

Many bodies having an affinity for oxygen reduce sulphuric acid by the aid of heat. Thus sulphur effects the reduction, being at the same time oxidized to sulphur dioxide.

$$2H^2SO^4 + S = 3SO^2 + 2H^2O$$

We have already studied the action of charcoal and copper upon sulphuric acid when boiled with that liquid, and we have seen that zinc and iron decompose the dilute acid with evolution of hydrogen and formation of a sulphate.

Sulphuric acid has a strong affinity for water. When four parts of sulphuric acid are quickly mixed with one part of water, the temperature rises to above 100°. If the experiment be made with large quantities, it is not without danger, and requires prudence lest part of the acid be projected from the vessel.

Experiments.—If four parts of sulphuric acid be quickly added to one part of snow, the latter is immediately liquefied and a notable elevation of temperature takes place; for the energy of the combination of the sulphuric acid with the water is so great that the heat produced by the union is greater than that consumed in the liquefaction of the ice.

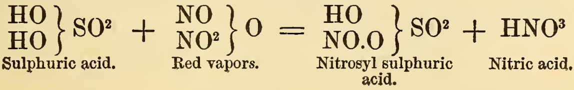
But if four parts of snow be mixed with one part of sulphuric acid, the result is the reverse; there is a lowering of temperature.

The affinity of sulphuric acid for water is manifested in a number of reactions. In the following it is sufficiently powerful to cause the formation of the water it requires:

If a morsel of sugar be moistened with sulphuric acid, it becomes blackened and carbonized in a few minutes. The sugar contains no water already formed, but independently of carbon it contains hydrogen and oxygen in the proportions necessary to form water, so that the latter compound is produced by the influence of the sulphuric acid, and a carbonaceous matter remains.

This water which is absorbed by sulphuric acid with so much energy, combines with the acid in a manner analogous to that in which water of crystallization combines with certain salts. Indeed, if sulphuric acid to which 18.3 per cent. of water has been added be exposed to a temperature of 0°, large prismatic crystals are formed, which remain solid even at a temperature of +7° or +8°. The composition of these crystals is expressed by the formula H^2SO^4,H^2O. They constitute a dihydrated acid, for they result from the union of two molecules of water with one molecule of sulphuric oxide.

Concentrated sulphuric acid will absorb red nitrous vapors (see page 165), forming colorless crystals that are often deposited in the leaden chambers. The compound is *nitrosulphonic acid*, or nitrosyl sulphuric acid.



$$\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO^2 + \left.\begin{matrix}NO\\NO^2\end{matrix}\right\}O = \left.\begin{matrix}HO\\NO.O\end{matrix}\right\}SO^2 + HNO^3$$

Sulphuric acid. Red vapors. Nitrosyl sulphuric acid. Nitric acid.

Sulphuric acid is a dibasic acid; that is, it contains two atoms of hydrogen that are replaceable by an equivalent quantity of metal. This substitution takes place when the acid is treated with a hydroxide, such as potassium hydroxide, or with an oxide, such as lead oxide.

$$H^2SO^4 + \underset{\text{Potassium hydroxide.}}{2KOH} = \underset{\text{Potassium sulphate.}}{K^2SO^4} + 2H^2O$$

$$H^2SO^4 + \underset{\text{Lead oxide.}}{PbO} = \underset{\text{Lead sulphate.}}{PbSO^4} + H^2O$$

When saturated with potassium hydroxide, the sulphuric acid is converted into potassium sulphate, and, in the salt, two atoms of potassium replace the two atoms of hydrogen of the acid. In the case of the lead oxide, on the contrary, the reaction, which is only a double decomposition, takes place so that a single atom of lead replaces the two atoms of hydrogen. The metal lead is then said to be diatomic; that is, one atom of lead is capable of replacing two atoms of a monatomic element such as hydrogen, and one atom of lead is equivalent to two atoms of potassium.

Sulphuric acid may be detected by the following reactions, which are also applicable to the soluble sulphates.

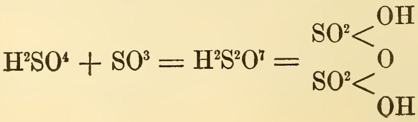
In solutions containing sulphuric acid or a sulphate, barium salts produce a white pulverulent precipitate, which is insoluble in either cold or hot nitric acid; this precipitate is barium sulphate. When mixed with an excess of charcoal and heated to whiteness, it is converted into barium sulphide.

$$\underset{\text{Barium sulphate.}}{BaSO^4} + 4C = \underset{\text{Carbon monoxide.}}{4CO} + \underset{\text{Barium sulphide.}}{BaS}$$

The sulphide of barium disengages hydrogen sulphide when it is moistened with hydrochloric acid; this gas may be recognized by its odor and by its blackening a paper impregnated with lead acetate.

PYROSULPHURIC ACID.

Fuming sulphuric acid, or *Nordhausen* acid, is a solution of sulphur trioxide in sulphuric acid, in which these bodies exist in combination as pyrosulphuric acid, $H^2S^2O^7$.



$$H^2SO^4 + SO^3 = H^2S^2O^7 = \begin{array}{l} SO^2 < {}^{OH} \\ \qquad\quad O \\ SO^2 < {}_{OH} \end{array}$$

This body is a colorless, fuming liquid, which, upon cooling, solidifies to a leafy mass which melts at 35°. When heated, it decomposes into sulphur trioxide and sulphuric acid. The commercial product is obtained either by dissolving sulphuric anhydride in sulphuric acid, or by distilling the ferric subsulphate which results from the roasting of green vitriol.

This subsulphate is calcined in stoneware retorts; it gives off sulphuric oxide when it is perfectly dry, but as it is difficult to entirely free it from water of crystallization, the vapor of sulphuric oxide is mixed with that of sulphuric acid, and the mixed vapors are condensed in cooled receivers. The residue of the distillation is ferric oxide, Fe^2O^3. Fuming sulphuric acid is used by dyers to dissolve indigo.

THIOSULPHURIC ACID.

$H^2S(SO^3)$

This acid, called also hyposulphurous and sulphosulphuric acid, is not known in the free state. When sodium thiosulphate is treated with dilute sulphuric acid, the thiosulphuric acid set free is at once decomposed into sulphurous acid and sulphur.

$$\underset{\text{Sodium thiosulphate.}}{Na^2S^2O^3} + H^2SO^4 = \underset{\text{Sodium sulphate.}}{Na^2SO^4} + H^2SO^3 + S$$

Sodium thiosulphate is formed when sulphur is boiled with a solution of sodium sulphite.

$$\underset{\text{Sodium sulphite.}}{Na^2SO^3} + S = \underset{\text{Sodium thiosulphate.}}{Na^2S(SO^3)}$$

It is a very soluble salt, forming voluminous crystals. It is used in photography and in the manufacture of paper.

HYPOSULPHURIC (DITHIONIC) ACID.

$H^2S^2O^6$

If fuming sulphuric acid represent a combination of sulphuric acid and sulphur trioxide, hyposulphuric acid can be regarded as resulting from the union of sulphuric acid with sulphur dioxide.

$SO^3.H^2SO^4$ pyrosulphuric acid.
$SO^2.H^2SO^4$ hyposulphuric acid.

Preparation.—Hyposulphuric acid is prepared by passing sulphur dioxide into water in which manganese dioxide is suspended.

$$2SO^2 + \underset{\text{Manganese dioxide.}}{MnO^2} = \underset{\text{Manganese hyposulphate.}}{MnS^2O^6}$$

Manganese hyposulphate is thus formed, and this is converted into barium hyposulphate by a double decomposition with barium sulphide. The liquid is separated from the manganese sulphide by filtration, and exactly decomposed with dilute sulphuric acid. Barium sulphate is precipitated, and the hyposulphuric acid remains in solution. The liquid is then concentrated in vacuo.

Properties.—Hyposulphuric acid is a very acid, syrupy liquid, having a density of 1.347. It is not stable; when boiled it decomposes into sulphuric acid and sulphurous oxide.

SULPHUR HEPTOXIDE AND PERSULPHURIC ACID.

S^2O^7 and HSO^4

When a mixture of equal volumes of perfectly dry sulphur dioxide and oxygen is subjected to the silent electric discharge, sulphur heptoxide is formed, and part of the oxygen remains (Berthelot).

$$4SO^2 + 4O^2 = \underset{\text{Sulphur heptoxide.}}{2S^2O^7} + O^2$$

Sulphur heptoxide is a viscous liquid which solidifies at 0^0, crystallizing sometimes in granules, sometimes in flexible needles. It is very unstable, and decomposes spontaneously, rapidly on heating, into sulphur trioxide and oxygen.

$$2S^2O^7 = 4SO^3 + O^2$$

Water dissolves it with production of dense fumes and a brisk effervescence due to the disengagement of oxygen. The liquid then contains sulphuric acid. At the same time a small quantity of persulphuric acid, $H^2S^2O^8$, or HSO^4, is formed, which soon decomposes into sulphuric acid and oxygen.

This persulphuric acid, which is very unstable, would be analogous to permanganic acid; its formation is expressed by the following equation:

$$S^2O^7 + H^2O = 2HSO^4$$

According to Berthelot, persulphuric acid is formed by the electrolysis of concentrated solutions of sulphuric acid. The potassium salt is obtained by electrolyzing a saturated solution of potassium acid sulphate; the salt being obtained at the anode, which must be artificially cooled.

$$2KHSO^4 + O = H^2O + 2KSO^4$$

Barium persulphate, $Ba(SO^4)^2 + 4H^2O$, is soluble in water.

SELENIUM AND TELLURIUM.

These two rare elements present a great analogy to sulphur.

Selenium was discovered by Berzelius in certain Swedish pyrites. It forms an essential part of but a few rare minerals, but appears to be widely distributed accompanying iron and copper pyrites. Like sulphur, selenium has two allotropic forms, one crystalline, the other vitreous and amorphous. The crystalline variety begins to melt above 217°, but liquefies only at 250° (Regnault); after rapid cooling it solidifies into a dark-brown mass. Its density is 4.8 when crystallized, and 4.3 when vitreous. When heated in the air to a temperature above its melting-point it takes fire and burns with a blue flame, being converted into selenious oxide, SeO^2. When sulphurous acid is added to a solution of selenious oxide the latter is reduced, sulphuric acid is formed, and the selenium is precipitated in the form of brown-red flakes. Its compound with hydrogen is a colorless gas having a fetid and irritating odor.

The electrical conductivity of selenium is remarkably modified by the action of light: when exposed to direct sunlight it conducts the current ten times as well as it does in the dark.

Tellurium is still more rare than selenium; it occurs combined with gold and other metals in certain minerals of Transylvania and Hungary, and also in the Rocky Mountain gold region in the United States. It has the external appearance and the lustre of a metal. Its color is silvery-white; its density 6.25. It melts at about 500°, and can be volatilized at a white heat in a current of hydrogen. It has a great tendency to crystallize. When heated in the air it burns with a greenish-blue flame, forming tellurous oxide, TeO^2. Its compound with hydrogen is a gas having an odor analogous to that of hydrogen sulphide.

The following table shows the analogy between the principal compounds of sulphur, selenium, and tellurium:

H^2S Hydrogen sulphide.	H^2Se Hydrogen selenide.	H^2Te Hydrogen telluride.
SO^2 Sulphurous oxide.	SeO^2 Selenious oxide.	TeO^2 Tellurous oxide.
SO^3 Sulphuric oxide.	$[SeO^3]$ Selenic oxide.	TeO^3 Telluric oxide.
$[H^2SO^3]$ Sulphurous acid.	H^2SeO^3 Selenious acid.	H^2TeO^3 Tellurous acid.
H^2SO^4 Sulphuric acid.	H^2SeO^4 Selenic acid.	H^2TeO^4 Telluric acid.

CHLORINE.

Density compared to air	2.44
Density compared to hydrogen	35.18
Atomic weight Cl	$=35.18$

Chlorine was discovered by Scheele in 1774, and was first recognized as an element by Gay-Lussac and Thenard in 1809, and by Sir Humphry Davy in 1810. It is one of the elements of common salt, or sodium chloride.

Preparation.—One part of manganese dioxide in coarse powder and six parts of common hydrochloric acid are introduced into a flask fitted with a safety-tube and delivery-tube (Fig. 37). The reaction begins in the cold; chlorine gas is

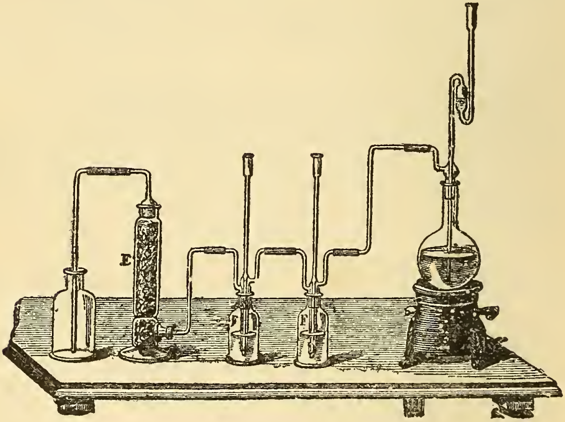


FIG. 37.

disengaged, and may be collected over salt water. As soon as the disengagement of gas diminishes, it may be re-established by the application of a gentle heat.

It is more convenient to collect the gas by dry displacement, and it may be obtained pure and dry by being washed with water, then passed through sulphuric acid, and finally through a tower, E, containing calcium chloride, as represented in the figure. It is then passed, by means of a tube bent at a right angle, into a dry jar. The chlorine being heavier than the air, collects at the bottom of the jar and gradually drives out the air, and the uniform greenish color of the whole of the gas in the jar indicates when the latter is completely filled.

The reaction which takes place in the preparation of chlorine is a double decomposition between the manganese dioxide and the hydrochloric acid. Water and manganese chloride are formed, and chlorine is set free.

$$\underset{\text{Manganese dioxide.}}{MnO^2} + \underset{\text{Hydrochloric acid.}}{4HCl} = 2H^2O + \underset{\text{Manganese chloride.}}{MnCl^2} + Cl^2$$

Large quantities of chlorine are required for the manufacture of bleaching-powder (page 329). The gas is generally prepared in large stone stills (Fig. 38) by the reaction just described; the heating is effected by injecting steam, and the manganese chloride solution is drawn off and treated with milk of lime, which precipitates manganous hydroxide, $Mn(OH)^2$. After washing this, steam and air are blown through it, and it is thus oxidized to Mn^3O^4 (Weldon). On treatment with hydrochloric acid this evolves chlorine, and the manganese is thus used continuously.

$$Mn^3O^4 + 8HCl = 3MnCl^2 + 4H^2O + Cl^2$$

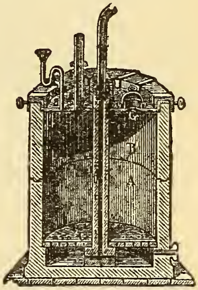


FIG. 38.

By another process air and hydrochloric acid gas are passed over pumice-stone saturated with cuprous chloride, Cu^2Cl^2. The reaction takes place in two phases: first cupric chloride and water are formed, and the former is decomposed into cuprous chloride and chlorine (Deacon).

$$Cu^2Cl^2 + O + 2HCl = 2CuCl^2 + H^2O$$
$$2CuCl^2 = Cu^2Cl^2 + Cl^2$$

Physical Properties.—Chlorine is a greenish-yellow gas having a strong and suffocating odor. A litre of this gas weighs 3.16 gr. It may be liquefied at 0° by a pressure of six atmospheres. A small quantity of the liquid may easily be prepared in the following manner:

Some crystals of chlorine hydrate are introduced into a tube of thick glass closed at one end and bent in the middle; the other end is then hermetically sealed at the blast-lamp. The branch containing the crystals is then heated in a water-bath, while the other branch is cooled in a freezing mixture (Fig. 39). The hydrate of chlorine breaks up into water and chlorine, and the greater part of the latter is disengaged, and condenses by its own pressure into a deep-yellow liquid, which collects in the cooler limb of the tube (Faraday).

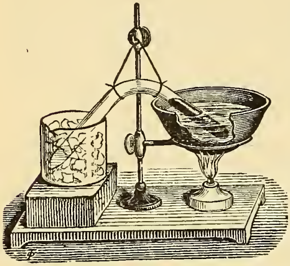


Fig. 39.

Chemical Properties.—One volume of water at 8° dissolves 3 volumes of chlorine; at 17°, 2.42 volumes. The saturated solution has a yellow color. When it is exposed to a temperature of 0°, it deposits crystals containing 27.7 per cent. of chlorine, and 72.3 per cent. of water, and constituting a hydrate of chlorine corresponding to the formula $Cl^2 + 10H^2O$ (Faraday).

Chlorine possesses powerful affinities. It unites directly with the greater number of the other elements, and the combination frequently takes place with such energy that luminous heat is produced.

Experiments.—If powdered antimony or arsenic be sprinkled into a jar containing dry chlorine, each particle of the black powder burns with a bright spark as soon as it enters the atmosphere of chlorine, producing thick, white fumes of antimony or arsenic chloride as the case may be.

If a morsel of phosphorus, contained in a deflagrating spoon, be plunged into a jar of chlorine, the phosphorus melts and inflames spontaneously, and the sides of the jar become covered with a yellow, crystalline deposit of phosphorus pentachloride, PCl^5.

But the affinity of chlorine is most strikingly manifested by its action on hydrogen and hydrogen compounds.

When a lighted taper is applied to a mixture of equal volumes of chlorine and hydrogen, the two gases unite instantly and explosively. Such a mixture will also explode violently on being exposed to direct sunlight; the rays of the sun may even be replaced by the flame of magnesium or that of carbon disulphide.

So great is the affinity of chlorine for hydrogen that it decomposes all hydrogen compounds, except hydrochloric and hydrofluoric acids. When it is dissolved in water, it slowly decomposes that liquid under the influence of sunlight, combining with the hydrogen and setting the oxygen at liberty.

If a tube filled with an aqueous solution of chlorine be inverted over the pneumatic trough and exposed to direct sunlight, small bubbles of gas will be seen to rise through the liquid and collect at the top of the tube. This is the oxygen resulting from the decomposition of the water.

At a red heat, the vapor of water is rapidly decomposed by chlorine; hydrogen sulphide gives up its hydrogen to chlorine at ordinary temperatures.

All organic substances contain hydrogen; they are therefore generally modified, and often destroyed by the action of chlorine. Coloring matters of organic origin are bleached.

Experiment.—If a solution of chlorine be added to a solution of litmus, sulphate of indigo, or ink, the intense colors peculiar to these substances disappear, giving place to a pale yellow or brown tint. This effect is due to the more or less profound decomposition which these coloring matters undergo by reason of the removal of a certain portion of their hydrogen in the form of hydrochloric acid.

This bleaching property of chlorine is of great service in the arts.

A wax taper will burn in chlorine gas with a red, smoky flame. The hydrogen of the wax combines with the chlorine, while the carbon is set free as smoke. A piece of paper saturated with oil of turpentine takes fire spontaneously when introduced into a jar of chlorine, producing a dense cloud of smoke; the turpentine contains only carbon and hydrogen the latter is attacked by the chlorine, the former being set free.

Chlorine is also an efficacious disinfectant. It decomposes hydrogen sulphide. It destroys odorous matters of organic origin, the effluvia resulting from putrid fermentation, and the miasms which are sometimes diffused in the air. It is employed to disinfect privys, etc., and to purify the air in certain epidemics.

The bleaching properties and disinfecting properties of chlorine are due to the same cause,—its powerful affinity for hydrogen.

HYDROCHLORIC ACID.

Density compared to air	1.27
Density compared to hydrogen	18.33
Molecular weight HCl	= 36.18

Hydrochloric acid exists among the gaseous products disengaged by volcanoes.

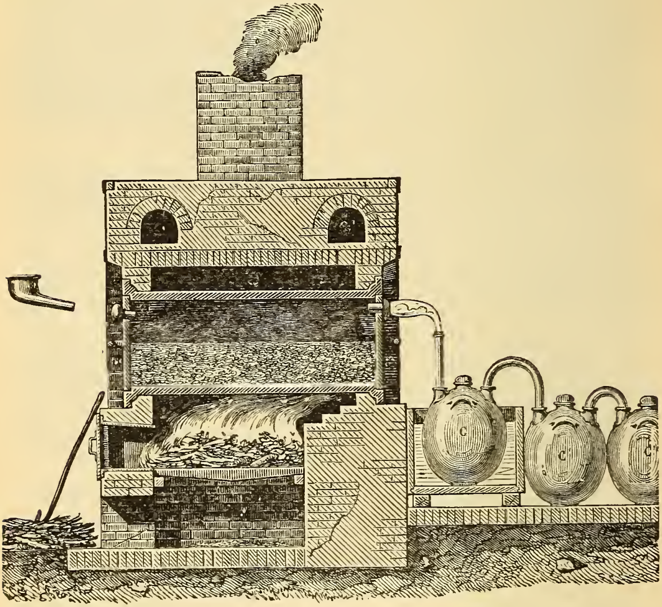


FIG. 41.

Preparation.—Fragments of fused common salt are introduced into a flask fitted with a safety-tube and delivery-tube, like that for the preparation of chlorine, and concentrated sulphuric acid is added. Hydrochloric acid gas is disengaged, and may be collected over mercury. Sodium acid sulphate remains in the retort.

$$\underset{}{H^2SO^4} + \underset{\text{Sodium chloride.}}{NaCl} = \underset{\text{Sodium acid sulphate.}}{NaHSO^4} + HCl$$

In the arts, the operation is conducted in cast-iron cylinders or furnaces (Fig. 41), at a high temperature. Under these conditions, one molecule of sulphuric acid acts upon two molecules of sodium chloride, yielding sodium neutral sulphate, and two molecules of hydrochloric acid.

$$H^2SO^4 + 2NaCl = \underset{\text{Sodium sulphate.}}{Na^2SO^4} + 2HCl$$

The hydrochloric acid gas evolved is passed into stoneware bottles, C, C′, C″, containing water. It is thus dissolved, and the solution obtained constitutes the muriatic acid of commerce.

A solution of hydrochloric acid may be prepared in the laboratory by passing the gas through water contained in a series of Wolff bottles surrounded by cold water, the contents of the first bottle being rejected (Fig. 42).

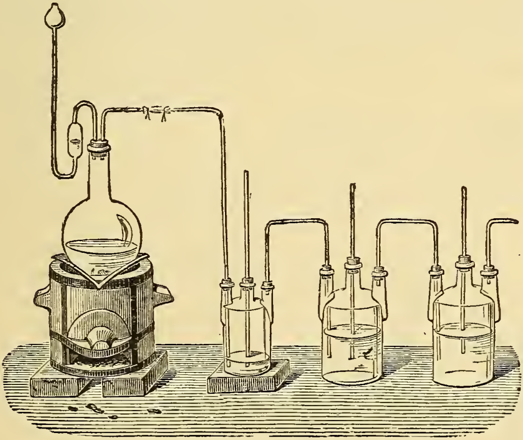


FIG. 42.

Composition of Hydrochloric Acid.—The composition of this gas may be deduced from the following experiments:

1. A bottle, B (Fig. 43), the neck of which is adapted by grinding with emery to the flask A, is filled with dry chlorine; A, which has exactly the same capacity as the bottle, is filled with dry hydrogen; the two vessels are then fitted together, and by means of the ground joint are hermetically sealed. The apparatus is now abandoned for a time to diffuse light, and as the two gases slowly mix they combine. The union is completed by exposing the apparatus to direct sunlight. When the tint of the chlorine has entirely disappeared, the two vessels are separated under the surface of mercury, and it is found that no change in volume has taken place. The chlorine and hydrogen have both disappeared to form hydrochloric acid, which occupies precisely the same volume as the two primitive gases. Consequently 2 volumes of hydrochloric gas contain 1 volume of chlorine and 1 volume of hydrogen; and if the weight of one volume of hydrogen (unity) be added to that of one volume of chlorine (its density compared to hydrogen as unity), the sum will be the weight of two volumes of hydrochloric acid, and will also represent the weight of the molecule.

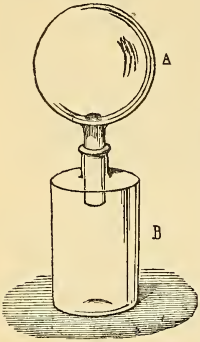


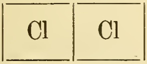
FIG. 43.

	Densities compared to H.	Densities compared to Air.
Weight of 1 volume of hydrogen	1	0.0693
Weight of 1 volume of chlorine	35.5	2.44
Weight of 2 volumes of hydrochloric acid	36.5	2.5093

2. Two volumes of hydrochloric acid gas are passed into a bent tube over mercury (Fig. 44), and a small piece of sodium is passed up into the bulb and heated by the flame of a spirit-lamp. The sodium combines with the chlorine setting the hydrogen at liberty, and after the experiment one volume of hydrogen remains in the tube.

FIG. 44.

This second experiment confirms the first, both proving that hydrogen and chlorine unite in equal volumes, and without condensation, to form hydrochloric acid. One volume of hydrochloric acid contains half a volume of hydrogen and half a volume of chlorine, but we cannot admit that the atoms of these elements are divided into two in the formation of hydrochloric acid; such a supposition would be contrary to all ideas of atoms, which represent the smallest particles of an element that can exist in a compound. It is more natural to conclude that two volumes of chlorine and two volumes of hydrogen react together in the formation of hydrochloric acid. Two volumes of chlorine contain two atoms, constituting one molecule of chlorine. In the same manner two volumes of hydrogen contain two atoms, constituting one molecule of hydrogen.



2 volumes or 1 molecule of chlorine = ClCl.

2 volumes or 1 molecule of hydrogen = HH.

It is these molecules which are separated into two when chlorine combines with hydrogen: they exchange their atoms, and from the exchange, which is a double decomposition, there result two molecules of hydrochloric acid, which occupy precisely the same volume as the two molecules of the simple gases.

2 vols. of chlorine + 2 vols. of hydrogen = 2 vols. of hydrochloric acid + 2 vols. of hydrochloric acid.

We encounter here again the notion that certain elements in the free state are composed of molecules, each of which contains two atoms of the same kind. The force which unites them is not different from affinity. It is affinity which unites chlorine to chlorine in the molecule of that element; hydrogen to hydrogen in the molecule of free hydrogen (Gerhardt). When, however, these two molecules are brought together, the affinity of chlorine for hydrogen preponderates, and brings about an exchange, a double decomposition.

Physical Properties.—Hydrochloric acid is a colorless gas having a pungent odor. It forms thick white fumes in the air by condensing the atmospheric moisture. It may be liquefied by a pressure of 40 atmospheres.

It is one of the most soluble of gases in water. If a jar filled with this gas and inverted on a plate containing mercury so that the mouth is sealed, be depressed in the pneumatic trough, and the plate be then quickly removed, the water immediately rushes into the jar as it would into a vacuum. The shock of the column of water is sometimes sufficient to break the jar.

One volume of water at 0° dissolves 500 volumes of hydrochloric acid; at ordinary temperatures, about 480 volumes. The water becomes heated and increases in volume. The cold saturated solution has a density of 1.21 and contains 42.4 per cent. by weight of the dry gas. It is a colorless liquid, giving off white fumes. When it is heated, it loses a large quantity of the gas which it holds in solution, but the whole of the gas is not disengaged, and when the temperature reaches 110° the liquid distils without further loss of gas. A dilute hydrochloric acid is thus obtained, having a uniform density of 1.10 and containing 20.24 per cent. of the acid.

Chemical Properties.—Hydrochloric acid is an energetic acid; it strongly reddens litmus-paper. It is not decomposable by heat, but is partly decomposed by a series of electric sparks. All of the metals which decompose water also decompose hydrochloric acid with the liberation of hydrogen and the formation of a chloride. Such metals are sodium, zinc, iron, aluminium, tin, etc.

Hydrochloric acid decomposes the metallic oxides and hydroxides with the formation of water and a chloride.

If hydrochloric acid be added in small quantities to a concentrated solution of potassium hydroxide, the liquid becomes heated and deposits potassium chloride as a crystalline powder.

$$\underset{}{HCl} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium chloride.}}{KCl} + H^2O$$

Hydrochloric acid is then a true acid, although it contains no oxygen, for it contains an atom of hydrogen that is replaceable by an atom of metal. In its action upon potassium hydroxide it resembles nitric acid, for this acid also contains one atom of hydrogen, which is replaceable by an atom of metal.

$$\underset{\text{Nitric acid.}}{HNO^3} + KOH = \underset{\text{Potassium nitrate.}}{KNO^3} + H^2O$$

It is seen that the acids are compounds containing a strongly electro-negative atom or group of atoms, united with hydrogen, which hydrogen can be replaced by a metal. In nitric acid, $H(NO^3)$, the group NO^3 plays the part taken by chlorine in hydrochloric acid; like the chlorine, it renders the hydrogen replaceable by a metal.

The action of hydrochloric acid upon the metallic oxides is analogous to that which it exerts upon the hydroxides.

If a current of hydrochloric acid be passed over mercuric oxide contained in a tube (Fig. 45), the oxide becomes heated, and is converted into a white powder which is mercuric chloride; at the same time water is formed and condenses in the bulb.

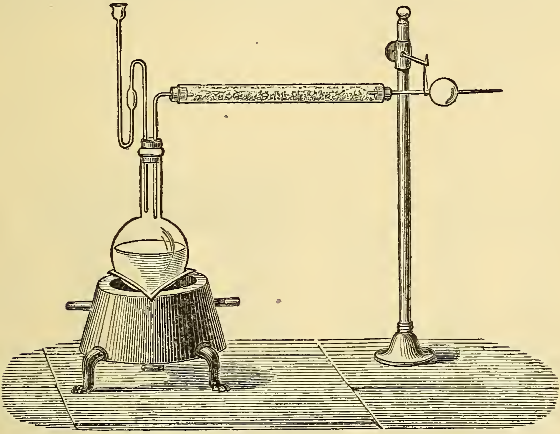


FIG. 45.

$$\underset{\text{Mercuric oxide.}}{HgO} + 2HCl = \underset{\text{Mercuric chloride.}}{HgCl^2} + H^2O$$

OXYGEN COMPOUNDS OF CHLORINE.

With oxygen, chlorine forms compounds which may be anhydrous or hydrated; the latter are acids.

The oxides are:

Hypochlorous oxide	Cl^2O
Chlorine peroxide	ClO^2

The acids are:

Hypochlorous acid	$HClO$
Chloric acid	$HClO^3$
Perchloric acid	$HClO^4$

HYPOCHLOROUS OXIDE.

Cl^2O

Hypochlorous oxide is prepared by passing a current of dry chlorine over mercuric oxide contained in a tube surrounded by cold water, and may be condensed in a long-necked matrass placed in a freezing mixture (Fig. 46).

$$\underset{\text{Mercuric oxide.}}{HgO} + 2Cl^2 = \underset{\text{Mercuric chloride.}}{HgCl^2} + Cl^2O$$

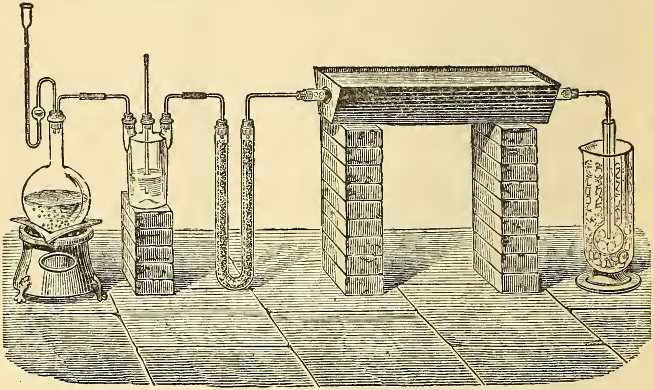


FIG. 46.

The oxide condenses as a brown-red liquid, boiling at 5°. Above that temperature it is a reddish-yellow vapor, having a density of 2.977, or, compared to hydrogen as unity, 43.5. Two volumes of this vapor contain two volumes of chlorine and one volume of oxygen, a composition represented by the formula Cl^2O.

Hypochlorous oxide is a dangerous body, and cannot be kept for more than a few hours without spontaneous decomposition; its vapor frequently explodes.

In combining with the elements of water, hypochlorous oxide forms hypochlorous acid, the solution of which is almost colorless.

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

HYPOCHLOROUS ACID.

$HClO$

This acid has never been obtained in the pure state. An aqueous solution may be prepared by agitating mercuric oxide with water in jars filled with chlorine gas. The water will then contain hypochlorous acid and mercuric chloride, and there remains a brown powder, which is mercury oxychloride. (Balard.)

$$2HgO + H^2O + 2Cl^2 = HgO.HgCl^2 + 2HClO$$

Another method consists in passing chlorine through water holding recently-precipitated calcium carbonate in suspension. The latter disappears, carbonic acid gas is disengaged, and the water becomes charged with calcium chloride and hypochlorous acid. The mixture is distilled, and the acid which passes with the water is condensed in a cooled receiver (Williamson).

$$\underset{\text{Calcium carbonate.}}{CaCO^3} + 2Cl^2 + H^2O = \underset{\text{Carbon dioxide.}}{CO^2} + \underset{\text{Calcium chloride.}}{CaCl^2} + \underset{\text{Hypochlorous acid.}}{2HClO}$$

When chlorine is passed into a rather dilute solution of an alkaline hydrate, a chloride and a hypochlorite are formed:

$$2KOH + 2Cl = KCl + KClO + H^2O$$

In this manner are prepared solutions containing potassium hypochlorite (eau de Javelle), and sodium hypochlorite (Labarraque's solution), extensively used for bleaching and disinfecting. The most important hypochlorite is the calcium salt, $Ca(ClO)^2$, which is the principal constituent of bleaching-powder.

Properties of Hypochlorous Acid.—Concentrated hypochlorous acid, obtained by distilling the aqueous solution, is a dark-yellow liquid, having the peculiar smell of chlorinated lime or bleaching-powder. It is very caustic and rapidly destroys the skin; its bleaching power is very energetic, double that of the chlorine it contains. Hydrochloric acid decomposes it into chlorine and water.

$$HClO + HCl = Cl^2 + H^2O$$

Hypochlorous acid is very unstable except in dilute solutions. It decomposes spontaneously into oxygen and hydrochloric acid.

$$2HClO = 2HCl + O^2$$

CHLORINE PEROXIDE.

ClO^2

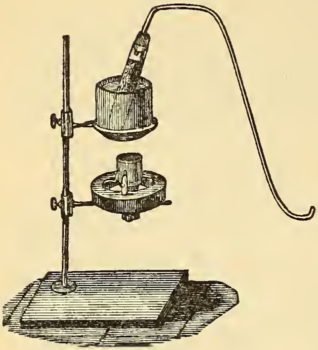


Fig. 47.

This compound, which was discovered by Sir Humphry Davy, is prepared by the action of concentrated sulphuric acid upon fused potassium chlorate. The salt is finely pulverized and added in small quantities to sulphuric acid cooled to —10°. The pasty mass is then introduced into a small test-tube fitted with a delivery-tube (Fig. 47), and is gently heated in a water-bath; the gas disengaged is collected in dry jars by downward displacement.

$$\underset{\text{Potassium chlorate.}}{3KClO^3} + 2H^2SO^4 = \underset{\text{Potassium perchlorate.}}{KClO^4} + \underset{\text{Potassium acid sulphate.}}{2KHSO^4} + H^2O + 2ClO^2$$

Chlorine peroxide is a yellow gas having a strong irritating odor. When strongly cooled, it condenses to a dark-red liquid, which boils at 9°, and solidifies at — 79°. Compared to hydrogen, the density of the gas is 33.47; hence the molecular weight is 66.94, corresponding to the formula ClO^2.

A mixture of this gas with chlorine is disengaged when hydrochloric acid is heated with potassium chlorate. This mixture is called *euchlorine*, and was formerly believed to be a definite compound.

$$4KClO^3 + 12HCl = 4KCl + 6H^2O + 3ClO^2 + 9Cl$$

Chlorine peroxide is a dangerous body; it sometimes decomposes spontaneously with violent explosions.

It is soluble in water, and the solution may be prepared by passing into water the mixture of carbonic acid gas and chlorine peroxide which is evolved when potassium chlorate is heated on a water-bath with an equal quantity of oxalic acid.

It acts as a powerful oxidizing agent. A jet of hydrogen sulphide passed into it takes fire spontaneously and continues to burn, and on contact with it sugar and other organic compounds are inflamed. If a drop of sulphuric acid be allowed to fall on a mixture of equal parts of sugar and potassium chlorate, both in powder, the chlorine peroxide disengaged at once ignites the sugar in contact with it, and the potassium chlorate yields its oxygen for the rapid combustion of the entire mass.

Chlorine peroxide is absorbed by alkaline solutions with the formation of a chlorate and a chlorite.

$$\underset{\text{Potassium hydroxide.}}{2KOH} + Cl^2O^4 = \underset{\text{Potassium chlorate.}}{KClO^3} + \underset{\text{Potassium chlorite.}}{KClO^2} + H^2O$$

Potassium chlorite is a salt of *chlorous acid* which has never been isolated.

CHLORIC ACID.

$HClO^3$

This acid is formed by the spontaneous decomposition of solutions of hypochlorous acid and chlorine peroxide.

It may be prepared by treating barium chlorate with dilute sulphuric acid. Barium sulphate precipitates, and is removed by filtration, and the solution of chloric acid is concentrated by evaporation in vacuo.

If chlorine be passed into a concentrated solution of an alkaline hydrate, a chloride and a chlorate are formed.

$$6KOH + 6Cl = 5KCl + KClO^3 + 3H^2O$$

Chloric acid is a syrupy liquid, ordinarily of a yellow color; it is not very stable; at a temperature of 40° it commences to decompose, and at a higher temperature it is resolved into perchloric acid, chlorine, oxygen, and water. It has extremely energetic oxidizing properties; when concentrated, it at once inflames sulphur, phosphorus, alcohol, and paper. It oxidizes sulphurous and phosphorous acids and hydrogen sulphide. With hydrochloric acid it forms water and chlorine.

$$HClO^3 + 5HCl = 3H^2O + 3Cl^2$$

PERCHLORIC ACID.

$HClO^4$

This is the most rich in oxygen of all the chlorine acids, and it is a curious circumstance that it is also the most stable.

It may be prepared by distilling potassium perchlorate with concentrated sulphuric acid. When a mixture of one part of the former with four parts of the latter is heated to 110°, pure perchloric acid distils over first; but if the distillation be continued, the liquid in the receiver is gradually converted into the crystalline monohydrate, $HClO^4 + H^2O$. The pure anhydrous acid may be prepared by carefully redistilling this hydrate at a temperature of 110°, part of the acid remaining in the retort as the dihydrate, $2HClO^4 + 2H^2O$, which boils at 203°.

Perchloric acid is a colorless, volatile liquid having a density of 1.782 at 15.5°. When strongly cooled, it solidifies to a crystalline mass which melts at 15°. It is extremely hygroscopic: absorbing moisture from the air, it emits dense fumes of the hydrate. Its contact with water is attended by a hissing noise and a great evolution of heat. Its oxidizing powers are so energetic that it explodes on contact with paper, wood, or charcoal.

Pure perchloric acid cannot be preserved or distilled: it suffers spontaneous decomposition even in the dark, and explodes with much violence when it is heated.

The salts of perchloric acid are very stable compounds. Unlike the chlorates, they are not reduced when heated with hydrochloric acid. Potassium perchlorate, $KClO^4$, is almost insoluble in water.

CHLORIDES OF SULPHUR.

When a current of dry chlorine is passed over sulphur heated in a retort, a liquid condenses in the receiver which fumes in the air, has a yellow color, and an irritating, fetid odor. This is *sulphurous chloride*, S^2Cl^2. In order that this compound may be formed, the sulphur must be maintained in excess, and the operation must be stopped before it has all disappeared. The product is purified by rectification, that part being collected which passes at 139°.

When chlorine is passed for several hours through the chloride of sulphur just described, the yellow color of the latter changes to deep red. The liquid obtained is mobile, fumes in the air, and continually disengages chlorine. It cannot be distilled without decomposition. The product which passes is at first red, but afterwards assumes a lighter color, and when the temperature reaches 139° there remains in the retort only sulphurous chloride, S^2Cl^2.

The red liquid has a composition which corresponds to the formula SCl^2. It is called perchloride of sulphur. Carius regards it as a mixture of the chloride S^2Cl^2 with a tetrachloride, SCl^4, corresponding to sulphur dioxide.

SO^2 sulphur dioxide.
SCl^4 sulphur tetrachloride.

This tetrachloride has been prepared by Michaelis, but it can only exist at a low temperature; it decomposes into chlorine and sulphurous chloride, S^2Cl^2, as soon as it is removed from the freezing mixture where it has been condensed.

The chlorides of sulphur are employed in vulcanizing caoutchouc.

BROMINE.

Vapor density compared to air	5.393
Vapor density compared to hydrogen	79.34
Atomic weight Br	= 79.34

Bromine was discovered by Balard in 1826.

Preparation.—It is obtained by decomposing potassium bromide by manganese dioxide and sulphuric acid. Potassium sulphate and manganese sulphate are formed, and the bromine is liberated.

$$\underset{\text{Potassium bromide.}}{2KBr} + \underset{\text{Manganese dioxide.}}{MnO^2} + 2H^2SO^4 = \underset{\text{Potassium sulphate.}}{K^2SO^4} + \underset{\text{Manganese sulphate.}}{MnSO^4} + 2H^2O + Br^2$$

The operation is conducted in a tubulated retort, heated on a sand-bath, and the bromine is condensed in a cooled receiver fitted to the retort by the aid of an adapter.

The potassium bromide may be replaced by magnesium bromide, which exists in the mother-liquors obtained in the manufacture of potassium chloride from carnallite and also in certain brine springs. The liberation of bromine from this salt is effected by the action of chlorine, thus—

$$MgBr^2 + Cl^2 = MgCl^2 + Br^2$$

Properties.—Bromine is a dark-red liquid, which solidifies at —7.3. Its density at 15° is 2.99. It boils at 63°, and at ordinary temperatures gives off red, irritating vapors, for its vapor tension is considerable even in the cold. It stains the skin yellow, and immediately corrodes the tissues. It dissolves in about 33 times its weight of water at 15°, forming an orange-red solution. At a low temperature it combines with water, forming a crystalline hydrate, $Br^2 + 10H^2O$, analogous to that formed by chlorine.

Bromine dissolves in carbon disulphide, in chloroform, and in ether.

Experiment.—A small quantity of solution of potassium bromide is introduced into a long tube, closed at one end, and the tube is then nearly filled with chlorine-water; when the two solutions are mixed, the liquor assumes an orange-red color from the liberation of the bromine. The tube is now filled up with ether and agitated briskly, the open end being closed with the finger. The ether passes through the aqueous solution and dissolves out all of the bromine, assuming at the same time a dark-red color.

The affinity of bromine for hydrogen is powerful, but not as energetic as that of chlorine. Like chlorine, it has remarkable bleaching properties.

HYDROBROMIC ACID.

Density compared to air	2.73
Density compared to hydrogen	40.5
Molecular weight HBr	= 80.34

Preparation.—This gas is prepared by the action of water upon phosphorus tribromide.

$$\underset{\text{Phosphorus tribromide.}}{PBr^3} + \underset{\text{3 molecules water.}}{\left.\begin{matrix}H^3\\H^3\end{matrix}\right\}O^3} = \underset{\text{Phosphorous acid.}}{\left.\begin{matrix}P\\H^3\end{matrix}\right\}O^3} + 3HBr$$

The operation may be conveniently conducted in a doubly-curved tube (Fig. 48). Into the long branch CD fragments of phosphorus are introduced, carefully separated from each other by moistened broken glass. The bromine is introduced into the bend A. The shorter end is then corked, a delivery-tube adapted to the end D, and the bromine is gently heated until it boils. The vapor comes into contact with the phosphorus and forms phosphorus tribromide, but this is at once decomposed by the water into phosphorous acid and hydrobromic acid. The latter may be collected in jars over the mercury-trough.

Amorphous phosphorus may be advantageously employed in this operation, and the process conducted as directed for hydriodic acid (Personne).

Another convenient process for preparing the acid depends upon the action of bromine on benzene in the presence of iron bromide. The gas which is disengaged is purified by passing it over ferrous bromide and anthracene.

When a mixture of hydrogen and bromine vapor is passed over heated platinum, the elements unite directly.

Properties.—Hydrobromic acid is a colorless gas, producing dense white fumes in the air. A litre of this gas weighs 3.547 grammes. It liquefies at —73°, and may be solidified at a lower temperature. It is formed by the union of equal volumes of bromine vapor and hydrogen without condensation, so that its composition corresponds to that of hydrochloric acid. It is very soluble in water; its concentrated solution fumes in the air, and is very corrosive.

Chlorine decomposes hydrobromic acid, liberating bromine.

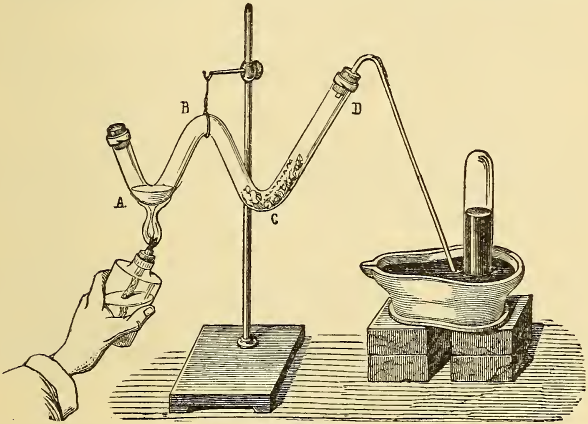


Fig. 48.

OXYGEN ACIDS OF BROMINE.

There are known three bromine oxygen acids:

Hypobromous acid, $HBrO$
Bromic acid, $HBrO^3$
Perbromic acid, $HBrO^4$

They correspond to hypochlorous, chloric, and perchloric acids.

Hypobromous Acid, $HBrO$.—When mercuric oxide is agitated with an aqueous solution of bromine, a yellowish liquid is obtained which contains hypobromous acid, and can be distilled in vacuo. W. Dancer has obtained this acid by the action of bromine upon silver oxide suspended in water.

$$2Br^2 + \underset{\text{Silver oxide.}}{Ag^2O} + H^2O = \underset{\text{Silver bromide.}}{2AgBr} + 2HBrO$$

In this process it is necessary to operate rapidly and avoid the contact of an excess of silver oxide with the hypobromous acid, as the latter would be destroyed by the oxide with evolution of oxygen.

$$2HBrO + Ag^2O = 2AgBr + H^2O + O^2$$

The solution of hypobromous acid has a yellow color and bleaching properties analogous to those of hypochlorous acid.

Bromic Acid, $HBrO^3$.—Potassium bromide and potassium bromate are formed by the action of bromine upon a concentrated solution of potassium hydroxide. This reaction is similar to that of chlorine upon potash.

Kämmerer recommends the preparation of bromic acid by the action of chlorine upon bromine in presence of water.

$$5Cl^2 + Br^2 + 6H^2O = 10HCl + 2HBrO^3$$

The hydrochloric acid is driven out by evaporation, and bromic acid remains in the form of a liquid that cannot be concentrated to a syrupy consistence without partial decomposition.

Perbromic Acid, $HBrO^4$.—Kämmerer has obtained this acid by decomposing perchloric acid with bromine: chlorine is disengaged. After concentration on a water-bath, the perbromic acid remains as a colorless oily liquid. It is relatively stable, as are the corresponding chlorine and iodine acids. Like them, it resists the reducing action of sulphurous acid and hydrogen sulphide.

IODINE.

Vapor density compared to air	8.716
Vapor density compared to hydrogen	125.9
Atomic weight I	= 125.9

Iodine was discovered by Courtois in 1811, and was studied by Gay-Lussac in 1813 and 1814.

Natural State.—Iodine is widely disseminated in nature. It is found in the mineral kingdom combined with various metals, such as potassium, sodium, calcium, magnesium, silver, mercury. The alkaline iodides exist in small quantity in sea-water, in a great number of salt-springs, and in certain rock-salts. The sodium nitrate found native in Chili contains traces of sodium iodate, and the mother-liquors from which the nitrate has been deposited contain enough iodate to be profitably employed for the preparation of iodine. The ashes of certain sea-plants, such as the algæ and fuci, are among the chief sources of iodine.

Preparation.—The ashes of sea-weeds, called kelp, are exhausted with water and the solution concentrated. Various salts, such as sodium and potassium sulphates and chlorides and sodium carbonate, are deposited, and the potassium iodide, which is contained in smaller quantity than these salts, remains in the mother-liquor.

A regulated current of chlorine is passed into this solution as long as it continues to set free iodine, which is deposited as a pulverulent, black precipitate. An excess of chlorine must be avoided, as this would redissolve a portion of the iodine, forming iodine chloride.

Still larger quantities of iodine are obtained from Chili saltpetre: the mother-liquor from the nitrates, which contains all the iodine in the form of iodates, is treated with the exact quantity of sulphur dioxide required for its decomposition.

$$2NaIO^3 + 5SO^2 + 4H^2O = I^2 + 4H^2SO^4 + Na^2SO^4$$

Impure iodine is precipitated and is refined by sublimation. In the laboratory, iodine is set free from the iodides by the action of nitric acid, a nitrate being formed and red vapors disengaged.

Properties of Iodine.—The iodine obtained by sublimation occurs as scales or crystalline plates, having a brilliant, dark bluish-gray surface, and a density of 4.948 at 17°. It may be obtained crystallized in rhombic octahedra by exposing to the air a solution of hydriodic acid.

Iodine melts at 107°. It boils at about 175°, but volatilizes sensibly at ordinary temperatures. Its vapor has an intense violet color. A litre of this vapor weighs 11.32 grammes.

Above 700° the density of iodine vapor diminishes, while its color becomes deep blue. At very high temperatures the molecule appears to be dissociated into single atoms.

Iodine is but very slightly soluble in water; one part of iodine requires 7000 parts of water for its solution, but communicates a light-brown color to the whole of that liquid. Alcohol and ether dissolve iodine freely, forming dark-brown solutions. Carbon disulphide, benzine, and chloroform also dissolve it, assuming a beautiful violet color.

Experiment.—If a few drops of chlorine-water be added to a very dilute solution of potassium iodide, the chlorine will combine with the potassium, displacing the iodine, which will color the liquid brown; if now the solution be agitated with a small quantity of chloroform, the latter will take up all of the iodine, assuming a violet color.

Iodine strikes an intense blue color with starch. The reaction is very delicate and permits the detection of the smallest trace of free iodine.

Experiment.—If a few drops of a solution of potassium iodide be added to a solution of starch, no coloration takes place, because the iodine is in combination; but if a drop or two of chlorine-water be added, the iodine will be set free, and combining with the starch will at once produce the characteristic blue color. An excess of chlorine will again destroy the color.

HYDRIODIC ACID.

Density compared to air	4.443
Density compared to hydrogen	64.1
Molecular weight HI	=126.9

Preparation.—Hydriodic acid is prepared by the action of iodine upon phosphorus in presence of water; phosphorus triiodide is first formed, and this is decomposed into phosphorous acid and hydriodic acid.

$$\underset{\text{Phosphorus triiodide.}}{PI^3} + \underset{\text{3 molecules of water.}}{\left.\begin{matrix}H^3\\H^3\end{matrix}\right\}O^3} = \underset{\text{Phosphorous acid.}}{\left.\begin{matrix}P\\H^3\end{matrix}\right\}O^3} + 3HI$$

Amorphous phosphorus in powder is introduced into a glass-stoppered retort the neck of which is soldered to the delivery-tube (Fig. 49), and covered with a layer of water; the iodine is then added, and on the application of a gentle heat a regular current of hydriodic acid is obtained. The gas may be collected, like chlorine, by downward displacement in dry jars.

Properties.—Hydriodic acid is a colorless gas producing white fumes in the air. It may be condensed to a colorless liquid by strong pressure or intense cold, and can even be solidified. Dry oxygen decomposes it at a high temperature, water being formed and the iodine being set at liberty.

If a lighted taper be applied to a mixture of hydriodic acid and oxygen, the violet vapor of the iodine set free is instantly apparent.

This decomposition of hydriodic acid by oxygen takes place at ordinary temperatures in the presence of water. A solution of hydriodic acid exposed to the air rapidly becomes brown, and after a time deposits crystals of iodine.

Solution of hydriodic acid is prepared by passing the gas into water cooled to 0°. It may also be made by passing a current of hydrogen sulphide through water holding iodine in suspension; hydriodic acid is formed, and sulphur is precipitated.

$$H^2S + I^2 = 2HI + S$$

The solution of hydriodic acid saturated at 0° has a density of 2, and fumes in the air. When freshly prepared, it is colorless; when heated, it loses part of its gas, and finally distils without further alteration at 126°. The solution then contains 57.7 per cent. of hydriodic acid.

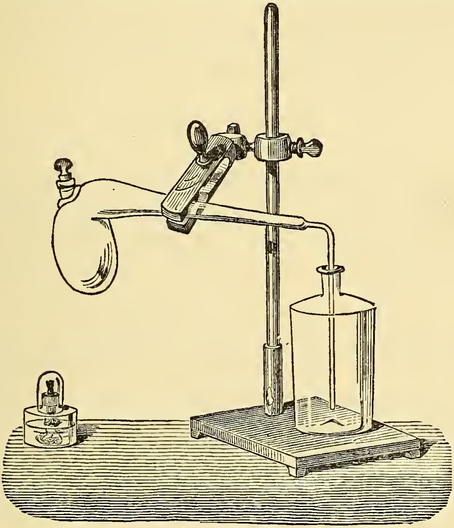


Fig. 49.

Chlorine and bromine at once decompose hydriodic acid, combining with the hydrogen and setting free the iodine. The experiment may be made by pouring a few drops of bromine into a jar filled with hydriodic acid gas, when the appearance of a violet vapor immediately indicates the liberation of iodine.

Potassium, zinc, iron, mercury, and silver decompose hydriodic acid, but with unequal energies, setting free the hydrogen.

Sulphuric acid also decomposes it, and is itself reduced to sulphurous oxide.

$$H^2SO^4 + 2HI = 2H^2O + SO^2 + I^2$$

Nitric acid is still more readily reduced by hydriodic acid.

$$\underset{\text{Nitric acid.}}{2HNO^3} + 2HI = 2H^2O + \underset{\text{Nitrogen peroxide.}}{2NO^2} + I^2$$

OXIDE AND OXYGEN ACIDS OF IODINE.

The only oxide of iodine known with certainty is the pentoxide, I^2O^5. It combines with water to form iodic acid, HIO^3 or $H^2I^2O^6$. There is also a periodic acid, H^5IO^6, corresponding to the unknown heptoxide, I^2O^7.

IODIC ACID.

$H^2I^2O^6$

Iodic acid is formed when iodine is subjected to the action of energetic oxidizing agents, such as concentrated nitric acid or a mixture of nitric acid and potassium chlorate. It is also formed by the action of an excess of chlorine on iodine in presence of water.

$$I^2 + 5Cl^2 + 6H^2O = 10HCl + H^2I^2O^6$$

Preparation.—Iodic acid may be conveniently prepared by heating iodine and potassium chlorate with dilute nitric acid. The oxygen of the chlorate oxidizes the iodine to iodic acid, and on adding barium nitrate to the liquid, barium iodate is precipitated. The latter salt is decomposed by sulphuric acid; iodic acid is set free in the solution, and barium sulphate is precipitated; the filtered solution is concentrated by evaporation in vacuo.

Properties.—Iodic acid is solid, and crystallizes in hexagonal tables. When heated to 170° it loses water and is converted into iodic oxide, and at a red heat the latter is decomposed into iodine and oxygen.

It is seen that iodic acid is much more stable than its analogue, chloric acid; nevertheless it is easily reduced by bodies avid of oxygen.

If sulphurous acid be added to a solution of iodic acid, a precipitate of iodine is formed instantly, but an excess of sulphurous acid redissolves the precipitate, part of the water being decomposed and hydriodic and sulphuric acids being formed.

Iodic acid is also decomposed by hydriodic acid. If a solution of iodic acid be poured into a solution of starch, no coloration appears, but the characteristic blue color is at once developed on adding a drop of hydriodic acid.

$$H^2I^2O^6 + 10HI = 6H^2O + 6I^2$$

PERIODIC ACID.

$$H^5IO^6 = IO(OH)^5$$

This acid has been obtained from disodic periodate, a salt which is precipitated when chlorine is passed through a solution of sodium iodate mixed with sodium hydroxide.

$$\underset{\text{Sodium iodate.}}{Na^2I^2O^6} + \underset{\text{Sodium hydroxide.}}{6NaOH} + 2Cl^2 = \underset{\text{Disodic periodate.}}{2Na^2H^3IO^6} + \underset{\text{Sodium chloride.}}{4NaCl}$$

The precipitate is dissolved in nitric acid, and lead nitrate is added to the solution; lead periodate is precipitated, and this salt is exactly decomposed by sulphuric acid; the liquid is filtered to separate the lead sulphate, and evaporated at a gentle heat. Periodic acid crystallizes out in colorless, deliquescent, rhombic prisms. It melts at 133°. When heated to 140°, it is decomposed into iodine pentoxide, water, and oxygen.

$$2H^5IO^6 = I^2O^5 + 5H^2O + O^2$$

Between 180 and 190° periodic oxide abandons oxygen, and is converted into iodic oxide, I^2O^5.

Analogy between Chlorine, Bromine, and Iodine.—Chlorine, bromine, and iodine present a striking analogy in their chemical properties, and this analogy is seen in all of their compounds. They combine with hydrogen, atom for atom, forming the acids HCl, HBr, HI, and the atoms of chlorine, bromine, and iodine are equivalent to each other and to an atom of hydrogen; each of these elements is monatomic.

Their affinities for hydrogen are far from being equal; in this respect chlorine is more powerful than bromine, and bromine than iodine. The contrary has been noticed regarding their affinities for oxygen, for the oxygen acids of iodine are more stable than those of chlorine.

The analogy between these three elements is followed out in the constitution of their oxides and acids, and in their combinations with the metals. The chlorides, iodides, and bromides possess in general the same constitution, and it is to be remarked that the greater number of these binary compounds are soluble in water and are crystallizable like salts, of which they otherwise present the characters. Hence the name *halogen bodies*, which was applied by Berzelius to this group of elements, to indicate that they form salts in combining with the metals.

FLUORINE.

$F = 19$

Fluorine belongs to the group of elements just considered, but its chemical energy is much greater than that of chlorine. It occurs chiefly in combination with calcium, and also with aluminium and sodium, forming the minerals *fluor spar*, CaF^2, and *cryolite*, $AlF^3.3NaF$. It was first isolated by Moissan, who obtained it by the electrolysis of anhydrous hydrofluoric acid in which hydrogen potassium fluoride was dissolved in order to give the necessary electrical conductivity. The decomposition was effected in a U-shaped tube of platinum (Fig. 50), each limb of which was provided with a side tube, and closed with a fluor spar stopper carrying and insulating the platinum electrodes. To prevent the escape of hydrofluoric acid, this apparatus was cooled to —40° by the rapid evaporation of methyl chloride surrounding it. A battery of 20 Bunsen cells furnished the current.

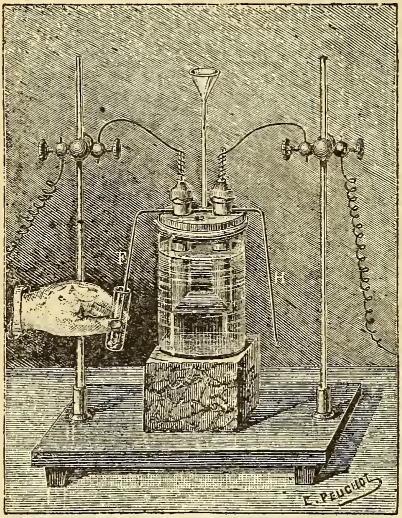


FIG. 50.

The affinities of fluorine are so energetic that it cannot be collected like other gases. It acts violently upon water, and readily combines with mercury, but may be received by dry displacement in platinum vessels. Fluorine has a greenish-yellow color and a powerful odor. Its density is 1.26. At —187° the gas condenses to a yellow liquid.

Fluorine combines with hydrogen even in the dark, and with explosive violence. Arsenic, antimony, sulphur, phosphorus, and silicon ignite spontaneously in the gas, and all the metals combine with it directly and, with few exceptions, at ordinary temperatures. Chlorine is displaced by fluorine in most of its compounds. Hydrofluoric acid and ozone result from its action upon water. Organic compounds, such as alcohol, benzene, turpentine, and even cork, are violently attacked and inflamed by it.

Fluorine does not combine with oxygen or argon.

HYDROFLUORIC ACID.

Molecular weight HF . . . . = 20

This compound is prepared by decomposing powdered calcium fluoride with sulphuric acid.

$$\underset{\text{Calcium fluoride.}}{CaF^2} + H^2SO^4 = \underset{\text{Calcium sulphate.}}{CaSO^4} + 2HF$$

The operation is conducted in a leaden retort, to which is adapted a receiver of the same metal surrounded by a freezing mixture (Fig. 51). The hydrofluoric acid condenses as a very acid liquid, which fumes strongly in the air. Its density is 1.06. In this state it still retains water; but Fremy obtained it anhydrous by decomposing dry hydrogen potassium double fluoride KF, HF, by heat in a platinum retort. This salt breaks up into potassium fluoride, which remains, and hydrofluoric acid, which is disengaged and must be condensed in a platinum receiver cooled to —20°. Pure hydrofluoric acid is liquid at ordinary temperatures; it is very mobile, it freezes at —92.3° and boils at 19.4°. It is extremely corrosive, and manipulations with it should be conducted with great care. Its affinity for water is so great that each drop of the acid let fall into that liquid produces a hissing noise, as would a red-hot iron. The solution is employed for etching upon glass, for hydrofluoric acid attacks and corrodes that substance. This effect is due to the action of the acid upon the silica of the glass, which it converts into either silicon fluoride or hydrofluosilicic acid, as will be seen farther on.

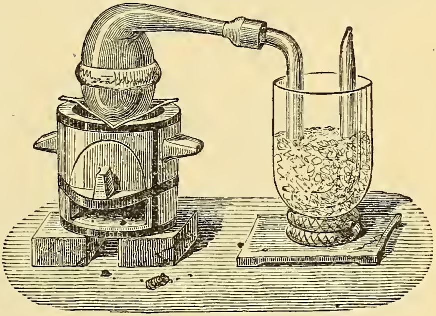


Fig. 51.

A design may readily be engraved on glass by covering the glass with a thin coating of wax, through which the design is traced with a sharp point; the glass is then placed over a leaden capsule containing a mixture of powdered calcium fluoride and strong sulphuric acid, which is gently heated by a spirit-lamp. Hydrofluoric acid vapor is disengaged and attacks the glass wherever it is not protected by the wax. When the wax is removed, the design is found to be permanently etched on the glass.

A dilute solution of hydrofluoric acid or a bath of hydrofluoride of potassium fluoride may be employed instead of the vapor in the former experiment, but in this case the etched portions are transparent and not opaque as when produced by the vapor; they may be rendered opaque by adding a salt, such as potassium or ammonium sulphate, to the bath.

NITROGEN.

Density compared to air	0.969
Density compared to hydrogen	13.93
Atomic weight N	= 13.93

Nitrogen was discovered by Rutherford in 1772. It is one of the elements of the air, and was first obtained free from oxygen by Lavoisier and Scheele, in 1777.

Preparation.—A flat piece of cork, B (Fig. 52), floating in the pneumatic-trough, supports a small capsule containing a fragment of phosphorus. The latter is inflamed, and the capsule immediately covered with a bell-jar. The heat produced by the combustion at first expands the air and drives out a portion, but in a few minutes the water rises in the jar, taking the place of the oxygen which has been consumed. When the phosphorus is extinguished, the experiment has terminated. The water gradually dissolves the white smoke of phosphoric oxide which fills the jar, and there remains a colorless, irrespirable gas that will not support combustion. This gas is nitrogen, still mixed with argon, traces of oxygen, and carbonic acid gas.

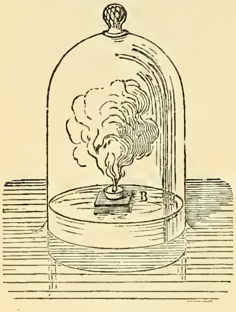


Fig. 52.

Nitrogen containing no impurity except argon may be obtained by passing a current of air, previously freed from moisture and carbon dioxide, through a porcelain tube containing incandescent copper. The copper absorbs the oxygen, and nitrogen passes out at the end of the tube and may be collected over the pneumatic trough.

Pure nitrogen is best obtained by heating a strong solution of ammonium nitrite; the products are nitrogen and water.

$$\underset{\text{Ammonium nitrite.}}{(NH^4)NO^2} = 2H^2O + N^2$$

Properties.—Nitrogen is a colorless gas, somewhat lighter than the air. A litre of this gas weighs 1.2505 grammes. It extinguishes burning bodies, and is not combustible itself; it produces no precipitate in lime-water. Water dissolves only $\frac{1}{50}$ of its volume of nitrogen at 0°. Animals are quickly suffocated in an atmosphere of pure nitrogen, but the gas does not exert a poisonous influence upon the economy.

It can be liquefied at temperatures below —146° (its critical temperature). Its critical pressure is 35 atmospheres. Under a pressure of one atmosphere this liquid boils at —190°. The affinities of nitrogen are not energetic. It combines directly with only a very small number of elements, among which may be mentioned magnesium, silicon, boron, and titanium. Under the influence of electrical discharges it will unite with oxygen, forming nitrogen peroxide, and with hydrogen, forming ammonia.

There are at present known three compounds of nitrogen and hydrogen,—ammonia, NH^3, hydrazine, N^2H^4, and hydrazoic acid, N^3H.

AMMONIA.

Density compared to air	0.596
Density compared to hydrogen	8.60
Molecular weight NH^3	$=16.93$

Ammonia was discovered by Priestley, studied by Scheele, and analyzed by Berthollet in 1785.

Preparation.—Equal weights of quick-lime and sal ammoniac, both in powder, are rapidly mixed in a mortar, and the mixture introduced into a glass flask, which is then filled up with fragments of quick-lime. A cork and delivery-tube are adapted to the flask, which is then gently heated and the gas disengaged collected over mercury.

The calcium oxide or lime decomposes the ammonium chloride (sal ammoniac), with the formation of calcium chloride, ammonia gas, and water; the latter is absorbed by the fragments of lime which fill up the flask.

$$\underset{\text{Ammonium chloride.}}{2NH^4Cl} + \underset{\text{Calcium oxide.}}{CaO} = \underset{\text{Ammonia.}}{2NH^3} + \underset{\text{Calcium chloride.}}{CaCl^2} + H^2O$$

A solution of ammonia in water may be prepared by passing the gas through a series of Wolff's bottles, about half filled with water, excepting the first, which should only contain a small quantity destined to wash the gas.

Physical Properties.—Ammonia is a colorless gas, having a powerful and pungent odor, which excites tears. Its taste is burning and caustic. It may be liquefied by a temperature of —40°, or at 10° under a pressure of 6½ atmospheres. Faraday's method of liquefying it is as follows: ammonia is passed over dry silver chloride, by which it is absorbed. The silver chloride, saturated with ammonia, is introduced into a bent tube (Fig. 53), the empty limb of which is then sealed at the blow-pipe. The end containing the chloride is now heated in a water-bath, while the empty end is cooled in a freezing mixture (Fig. 54). The ammonia is driven out from the silver chloride, and condenses into a transparent liquid in the cooler branch. Faraday succeeded in solidifying ammonia by subjecting this liquid to rapid evaporation. In the solid state it is a white, crystalline, transparent substance, fusible at —75°, and having only a feeble odor. According to Bunsen, liquid ammonia boils at — 33.7°; its density at 0° is 0.6233.

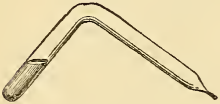


FIG. 53.

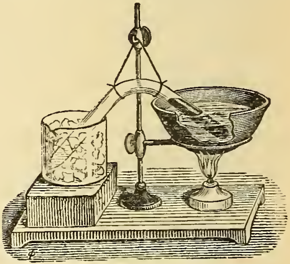


FIG. 54.

Ammonia gas is very soluble in water, which dissolves 1000 times its volume at 0°, and about 740 times its volume at 15°. The rapid absorption of ammonia by water may be strikingly shown by the following experiment. A bottle, A (Fig. 55), is filled with ammonia gas, and fitted with a cork, through which passes a tube drawn out at both extremities, and the outer end of which is sealed. If this end be plunged under water and the point be broken off, the water at once rises into the bottle, forming a fountain, and the vessel becomes filled with water in a very short time.

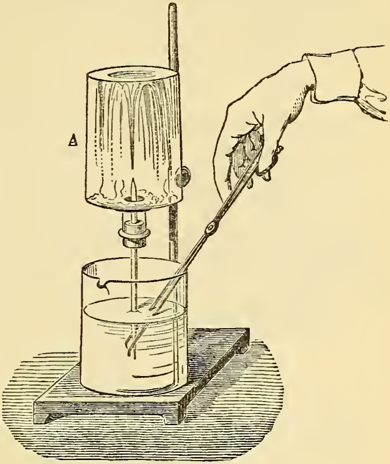


Fig. 55.

The aqueous solution of ammonia possesses the odor of the gas; it is caustic, and was formerly called volatile alkali and spirits of hartshorn. It is largely used in the arts and as a reagent. Its density is 0.882 at 15°. When heated, it loses ammonia gas, the whole of which may be driven out by boiling.

Composition of Ammonia.—200 volumes of ammonia gas are introduced into an eudiometer, and electric sparks are passed through the gas for some time by means of a Ruhmkorff coil (Fig. 56). When the experiment has terminated, the volume of gas will be found to have doubled. 200 volumes of oxygen are added to the 400 volumes of gas thus obtained, and a spark is passed; an explosion takes place, and after making the necessary corrections for temperature and pressure, the 600 volumes of gas are found to be reduced to 150 volumes; 450 volumes have thus disappeared to form water.

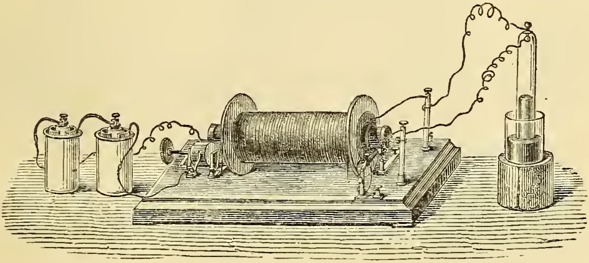


Fig. 56.

These 450 volumes must have contained

300 volumes of hydrogen,
150 volumes of oxygen.

Consequently the 200 volumes of ammonia gas, which were decomposed by the spark into 400 volumes, must have been formed by the union of

300 volumes of hydrogen,
100 volumes of nitrogen.

The latter gas remains in the eudiometer, together with the 50 volumes of oxygen that were employed in excess.

From this analysis it is seen that two volumes of ammonia contain three volumes of hydrogen and one volume of nitrogen, a composition which is expressed by the formula NH^3.

Chemical Properties.—Ammonia gas is decomposed by a high temperature, as by a series of electric sparks. The experiment may be made by passing the gas through a porcelain tube filled with fragments of broken porcelain and heated to whiteness, and collecting the gas resulting from the decomposition in vessels filled with water (Fig. 57). This gas is found to be a mixture of three volumes of hydrogen and one volume of nitrogen.

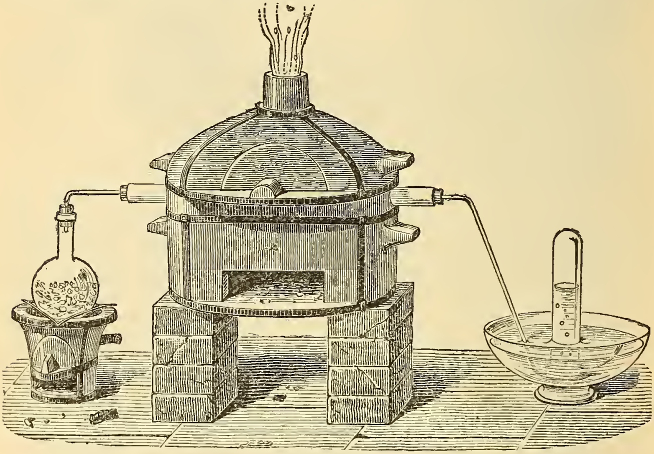


Fig. 57.

The decomposition takes place more readily if iron, copper, or platinum wires be introduced into the porcelain tube. The latter metal is not altered, but the iron and copper become brittle and retain a few per cent. of nitrogen. The decomposition of the ammonia seems here to be favored by the formation of metallic nitrides, unstable compounds which are almost entirely decomposed by the prolonged action of the heat.

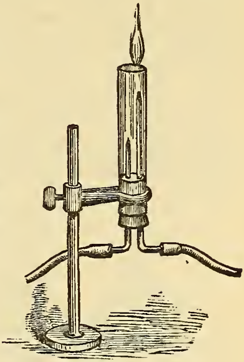


FIG. 58.

Ammonia will not burn in air, but will burn in an atmosphere of oxygen. A glass tube about 25 millimetres in diameter and 15 centimetres long is fitted with a cork through which pass two bent tubes, one reaching nearly to the open end of the tube, the other only a little beyond the cork (Fig. 58), and some cotton-wool or loose asbestos is thrust into the wide tube beyond this point. Ammonia gas, conveniently obtained by heating strong ammonia water, is passed through the longer tube, while oxygen gas is delivered through the shorter. The ammonia may then be ignited, and will burn with a yellow flame. $4NH^3 + 3O^2 = 6H^2O + 2N^2$. A mixture of four volumes of ammonia with three of oxygen will explode on the application of flame.

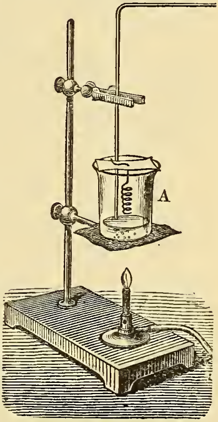


FIG. 59.

Independently of this rapid combustion, ammonia may undergo slow combustion. A spiral of platinum wire is suspended above a little ammonia water in a beaker (A, Fig. 59). The latter is gently heated, and oxygen is passed through the liquid. The mixed ammonia and oxygen gases in contact with the platinum spiral combine and develop so much heat that the spiral is heated to redness. The vessel sometimes becomes filled with white fumes of ammonium nitrite, produced by the slow oxidation of the ammonia. If a mixture of oxygen and ammonia be passed through a heated tube containing spongy platinum, nitric acid and water will be formed and disengaged in vapor.

Action of Chlorine and Iodine upon Ammonia.—Chlorine instantly decomposes ammonia, combining with its hydrogen. If a drawn-out tube through which a jet of ammonia is escaping be plunged into a bottle filled with dry chlorine (Fig. 60), the ammonia takes fire immediately, and white vapors of ammonium chloride are formed.

$$4NH^3 + Cl^3 = 3NH^4Cl + N$$

If a long tube closed at one end be almost filled with saturated chlorine-water, and then filled up with ammonia-water, and quickly inverted on the pneumatic trough, the lighter solution of ammonia will rise through the chlorine-water, and reaction occurs according to the preceding equation. Ammonium chloride remains in solution, while the nitrogen collects in the tube.

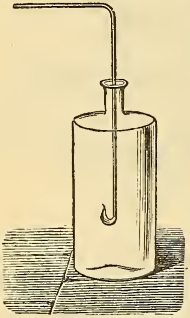


Fig. 60.

Nitrogen Chloride.—Under certain conditions the nitrogen combines with chlorine, forming a very explosive and dangerous compound, nitrogen chloride, NCl^3. This is an oily yellow liquid, heavier than water, which explodes violently on contact with phosphorus, turpentine, and other combustible substances.

A small jar of chlorine is inverted in a saucer containing a solution of ammonium chloride; the salt is slowly decomposed by the chlorine, with the formation of hydrochloric acid and nitrogen chloride, and a drop of yellow liquid soon collects on the surface. A light tap on the vessel causes it to sink through the solution into the saucer. The jar is now removed and a small piece of phosphorus pushed into the drop of nitrogen chloride by the aid of a long wooden rod. Instantly the nitrogen chloride explodes and the saucer is broken into pieces.

When a warm saturated solution of ammonium chloride is electrolyzed, the chlorine set free at the anode reacts with the solution; nitrogen chloride is formed, and carried to the surface with the escaping gases. If a little turpentine be poured on the surface of the liquid, on contact with this each little globule of the chloride explodes with a flash and a continual crackling is kept up.

Nitrogen chloride has been carefully investigated by Gattermann, who found that it explodes also when exposed to direct sunlight.

Nitrogen Iodide.—There is another explosive compound analogous to nitrogen chloride, but containing iodine. It is obtained as a black powder by treating powdered iodine with ammonia; when dry it explodes with great violence on the lightest touch, and sometimes spontaneously. Bunsen has attributed to it the formula $N^2H^3I^3$.

According to Stahlschmidt, the composition of nitrogen iodide corresponds to the formula NI^3, when this body is prepared by the action of an alcoholic solution of iodine upon aqueous ammonia; but if both bodies be in alcoholic solution, an iodide is obtained having the formula NHI^2. If this be correct, these bodies present very simple relations with ammonia.

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

Ammonia. Nitrogen chloride. Triiodammonia. Diiodammonia.
Trichlorammonia. Nitrogen iodides.

The last-named compound has been recently carefully studied by Szuhay, who obtained it by the action of aqueous solution of ammonia upon a strong solution of iodine in potassium iodide. Its hydrogen is replaceable by metals.

Action of Potassium upon Ammonia.—When potassium is heated in an atmosphere of ammonia, the brilliant surface of the metal becomes covered with a greenish-black liquid, and at the same time hydrogen is disengaged. The metal entirely disappears little by little, and, on cooling, the liquid solidifies to an olive-green mass. This substance represents ammonia in which one atom of hydrogen has been replaced by an atom of potassium.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N = \text{Ammonia.} \qquad \left.\begin{matrix}K\\H\\H\end{matrix}\right\}N = \text{Potassium amide.}$$

It reacts with water, forming ammonia and potassium hydrate.

$$\underset{\text{Potassium amide.}}{KNH^2} + H^2O = \underset{\text{Potassium hydrate.}}{KOH} + NH^3$$

Ammonium Amalgam.—If liquid amalgam of potassium or sodium and mercury be treated with a saturated solution of ammonium chloride, the amalgam increases in volume, assumes a buttery consistence, and is converted into a soft, light mass having the metallic lustre of mercury. It will retain the impression of the finger, and will float upon water; but it gradually decomposes, losing hydrogen and ammonia, and only mercury remains. This unstable body is called ammonium amalgam. Whether it is really an amalgam of the group NH^4

with mercury or is simply metallic mercury containing hydrogen and ammonia gases is still doubtful.

Although the ammonium group has not been isolated, there can be no doubt that it exists in many compounds, and plays in them a part analogous to that of a metallic atom. Thus ammonium may replace potassium in the potassium salts, producing compounds similar and analogous to the latter.

$$NH^3.HCl = (NH^4)Cl \quad \text{analogous to} \quad KCl$$

Ammonium chloride. Potassium chloride.

$$NH^3.HNO^3 = (NH^4)NO^3 \quad \text{analogous to} \quad KNO^3$$

Ammonium nitrate. Potassium nitrate.

$$NH^3.H^2S = \left.\begin{matrix} NH^4 \\ H \end{matrix}\right\} S \quad \text{analogous to} \quad \left.\begin{matrix} K \\ H \end{matrix}\right\} S$$

Ammonium sulphydrate. Potassium sulphydrate.

$$(NH^3)^2.H^2S = \left.\begin{matrix} NH^4 \\ NH^4 \end{matrix}\right\} S \quad \text{analogous to} \quad \left.\begin{matrix} K \\ K \end{matrix}\right\} S$$

Ammonium sulphide. Potassium sulphide.

AMMONIUM CHLORIDE.

NH^4Cl

This salt was formerly obtained from Egypt, where it was made by subliming the soot produced by the combustion of camel's dung. It is now prepared in large quantities from gas-liquor, or the water condensed in the manufacture and purification of illuminating gas from coal. This liquor is heated with lime, ammonia is disengaged and is conducted into hydrochloric acid. Ammonium chloride is obtained by simply evaporating the solution. It is purified by sublimation in stoneware pots which are heated in a furnace out of which the upper parts of the pots project. There the volatilized chloride condenses, and the sublimed product is known in commerce as sal ammoniac, or muriate of ammonia.

It generally occurs as white or grayish, compact masses, having a crystalline fibrous structure. Its taste is sharp and salty. It dissolves in two and a half parts of cold, and in its own weight of boiling water. It is deposited from a saturated solution in small octahedra, grouped together in needles, and presenting a fern-leaf-like appearance. At a high temperature it volatilizes without melting; its vapor is dissociated, but the resulting NH^3 and HCl at once recombine on cooling.

Ammonium chloride is formed by the union of equal volumes of hydrochloric acid and ammonia gases.

AMMONIUM HYDROSULPHIDE AND AMMONIUM SULPHIDE.

Hydrogen sulphide and ammonia gases unite in the cold in two different proportions, forming two compounds, ammonium hydrosulphide and ammonium sulphide.

$$\underset{\substack{\text{Hydrogen sulphide.}\\ \text{(2 vol.)}}}{H^2S} \quad + \quad \underset{\substack{\text{Ammonia.}\\ \text{(2 vol.)}}}{NH^3} \quad = \quad \underset{\text{Ammonium hydrosulphide.}}{\left.\begin{matrix}NH^4\\ H\end{matrix}\right\}S}$$

$$\underset{\substack{\text{Hydrogen sulphide.}\\ \text{(2 vol.)}}}{H^2S} \quad + \quad \underset{\substack{\text{Ammonia.}\\ \text{(4 vol.)}}}{2NH^3} \quad = \quad \underset{\text{Ammonium sulphide.}}{\left.\begin{matrix}NH^4\\ NH^4\end{matrix}\right\}S}$$

These compounds are definite, but are decomposed into their elements by heat. Horstmann and Salet have shown that hydrogen sulphide and ammonia gases may be mixed in all proportions without contraction in volume taking place, provided the temperature be maintained above 60°.

Ammonium hydrosulphide is generally obtained in solution by saturating aqueous ammonia with hydrogen sulphide. This solution is colorless, but acquires a yellow color on exposure to the air. When a quantity of ammonia is added to it equal to that which it already contains, ammonium sulphide, $(NH^4)^2S$, is formed, which corresponds to potassium sulphide, K^2S.

Ammonium sulphide is largely employed in the laboratory as a reagent for the detection of certain metals.

If ammonium sulphide be added to a solution of ferrous sulphate, a double decomposition takes place; ammonium sulphate is formed and remains in solution, while ferrous sulphide forms a black precipitate.

$$\underset{\text{Ferrous sulphate.}}{FeSO^4} \quad + \quad (NH^4)^2S \quad = \quad \underset{\text{Ferrous sulphide.}}{FeS} \quad + \quad \underset{\text{Ammonium sulphate.}}{(NH^4)^2SO^4}$$

The salts of zinc, manganese, cobalt, and nickel are likewise precipitated as sulphides by ammonium sulphide.

The salts of aluminium and chromium are precipitated as hydroxides, hydrogen sulphide being disengaged.

The preceding salts are not precipitated by hydrogen sulphide (the zinc salts are not precipitated if they be acid), but the latter reagent precipitates in the form of sulphides the salts of lead, bismuth, copper, cadmium, mercury, silver, antimony, tin, gold, and platinum. The sulphides of the latter four metals dissolve in an excess of ammonium sulphide.

The sulphides of arsenic, tin, antimony, gold, and platinum all form compounds with ammonium sulphide, in which the latter plays the part of a base.

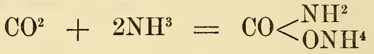
AMMONIUM NITRATE.

$(NH^4)NO^3$

Ammonium nitrate is prepared by saturating nitric acid with ammonia. It crystallizes in large, transparent, fusible prisms, which are very soluble in water and produce a notable depression of temperature in the act of solution, extending even to —15°. At 300° ammonium nitrate is decomposed into nitrogen monoxide and water. It is used for the preparation of nitrous oxide, much used as an anæsthetic.

AMMONIUM CARBONATE.

When dry carbon dioxide and ammonia gases are mixed in the proportion of 2 volumes of the first to 4 volumes of the second, they condense, forming a white powder, which is ammonium carbamate, a compound which was formerly called anhydrous carbonate of ammonia.



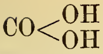
$$CO^2 + 2NH^3 = CO{<}\begin{matrix}NH^2\\ONH^4\end{matrix}$$

Ammonium carbamate.

The ammonium carbonate of commerce is generally considered as a sesquicarbonate. It contains $2[CO^3(NH^4)^2] + CO^2 + 2H^2O$. It is obtained by heating a mixture of equal parts of ammonium sulphate and chalk in a subliming apparatus. Ammonia and water are disengaged, and the sesquicarbonate of ammonium sublimes.

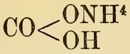
Recently sublimed ammonium sesquicarbonate is transparent and crystalline. It has a strong ammoniacal odor and a sharp caustic taste. When exposed to the air it gradually loses ammonia and is converted into ammonium acid carbonate.

Ammonium Acid Carbonate.—This salt, which is commonly known as bicarbonate of ammonia, may be obtained by passing a current of carbonic acid gas into aqueous ammonia, to saturation. The acid salt separates in right rhombic prisms. The neutral carbonate of ammonium crystallizes from a cooled solution of the sesquicarbonate in ammonia-water. These salts present the following relations to the hypothetical carbonic acid:



$$CO{<}{\begin{matrix}OH\\OH\end{matrix}}$$

Carbonic acid.
(Hypothetical.)



$$CO{<}{\begin{matrix}ONH^4\\OH\end{matrix}}$$

Ammonium acid
carbonate.

$$CO{<}{\begin{matrix}ONH^4\\ONH^4\end{matrix}}$$

Ammonium
carbonate.

AMMONIUM SULPHATE.

$(NH^4)^2SO^4$

This salt is obtained in the arts by passing the ammonia that is disengaged when gas-liquor is heated with lime into dilute sulphuric acid. It crystallizes in right rhombic prisms.

It is colorless and has a sharp taste. It dissolves in two parts of cold, and in its own weight of boiling, water. It is insoluble in alcohol.

Ammonium sulphate is manufactured on an enormous scale, and is used as a fertilizer and for the preparation of other ammonium compounds.

HYDROXYLAMINE.[1]

$NH^2(OH)$

This remarkable compound was discovered by Lossen in 1865, and first obtained in a state of purity by Lobry de Bruyn in 1891. It is produced by the action of *nascent* hydrogen—that is, hydrogen at the instant when it is set free—upon nitric oxide, nitric acid, and certain nitrates.

$$NO + 3H^2 = 2NH^2(OH)$$
$$HNO^3 + 3H^2 = NH^2(OH) + 2H^2O$$

When a current of nitric oxide is passed into a mixture of tin and hydrochloric acid, the hydroxylamine formed remains in solution combined with an excess of the acid.

A more convenient method of preparation consists in adding a concentrated cold solution of sodium nitrite to one of sodium acid sulphite, and heating the resulting compound—*sodium hydroxylamine disulphonate*, $N(OH)(SO^3Na)^2$—with water at 130° in closed vessels. The products are hydroxylamine, sulphuric acid, and sodium sulphate.

$$NaNO^2 + 2NaHSO^3 = N(OH)(SO^3Na)^2 + NaOH$$
$$2N(OH)(SO^3Na)^2 + 4H^2O = (NH^3OH)^2SO^4 + H^2SO^4 + 2Na^2SO^4$$

The sulphate of hydroxylamine is thus obtained. Hydroxylamine is an energetic base which, like ammonia, forms definite salts with the acids. It may be regarded as ammonia, in which the group OH (hydroxyl) has been substituted for one atom of hydrogen.

The free base has been prepared by the action of sodium methoxide (page 486) upon hydroxylamine hydrochloride dissolved in methyl alcohol.

$$\underset{\substack{\text{Hydroxylamine}\\\text{hydrochloride.}}}{NH^3(OH)Cl} + \underset{\substack{\text{Sodium}\\\text{methoxide.}}}{NaOCH^3} = NH^2(OH) + NaCl + \underset{\substack{\text{Methyl}\\\text{alcohol.}}}{CH^3OH}$$

---

[1] An amine is a compound representing NH^3 in which one or more atoms of H are replaced by equivalent atoms or groups.

Hydroxylamine is an odorless and colorless solid, crystallizing in plates or needles which deliquesce on exposure to the air. Its density is 1.35. It melts at 33°, and boils at 58° under 22 mm. pressure. Heated above 100° it explodes violently.

Its aqueous solution has powerful reducing properties: it precipitates gold and mercury from solutions of their salts, and, on boiling with a cupric salt, throws down red cuprous oxide.

HYDRAZINE.

$NH^2—NH^2$

By warming triazoacetic acid $(CHN^2—COOH)^3$ with sulphuric acid, Curtius obtained the sulphate of a new compound of hydrogen and nitrogen, $(NH^2)^2=H^2N—NH^2$, which is named hydrazine. This base forms a dihydrochloride $(NH^2)^2 2HCl$, and a hydrochloride $(NH^2)^2 HCl$, both of which are crystallizable solids.

Hydrazine hydrate, $(NH^2)^2.H^2O$, is prepared by distilling the hydrochloride with potassium hydroxide. It is a fuming, caustic liquid, of peculiar odor, and boils at 119°. It destroys cork and caoutchouc, and even corrodes glass. The free base, $(NH^2)^2$, is obtained by treating the hydrate with an excess of barium oxide and distilling in vacuo. It is a fuming, inflammable liquid, which boils at 112.5° (Lobry de Bruyn).

HYDRAZOIC ACID.

HN^3

Curtius has isolated a remarkable compound of the composition N^3H, which closely resembles hydrochloric acid in its properties. It is called hydrazoic acid. Its sodium salt is readily obtained by passing nitrous oxide over heated sodium amide (W. Wislicenus).

$$\underset{\text{Sodium amide.}}{2NaNH^2} + N^2O = \underset{\text{Sodium hydrazoate.}}{NaN^3} + NaOH + NH^3$$

An aqueous solution of the free acid may be prepared by treating this sodium salt with dilute sulphuric acid, or by conducting red nitrous vapors into a solution of hydrazine hydrate at 0°.

Hydrazoic acid is a colorless, mobile liquid, having a very penetrating odor. Its boiling point is 37°. Its solution is strongly acid. It dissolves many metals with evolution of hydrogen. The resulting hydrazoates are in many respects analogous to the chlorides. Silver hydrazoate forms a white curdy precipitate.

Hydrazoic acid and many of its salts are explosive.

OXYGEN COMPOUNDS OF NITROGEN.

Five compounds of nitrogen and oxygen are known.

	ATOMIC COMPOSITION.	VOLUMETRIC COMPOSITION.
Nitrous oxide	N^2O	2 vol. N and 1 v. O condensed in 2 v.
Nitric oxide	NO	1 vol. N and 1 v. O = 2 v.
Nitrogen trioxide	N^2O^3	2 vol. N and 3 v. O condensed in 2 v.
Nitrogen peroxide .	NO^2 and N^2O^4	2 vol. N and 4 v. O condensed in 2 v.
Nitrogen pentoxide	N^2O^5	2 vol. N and 5 v. O condensed in 2 v.

Nitrogen trioxide and nitrogen pentoxide combine with water, forming nitrous and nitric acids.

$$N^2O^3 + H^2O = 2HNO^2$$
$$N^2O^5 + H^2O = 2HNO^3$$

NITROUS OXIDE.

Density compared to air 1.527
Density compared to hydrogen . . . . 22.
Molecular weight N^2O . . . . $=44$.

This gas, known also as protoxide or monoxide of nitrogen, and laughing-gas, was discovered by Priestley in 1776.

Preparation.—It is obtained by gently heating ammonium nitrate in a glass retort. The salt melts, and then decomposes with effervescence into water and nitrous oxide, which may be collected over water (Fig. 61).

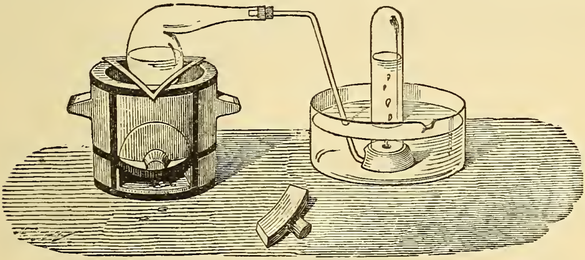


FIG. 61.

$$(NH^4)NO^3 = N^2O + 2H^2O$$

Properties.—Nitrous oxide is colorless and odorless, but possesses a sweetish taste. It is not permanent, and may be liquefied by strong pressure. It is liquefied on a considerable scale at present, that it may be transported in small bulk for the use of dentists. For this purpose it is compressed in strong iron reservoirs from which it may be easily drawn in the liquid state for experiments after first cooling the reservoir in ice and salt.

A remarkable experiment can be performed as follows: A quantity of liquid nitrous oxide is poured into a test-tube fixed by a cork in the neck of a bottle; a portion of it instantly volatilizes, producing intense cold. If now a little mercury be poured into the tube, it will sink through the liquid monoxide and immediately be solidified. A small piece of incandescent charcoal let fall into the tube will float upon the surface of the liquid, and burn with great brilliancy, notwithstanding the intense cold by which it is surrounded, as evidenced by the freezing of the mercury (Fig. 62).

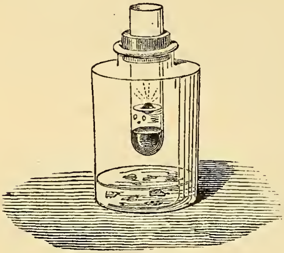


Fig. 62.

Water dissolves about its own volume of nitrous oxide at ordinary temperatures.

A taper which has been extinguished, but still bears a spark of fire, is relighted, and burns brilliantly when plunged into a jar of nitrous oxide (Fig. 63). In the same manner, the combustion of sulphur and phosphorus is effected with great energy in an atmosphere of this gas.

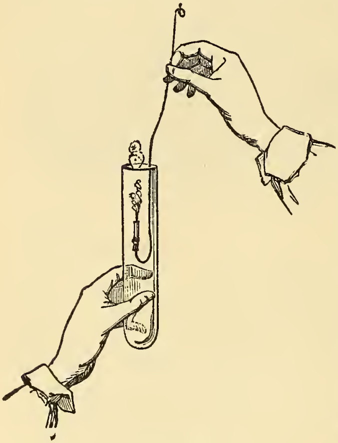


Fig. 63.

Equal volumes of nitrous oxide and hydrogen form a mixture which explodes on the passage of an electric spark or on the application of flame.

$$\underset{\text{2 volumes.}}{N^2O} + \underset{\text{2 volumes.}}{H^2} = \underset{\text{2 volumes.}}{H^2O} + \underset{\text{2 volumes.}}{N^2}$$

Respiration is a slow combustion and may be sustained for a few seconds by nitrous oxide. Such inhalation does not suffocate but it disturbs the functions of the nervous system, producing anæsthesia, and for this purpose nitrous oxide is now largely employed by surgeons and dentists. The insensibility is frequently preceded by a stage of intoxication, hence the name *laughing-gas*, which was given by Davy.

It must be added that these exhilarating effects have not been observed in recent experiments with perfectly pure nitrous oxide.

NITRIC OXIDE.

Density compared to air	1.039
Density compared to hydrogen	15.
Molecular weight NO	$=30.$

Preparation.—This gas was discovered in 1772 by Hales; it is prepared by decomposing cold, dilute nitric acid by metallic copper.

$$\underset{\text{Copper.}}{3Cu} + \underset{\text{Nitric acid.}}{8HNO^3} = \underset{\text{Cupric nitrate.}}{3Cu(NO^3)^2} + 4H^2O + 2NO$$

The copper and water are introduced into a gas-bottle, and ordinary nitric acid is added by means of a funnel-tube; the copper is immediately attacked and dissolved, forming cupric nitrate (Fig. 64), and at the same time nitric oxide gas is disengaged. This gas absorbs oxygen from the air and is converted into red vapors, which are at first apparent in the gas-bottle, but as the evolution of nitric oxide continues, the gas in the flask gradually becomes colorless, and may then be collected in jars over water.

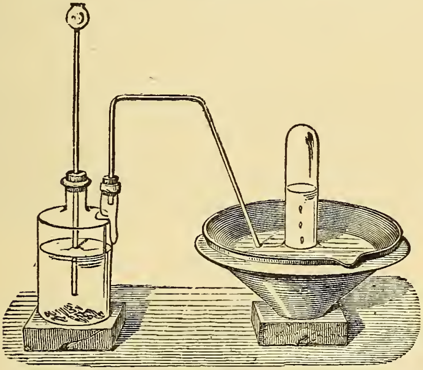


Fig. 64.

Properties.—Nitric oxide is a colorless gas. Its liquefaction was first effected by Cailletet. It is decomposable by heat, but less easily than the monoxide. It is scarcely soluble in water, which only takes up a twentieth of its volume. Its most characteristic property is the energy with which it absorbs half its volume of oxygen, passing into the state of nitrogen peroxide or red vapors.

If a jar filled with nitric oxide be opened to the air, the red vapors appear at once.

$$2NO + O^2 = N^2O^4$$

Nitric oxide supports the combustion of certain substances. Phosphorus burns in it brilliantly, but the gas does not, like oxygen and nitrogen monoxide, relight a taper still presenting a spark.

Hydrogen decomposes nitric oxide at a temperature but slightly elevated, forming water and nitrogen.

$$NO + H^2 = N + H^2O$$

The mixture of the two gases in equal volumes takes fire on the application of flame.

If a few drops of carbon disulphide be poured into a jar of nitric oxide, the vapor of the volatile liquid is at once diffused throughout the gas, and on the approach of a lighted taper a brilliant flash of light is produced, the sulphur and carbon being burned by the oxygen of the nitric oxide.

The light produced by this combustion is rich in actinic rays: like the solar light, it effects the explosive combination of chlorine and hydrogen.

When a mixture of nitric oxide with an excess of hydrogen is passed through a heated tube containing platinum sponge, water and ammonia are formed.

$$NO + 5H = H^2O + NH^3$$

Under other circumstances hydroxylamine may be produced.

A solution of ferrous sulphate absorbs nitric oxide with avidity, assuming a dark-brown color; this is a characteristic property, by which nitric oxide may be recognized.

NITROGEN TRIOXIDE.

N^2O^3

This compound does not appear to exist except at very low temperatures. It is formed by passing nitric oxide into liquid nitrogen peroxide at —21°.

$$2NO + N^2O^4 = 2N^2O^3$$

It is a blue liquid, which congeals at —82°, and boils, with decomposition, at 3.5°. Even below this temperature the liquid appears to suffer partial decomposition.

NITROGEN PEROXIDE.

NO^2 or N^2O^4

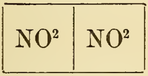
Preparation.—When well dried lead nitrate is heated to redness it is decomposed into lead oxide and nitrogen peroxide, which may be condensed in a well-cooled receiver.

$$\underset{\text{Lead nitrate.}}{Pb(NO^3)^2} = \underset{\text{Lead oxide.}}{PbO} + O + N^2O^4$$

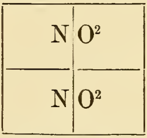
The first portions of nitrogen peroxide that are condensed generally retain a trace of moisture, and present a green color; if the receiver be then changed, there collects a yellow liquid which solidifies to a crystalline mass at —10°.

Properties.—Nitrogen peroxide is a mobile liquid, almost colorless at very low temperatures; at 0° it has a somewhat darker color, and at 15° it is orange-brown. It boils at 22°, and its vapor is red. Near the point of ebullition its volumetric composition corresponds to the formula N^2O^4; that is, two volumes of nitrogen and four volumes of oxygen are condensed into two volumes of N^2O^4, and occupy the same space as two atoms (one molecule) of hydrogen.

But at a higher temperature this vapor is dissociated; that is, it is gradually decomposed in such a manner as to occupy double its primitive volume. The two atoms of nitrogen and four atoms of oxygen which constitute two volumes of N^2O^4 at a low temperature, occupy four volumes at about 140°.



Red vapors at 20°.



Red vapors at 140°.

The vapor of nitrogen peroxide is very corrosive, and dangerous to inhale.

A small quantity of cold water decomposes nitrogen peroxide into nitrogen trioxide and nitric acid; a larger quantity of water causes the formation of nitrous and nitric acids.

$$N^2O^4 + H^2O = \underset{\text{Nitrous acid.}}{HNO^2} + \underset{\text{Nitric acid.}}{HNO^3}$$

At ordinary temperatures and in presence of much water, nitric oxide is formed.

$$3NO^2 + H^2O = 2HNO^3 + NO$$

When a mixture of nitrogen peroxide and hydrogen is passed over heated platinum sponge, water and ammonia are formed.

Certain very finely divided metals, especially copper, nickel, and cobalt, have the property of absorbing large quantities of nitrogen peroxide, apparently combining with it to form definite compounds that have been named *nitro-metals.* The copper compound, Cu^2NO^2, is a dark-brown powder, which is decomposed at 90°, and also by water, into copper and nitrogen peroxide.

Nitryl Chloride and Bromide.—Like nitric oxide, which may be called nitrosyl, nitrogen peroxide may play the part of a radical. There exists a chloride and also a bromide of nitrogen peroxide or nitryl.

$$\underset{\text{Nitryl chloride.}}{NO^2Cl} \qquad \underset{\text{Nitryl bromide.}}{NO^2Br}$$

The latter compound is formed, together with other products, when bromine acts upon nitrogen peroxide at a very low temperature. The chloride of nitryl has recently been obtained by the reaction of phosphorus oxychloride upon silver nitrate.

$$\underset{\substack{\text{Phosphorus}\\\text{oxychloride.}}}{POCl^3} + \underset{\text{Silver nitrate.}}{3AgNO^3} = \underset{\text{Silver phosphate.}}{Ag^3PO^4} + \underset{\text{Nitryl chloride.}}{3(NO^2Cl)}$$

Nitryl chloride is a light-yellow liquid, boiling at +5° and solidifying at —31°.

In contact with water, it forms nitryl hydrate (nitric acid), and hydrochloric acid.

$$NO^2Cl + H^2O = HCl + NO^2.OH$$

The nitric acid is formed at the expense of the water, of which one atom of hydrogen is removed by the chlorine and replaced by the radical nitryl. Hence in nitric acid the group NO^2 replaces one atom of hydrogen in water; this group is therefore monatomic.

But the atom of hydrogen in nitric acid may also be replaced by another nitryl group, and the result is an oxide of nitryl, the anhydride of nitric acid, or nitrogen pentoxide. The following formulæ will illustrate the relations between these compounds and water which is their type:

$$\underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} \qquad \underset{\substack{\text{Nitric acid.}\\\text{(Nitryl hydrate.)}}}{\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O} \qquad \underset{\substack{\text{Nitrogen pentoxide.}\\\text{(Nitryl oxide.)}}}{\left.\begin{matrix}NO^2\\NO^2\end{matrix}\right\}O}$$

NITROGEN PENTOXIDE.

(NITRIC ANHYDRIDE.)

N^2O^5

This compound was obtained by H. Sainte-Claire Deville by the action of chlorine upon dry silver nitrate heated to between 58 and 60°.

$$\underset{\text{Silver nitrate.}}{2AgNO^3} + Cl^2 = \underset{\text{Nitrogen pentoxide.}}{N^2O^5} + \underset{\text{Silver chloride.}}{2AgCl} + O$$

It may also be obtained by passing the vapor of nitryl chloride over silver nitrate heated to 70°.

$$\underset{\text{Silver nitrate.}}{AgO.NO^2} + \underset{\text{Nitryl chloride.}}{NO^2Cl} = AgCl + \underset{\text{Nitrogen pentoxide.}}{(NO^2)^2O}$$

Also, as shown by Berthelot, by the action of phosphorus pentoxide upon concentrated nitric acid.

$$2HNO^3 - H^2O = N^2O^5$$

Nitrogen pentoxide is solid and crystallizes in right-rhombic prisms. It melts at 29.5°, and boils between 48 and 50°. It is very unstable and explodes spontaneously even when it is preserved at a low temperature.

NITRIC ACID.

HNO^3

The atmosphere frequently contains a trace of nitric acid vapor or other compounds of nitrogen and oxygen, and small quantities of ammonium nitrate and nitrite may be detected in rain-water. After passing a current of air for a long time through a solution of potassium carbonate, the liquid is found to contain potassium nitrate (Cloez). It may be admitted that the compounds of nitrogen and oxygen are formed directly by the action of electricity upon the elements of the air.

The nitrates of potassium, sodium, magnesium, and calcium are met with in certain soils, often in abundance. They are formed wherever nitrogenized organic matters decompose in contact with the air and in presence of porous matters and alkaline bases.

By the activity of peculiar micro-organisms, ammonia and ammonium nitrite are first produced, and these are oxidized and converted into nitrates. In rainless regions these nitrates form extensive deposits.

Preparation.—Nitric acid is obtained by decomposing an alkaline nitrate with sulphuric acid. In the laboratory, the operation may be conducted in a glass retort, the neck of which passes, without cork, into a cooled receiver. 98 parts of concentrated sulphuric acid and 85 parts of sodium nitrate are employed. On the application of heat, nitric acid is volatilized, mixed at the commencement of the operation with red vapors. The acid condenses in the receiver as a yellow liquid, fuming in the air. Sodium acid sulphate remains in the retort.

$$H^2SO^4 + \underset{\text{Sodium nitrate.}}{NaNO^3} = \underset{\text{Sodium acid sulphate.}}{\left.\begin{matrix}Na\\H\end{matrix}\right\}SO^4} + HNO^3$$

In the arts, the sodium nitrate is decomposed with a less concentrated sulphuric acid, the decomposition of the nitric acid during the operation being thus avoided. The operation is conducted in cast-iron retorts, A (Fig. 65), the lateral tubes of which, B, are adapted to stoneware tubes communicating with a series of stoneware bottles, D, where the acid condenses. The temperature is elevated towards the close of the operation, and sodium neutral sulphate is formed.

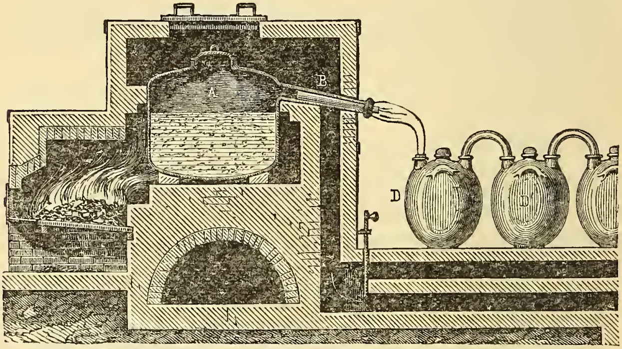


Fig. 65.

$$H^2SO^4 + 2NaNO^3 = Na^2SO^4 + 2HNO^3$$

Properties.—When perfectly pure, nitric acid is colorless, but it rapidly becomes yellow under the influence of light, undergoing a partial decomposition. When exposed to the air, it gives off abundant white fumes. Its density is 1.52; it solidifies at —49°, and boils at 86°.

When its vapor is passed through a red-hot porcelain tube, it is decomposed into nitrogen peroxide, oxygen, and water.

$$2HNO^3 = H^2O + N^2O^4 + O$$

The same decomposition takes place when the concentrated acid is boiled under ordinary pressures: its boiling-point gradually rises while the acid becomes weaker until a temperature of 120.5° is reached. The residual liquid, which distils without further decomposition, contains 68 per cent. of the acid and has a density of 1.414. The same acid results when a weaker acid is distilled; it becomes gradually stronger until a boiling-point of 120.5° is attained. However, the acid which distils at a temperature higher than 86° cannot be considered a definite hydrate; its composition depends on the pressure.

Nitric acid readily gives up a portion of its oxygen to bodies having an affinity for that element. It energetically oxidizes sulphur, phosphorus, arsenic, iodine, silicon, carbon, and most of the metals.

If nitric acid be poured upon red-hot charcoal, the combustion is vividly intensified by the decomposition of the nitric acid, and red fumes appear at the same time.

Copper decomposes nitric acid with an abundant disengagement of nitric oxide, which is converted into nitrogen peroxide by contact with the air.

If dilute nitric acid be poured upon clean iron wire, chemical action at once takes place, and there is an abundant evolution of red vapor; but if the same wire be plunged into the concentrated acid, no action is manifested; and further, if the strong acid be poured off and replaced by dilute acid, the latter undergoes no decomposition; the iron has become *passive* by becoming covered with a thin film of oxide of iron. This passive state of iron may also be brought about by means of other oxidizing agents, such as chromic and chloric acids.

The action of tin upon nitric acid is worthy of notice. Torrents of red vapor are disengaged, and the metal is converted into a white powder, which is stannic acid. In this reaction small quantities of ammonia and hydroxylamine are formed at the expense of the elements of the nitric acid, and remain combined with the excess of acid.

The conversion of nitric acid into ammonia may be more complete. If zinc be introduced into very dilute nitric acid, the metal dissolves slowly and without disengagement of gas; the liquid is then found to contain zinc nitrate and ammonium nitrate. The nascent hydrogen set free from a portion of the nitric acid by the zinc reduces another portion of the acid, forming water and ammonia.

$$\underset{\text{Zinc.}}{Zn} + 2HNO^3 = \underset{\text{Zinc nitrate.}}{Zn(NO^3)^2} + H^2$$

$$2HNO^3 + 4H^2 = 3H^2O + \underset{\text{Ammonium nitrate.}}{(NH^4)NO^3}$$

Nitric oxide decomposes nitric acid. The acid is reduced, and either nitrogen peroxide or nitrous acid is formed and remains dissolved in the liquid, the former communicating a brown, the second a blue or green color.

Nitric acid is one of the most important acids. It is employed in the manufacture of sulphuric acid, and also to oxidize certain organic matters, such as starch and sugar, which it converts into oxalic acid. It is also used in parting gold, in the manufacture of nitrates, nitroglycerin, picric acid, and coal-tar colors, and is the most generally useful oxidizing agent in the laboratory.

Nitro-hydrochloric Acid.—A mixture of nitric and hydrochloric acids is called nitro-hydrochloric or nitro-muriatic acid, or aqua regia. This liquid dissolves gold and platinum, and it owes this property to the chlorine, which is set at liberty by the mutual action of the two acids.

$$6HCl + 2HNO^3 = 4H^2O + 2NO + 3Cl^2$$

When the mixture is left to itself it gradually assumes a yellow color, undergoing a partial decomposition. But this decomposition is limited, and only complete in the presence of metals which are capable of absorbing free chlorine.

The reaction between hydrochloric and nitric acids gives rise to the formation of another product, consisting of oxygen, nitrogen, and chlorine. It is *nitrosyl chloride*, NO.Cl.

$$3HCl + HNO^3 = 2H^2O + NOCl + Cl^2$$

Nitrosyl chloride is an orange-colored gas which, with the aid of a freezing mixture, is readily condensed to a liquid of the same color. This boils at —5°. By reacting with water nitrosyl chloride forms hydrochloric and nitrous acids.

$$NO.Cl + H^2O = HCl + NO.OH$$

Similarly a chloride and a nitrite result when nitrosyl chloride is treated with an alkaline hydroxide.

$$NO.Cl + 2KOH = KCl + NO.OK + H^2O$$

It will be noticed that nitrosyl chloride bears the same relation to nitrous acid that nitryl chloride bears to nitric acid. The following formulæ will illustrate the constitution of these bodies:

$NO.Cl$	$\left.\begin{matrix}NO\\H\end{matrix}\right\}O$	$\left.\begin{matrix}NO\\NO\end{matrix}\right\}O$
Nitrosyl chloride.	**Nitrous acid.**	**Nitrogen trioxide.**
$NO^2.Cl$	$\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O$	$\left.\begin{matrix}NO^2\\NO^2\end{matrix}\right\}O$
Nitryl chloride.	**Nitric acid.**	**Nitrogen pentoxide.**

PHOSPHORUS.

Vapor density compared to air	4.32
Vapor density compared to hydrogen	61.1
Atomic weight P	= 30.75

Brand, an alchemist of Hamburg, while attempting to extract the philosopher's stone from urine, discovered phosphorus in 1669. But urine contains only a small quantity of phosphates and can yield but traces of phosphorus, so that this body only became generally known to chemists after Gahn demonstrated its existence in bones, and Scheele discovered the process for its extraction.

The process of the latter chemist is still in use; it consists in treating bone-ash with dilute sulphuric acid, by which means the tricalcium phosphate of the bones is converted into monocalcium phosphate, ordinarily called acid phosphate of lime.

$$\underset{\text{Tricalcium phosphate.}}{Ca^3(PO^4)^2} + 2H^2SO^4 = \underset{\text{Calcium acid phosphate.}}{CaH^4(PO^4)^2} + \underset{\text{Calcium sulphate.}}{2CaSO^4}$$

The latter phosphate being soluble is separated from the calcium sulphate by filtration, and the solution is evaporated and mixed with powdered charcoal. The mixture is dried and gradually heated to redness in cast-iron vessels. By this means the calcium acid phosphate is converted into calcium metaphosphate by the expulsion of two molecules of water.

$$\underset{\text{Calcium acid phosphate.}}{CaH^4(PO^4)^2} = 2H^2O + \underset{\text{Calcium metaphosphate.}}{Ca(PO^3)^2}$$

The latter is strongly heated with charcoal in clay retorts (Fig. 66), and is decomposed, yielding carbon monoxide and phosphorus which distils over, and leaving a residue of calcium pyrophosphate.

$$\underset{\text{Calcium metaphosphate.}}{2Ca(PO^3)^2} + 5C = \underset{\text{Calcium pyrophosphate.}}{Ca^2P^2O^7} + \underset{\text{Carbon monoxide.}}{5CO} + P^2$$

The phosphorus condenses in the water in the receiver A, in which the neck of the retort C is engaged.

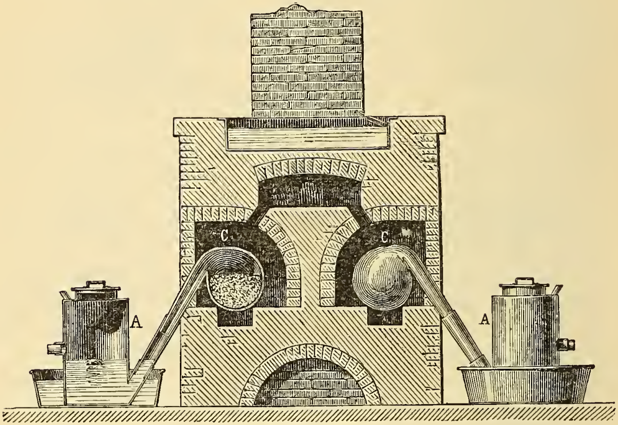


FIG. 66.

The crude product is purified either by redistilling it, or by enclosing it in a chamois-skin sack and strongly compressing it under water at 50°; the phosphorus passes through the leather and collects under the water. It is moulded into sticks by being drawn up into slightly conical glass tubes, which are then plunged into cold water. The phosphorus solidifies and is easily drawn from the tubes.

A newer process of manufacturing phosphorus consists in directly reducing the calcium phosphate by charcoal at the high temperatures attainable in the electric furnace (page 210). A flux is added to form a liquid slag with the lime, which remains in the furnace while the phosphorus distils.

Physical Properties.—Recently-fused phosphorus is transparent, colorless, or having a pale-yellow tint, flexible, and soft enough to be easily scratched by the nail. One-tenth per cent. of sulphur renders it hard and brittle. It has a well-marked odor, slightly resembling that of garlic. Its density at 10° is 1.83. It melts at 44° and boils at 290°; its vapor is colorless and has a density of 4.32 compared to air, or 61.1 compared to hydrogen.

If one volume of hydrogen weighs 1, one volume of vapor of phosphorus weighs 61.1, and this number should represent the weight of one atom of phosphorus; now it represents the weight of two atoms, and the vapor of phosphorus presents the singular anomaly that it contains in the same volume twice as many atoms as the simple gases, such as hydrogen or nitrogen. If one volume of hydrogen contain one atom, one volume of phosphorus vapor contains two. It has been found, however, that at temperatures considerably above 1000° the density of phosphorus vapor is diminished: the molecules consisting of four atoms are dissociated into simpler ones.

$$P^4 = 2P^2$$

The vapor density of arsenic is likewise anomalous, corresponding to the molecular formula As^4.

Phosphorus volatilizes below its boiling-point and even below its melting-point. At ordinary temperatures it emits vapors in a vacuum and even in the air. It is luminous in the dark, from which property it derives its name, which signifies light-bearer. The cause of this phenomenon is still obscure, but is generally attributed to the slow oxidation which phosphorus undergoes in the air.

When a stick of transparent phosphorus is kept under water, it gradually becomes opaque and covered with a yellowish-white pulverulent powder, while the central parts retain their transparence. This white phosphorus is still pure, but the surface of the stick has divided into a multitude of little particles which present a crystalline appearance. Some of them become detached and remain suspended in the water, giving to the latter the property of being luminous in the dark.

Phosphorus is rapidly dissolved by carbon disulphide and is deposited in rhombic dodecahedra on the slow evaporation of the solution.

There is an amorphous variety of phosphorus which differs so much from ordinary phosphorus that it presents the properties of an entirely different substance. It has a dark brown-red color, and is not luminous in the dark. It is insoluble in carbon disulphide; it does not melt and take fire like ordinary phosphorus when heated to 60°. It is amorphous, and presents a conchoidal fracture. Its density is 2.14. Ordinary phosphorus is one of the most dangerous poisons, but this red body exerts no action upon the economy. At 260° amorphous phosphorus melts and again becomes ordinary phosphorus.

Amorphous phosphorus results from a physical change brought about by the action of light or heat on the ordinary variety. If a stick of phosphorus be exposed to direct sunlight, its surface assumes a red color; or if it be maintained for a long time at a temperature of 240°, it is entirely converted into the amorphous variety.

This transformation is also accomplished by the influence of certain chemical agents. If a small stick of ordinary phosphorus be introduced into a test-tube and a very minute portion of iodine be allowed to fall upon it, the iodine unites with the phosphorus with the production of light and heat. A trace of phosphorus iodide is formed, and the remainder of the phosphorus is converted into a hard, black mass, which yields a red powder; this is amorphous phosphorus (E. Kopp, Brodie).

Thus prepared, this body volatilizes like arsenic, without melting, and can be distilled without alteration, condensing in a black mass, which contains only traces of iodine.

Chemical Properties.—Ordinary phosphorus possesses a strong affinity for oxygen. When exposed to the air it slowly oxidizes, and the slow combustion, aided by the moisture of the air, produces a mixture of phosphorous and phosphoric acids. Schönbein has shown that the slow oxidation of phosphorus is accompanied by the formation of small quantities of ozone and hydrogen dioxide.

When heated in the air to a temperature of 60°, phosphorus takes fire and burns, producing a bright light and white vapors of phosphorus pentoxide mixed with some phosphorus trioxide. In oxygen the combustion takes place with great brilliancy. It is remarkable that under ordinary pressures phosphorus will not burn in pure and dry oxygen: it can be melted and even distilled in such an atmosphere (Dixon).

Phosphorus may be burned under warm water by passing a current of oxygen through the melted element by means of a tube drawn out to a point (Fig. 67); each bubble of oxygen which comes in contact with the phosphorus produces a bright flash.

Phosphorus takes fire spontaneously in an atmosphere of dry chlorine, phosphorus pentachloride being produced.

Uses of Phosphorus.—This body is principally employed in the manufacture of matches. The inflammable tips of friction-matches contain either ordinary or amorphous phosphorus. In the first case, the phosphorus is mixed with inert substances, such as sand or ochre, held together by strong glue; in the second case, the ignition of the amorphous phosphorus, which is but slightly combustible, is determined by potassium chlorate, to which is also added antimony sulphide. All of these substances are made into a paste, into which the ends of the matches are dipped. Sometimes the match-sticks are tipped with a paste composed of potassium chlorate and antimony sulphide, a mixture which only takes fire by friction upon a prepared surface, composed generally of amorphous phosphorus and antimony sulphide. All of these mixtures are held together by strong glue.

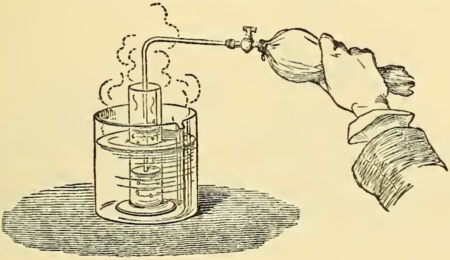


FIG. 67.

HYDROGEN PHOSPHIDE (PHOSPHINE).

Density compared to air 1.178
Density compared to hydrogen . . . . 17.
Molecular weight PH^3 . . . . $= 34.$

This gas was discovered by Gengembre in 1783.

When phosphorus is heated with a solution of caustic potash, there is a gas disengaged, which inflames spontaneously on contact with the air; this is hydrogen phosphide. It is formed according to the following equation:

$$\underset{\text{Potassium hydrate.}}{3KOH} + 4P + 3H^2O = \underset{\text{Potassium hypophosphite.}}{3KH^2PO^2} + PH^3$$

Preparation.—1. Hydrogen phosphide may be prepared by heating phosphorus with a strong solution of potassium hydrate, or with thick milk of lime, with which the flask (Fig. 68) should be almost entirely filled. The gas is conducted under the surface of water, and as each bubble arrives in contact with the air it takes fire spontaneously, producing a bright flash and a wreath of white smoke, which enlarges as it rises in the air.

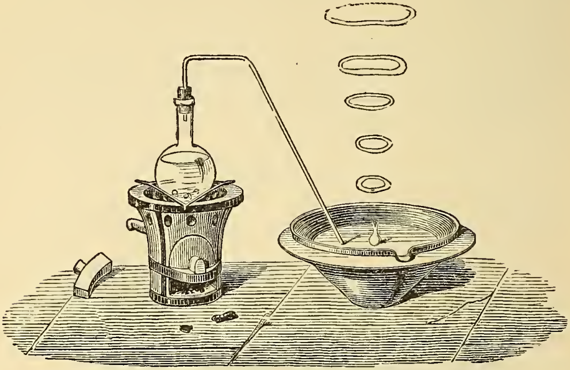


Fig. 68.

2. The same spontaneously inflammable gas is evolved when calcium phosphide is thrown into water (Fig. 69). The phosphide of calcium is prepared by passing vapor of phosphorus over fragments of incandescent lime; it instantly decomposes water with formation of calcium hypophosphite and spontaneously inflammable hydrogen phosphide.

However, when calcium phosphide is treated with hydrochloric acid, hydrogen phosphide is produced, which does not take fire without the application of heat (Fig. 70).

In this case, the gas is formed by double decomposition between the hydrochloric acid and the calcium phosphide; the calcium combines with the chlorine, forming calcium chloride, and the hydrogen of the acid combines with the phosphorus.

3. In the same manner, when phosphorous acid is strongly heated in a small retort, it evolves a hydrogen phosphide which is not spontaneously inflammable.

$$\underset{\text{Phosphorous acid.}}{4H^3PO^3} = PH^3 + \underset{\text{Phosphoric acid.}}{3H^3PO^4}$$

Properties.—The gas thus obtained is colorless, and possesses a garlicky odor. It is but slightly soluble in water, but is soluble in alcohol and in ether. When it is pure it does not take fire in the air at a temperature below 100°, and then burns with a very luminous white flame. According to Paul Thenard, the spontaneous inflammability of the hydrogen phosphide prepared by the methods first mentioned is due to the presence of another phosphide, P^2H^4; this is a very volatile liquid, extremely inflammable, and the least trace of its vapor in hydrogen phosphide gas communicates to the latter the property of spontaneous inflammability.

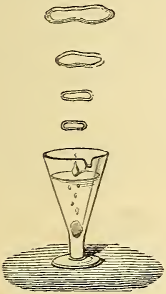


FIG. 69.

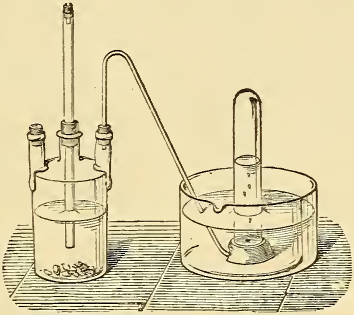


FIG. 70.

Hydrogen phosphide liquefies at about —85°, and freezes at —132.5° ; it is absorbed by a solution of cuprous chloride in hydrochloric acid, with the formation of the compound $CuClPH^3$.

The composition of hydrogen phosphide, PH^3, recalls that of ammonia, NH^3, and the analogy between the two gases is further revealed by the property common to both of uniting with hydriodic acid. *Phosphonium iodide*, $PH^3.HI$ or PH^4I, is a well-defined solid body, crystallizing in brilliant tetragonal prisms. Caustic alkalies decompose it with formation of phosphine.

The existence of a solid phosphide of hydrogen has been demonstrated, and the formula P^2H attributed to it.

COMPOUNDS OF PHOSPHORUS AND CHLORINE.

There are two chlorides of phosphorus :

Phosphorus trichloride	PCl^3
Phosphorus pentachloride	PCl^5

There are, besides,

Phosphorus oxychloride	$POCl^3$
Phosphorus sulphochloride	$PSCl^3$

PHOSPHORUS TRICHLORIDE.

PCl^3

When a current of dry chlorine is passed over phosphorus heated in a small tubulated retort, a liquid compound of chlorine and phosphorus is formed and may be condensed in a cooled receiver. This is phosphorus trichloride. It is a fuming, colorless liquid, having a density of 1.61 and boiling at 76°. It solidifies at —112°.

If it be poured into water, it at first sinks to the bottom, and then rapidly disappears, evolving white fumes of hydrochloric acid, and forming phosphorous acid, which remains in solution.

$$PCl^3 + 3H^2O = H^3PO^3 + 3HCl$$

PHOSPHORUS PENTACHLORIDE.

PCl^5

In contact with an excess of chlorine, phosphorus trichloride absorbs two more atoms of that gas, and condenses into a yellow crystalline solid, phosphorus pentachloride.

This body is volatile, and sublimes without fusion when heated, even below 100°. When heated under pressure, it melts at 148° and boils at a slightly higher temperature. Its vapor density, taken at 336° and reduced to 0°, is equal to 3.656. This density should be double, supposing that the molecule PCl^5 occupies two volumes. The anomaly, however, is only apparent, for there are good reasons for believing that at the temperature 336° the vapor of phosphorus pentachloride no longer exists, and that the compound is decomposed or dissociated into a mixture of phosphorus trichloride and chlorine, a mixture which would give four volumes of vapor for one molecule of PCl^5.

$$PCl^5 = \begin{cases} PCl^3 = 2 \text{ volumes.} \\ Cl^2 \;\;= \underline{2 \text{ volumes.}} \end{cases}$$
$$\qquad\qquad\qquad 4 \text{ volumes.}$$

Indeed, when the vapor density of phosphorus pentachloride is taken by diffusing it in the vapor of the protochloride, which prevents the dissociation before mentioned, a figure is found which corresponds very nearly with the theoretic density 7.21 (A. Wurtz).

Phosphorus pentachloride decomposes water with energy, forming hydrochloric and phosphoric acids.

$$PCl^5 + 4H^2O = H^3PO^4 + 5HCl$$

When only a small quantity of water is present, hydrochloric acid is disengaged, by the exchange of two atoms of chlorine for one atom of oxygen, and a colorless liquid is formed which is called phosphorus oxychloride. When heated in a current of hydrogen sulphide, phosphorus pentachloride is converted into the sulphochloride, a colorless liquid boiling at 126°.

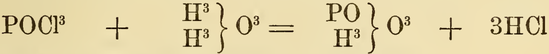
$$\begin{aligned} PCl^5 + H^2O &= 2HCl + POCl^3 \\ PCl^5 + H^2S &= 2HCl + PSCl^3 \end{aligned}$$

PHOSPHORUS OXYCHLORIDE.

POCl^3

This body is readily obtained by exposing phosphorus pentachloride to moist air until it becomes liquid, and subsequently distilling the liquid (A. Wurtz). It is formed in a great number of reactions when phosphorus pentachloride is heated with hydrated acids, such as oxalic acid, boric acid, etc., or with oxides, such as phosphoric oxide. In these cases, one atom of oxygen from the oxidized body is exchanged for two atoms of chlorine from the pentachloride (Gerhardt).

Phosphorus oxychloride is a colorless liquid, boiling at 110°. When poured into water, it sinks and is at once decomposed, hydrochloric and phosphoric acids being formed.



$$POCl^3 \quad + \quad \left.\begin{matrix} H^3 \\ H^3 \end{matrix}\right\} O^3 = \left.\begin{matrix} PO \\ H^3 \end{matrix}\right\} O^3 \quad + \quad 3HCl$$

Phosphorus oxychloride. 3 molecules water. Phosphoric acid.

COMPOUNDS OF PHOSPHORUS WITH BROMINE AND IODINE.

Two bromides of phosphorus are known:

Phosphorus tribromide, PBr^3, a colorless liquid.

Phosphorus pentabromide, PBr^5, a yellow, crystalline mass.

To the trichloride and tribromide of phosphorus there corresponds a triiodide, concerning which but little is known.

The best defined and most important combination of phosphorus with iodine is the compound P^2I^4.

Phosphorus Iodide, P^2I^4.—This body is obtained by dissolving dry phosphorus in carbon disulphide and gradually adding iodine to the solution. The liquor is distilled on the water-bath, and leaves a bright-red, crystalline mass. This is the iodide P^2I^4.

It crystallizes in long, brilliant, flexible needles, which melt at 110°. On contact with water it is decomposed, forming phosphorous and hydriodic acids.

Phosphorus Fluorides.—A trifluoride, PF^3, and a pentafluoride, PF^5, are known. Both are colorless gases at ordinary temperatures. The pentafluoride is the only compound of pentavalent phosphorus which can exist as a gas without dissociation. It is stable at high temperatures.

COMPOUNDS OF PHOSPHORUS AND OXYGEN.

Phosphorus combines with oxygen, forming two oxides:

Phosphorus trioxide, or phosphorous oxide . .	P^4O^6
Phosphorus pentoxide, or phosphoric oxide . .	P^2O^5

Recent investigations by Thorpe and Tutton seem to show that the products of the slow combustion of phosphorus contain also an oxide having the composition P^2O^4, corresponding to nitrogen tetroxide. Both the trioxide and the pentoxide can combine with three molecules of water, phosphorous and phosphoric acids being thus formed.

$$2P^4O^6 + 6H^2O = 4H^3PO^3$$
$$P^2O^5 + 3H^2O = 2H^3PO^4$$

Besides these two acids there is another containing less oxygen; it is hypophosphorous acid, whose corresponding oxide is unknown. These three acids form a series containing for three atoms of hydrogen and one atom of phosphorus regularly-increasing quantities of oxygen; they may be said to constitute different degrees of oxidation of hydrogen phosphide.

PH^3 hydrogen phosphide.
PH^3O (missing).
PH^3O^2 hypophosphorous acid.
PH^3O^3 phosphorous acid.
PH^3O^4 phosphoric acid.

Phosphoric acid is formed from phosphorus oxychloride (phosphoryl trichloride) by the action of water.

$$(PO)'''Cl^3 + 3H^2O = (PO)'''(OH)^3 + 3HCl$$

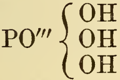
The same product is obtained when water acts upon phosphorus pentachloride, PCl^5. It may be assumed that the five chlorine atoms are replaced by hydroxyl groups, and the resulting (unknown) compound, $P(OH)^5$, is, by the loss of a molecule of water, converted into phosphoric acid.

$$P(OH)^5 = H^2O + (PO)(OH)^3$$

Phosphorous acid results from the action of water on phosphorus trichloride, and might, therefore, be supposed to be derived from the latter by the replacement of the three chlorine atoms by three hydroxyl groups. Its chemical properties indicate, however, that in it the phosphorus plays the part of a pentatomic element: it is phosphoryl, $(PO)'''$, combined with one hydrogen atom and two hydroxyl groups.

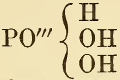
In hypophosphorous acid it must be admitted that phosphoryl is united to two atoms of hydrogen and one hydroxyl group.

The constitution of the three acids is expressed by the formulæ



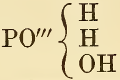
$$PO'''\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$$

Phosphoric acid.



$$PO'''\left\{\begin{matrix}H\\OH\\OH\end{matrix}\right.$$

Phosphorous acid.



$$PO'''\left\{\begin{matrix}H\\H\\OH\end{matrix}\right.$$

Hypophosphorous acid.

HYPOPHOSPHOROUS ACID.

H^3PO^2

When phosphorus is boiled with milk of lime or with a concentrated solution of baryta, a soluble hypophosphite is produced, and on treating the solution of barium hypophosphite with sulphuric acid, a precipitate of barium sulphate and a solution of hypophosphorous acid are obtained; they may be separated by filtration. When sufficiently concentrated, the liquor leaves a colorless and syrupy residue, which, when cooled to 0°, deposits white crystals of the acid.

This acid is decomposed at a high temperature, yielding phosphoric acid and hydrogen phosphide. It is gifted with energetic reducing properties: it instantly decomposes the salts of mercury and silver, setting free the metal. An excess of hypophosphorous acid added to a solution of cupric sulphate precipitates, by the aid of a gentle heat, hydride of copper, Cu^2H^2, which is decomposed at 100° into copper and hydrogen (A. Wurtz).

Hypophosphorous acid contains three atoms of hydrogen, only one of which is capable of being replaced by an equivalent quantity of a metal. The composition of the hypophosphites is consequently expressed by the following general formula:

$$R'H^2PO^2$$

in which R′ represents a monatomic metal, such as potassium, capable of replacing hydrogen atom for atom.

PHOSPHOROUS ACID.

$$H^3PO^3$$

Preparation.—Phosphorous acid results from the action of water upon phosphorus trichloride, as already seen. It may be obtained in a state of purity by evaporating the acid liquor resulting from this reaction, and heating the syrupy residue in a platinum capsule until the odor of hydrogen phosphide is perceptible. On cooling, the acid solidifies to a crystalline mass.

Properties.—These crystals absorb moisture when exposed to the air, and are resolved into an intensely acid liquid; they melt at a gentle heat, and are decomposed by a high temperature into hydrogen phosphide and phosphoric acid.

Like hypophosphorous acid, phosphorous acid possesses reducing properties.

Its boiling aqueous solution reduces the salts of mercury, silver, and gold, and this reduction is favored by the presence of ammonia. It converts arsenic acid into arsenious acid.

Chlorine, bromine, and iodine convert it into phosphoric acid in presence of water.

$$H^3PO^3 + H^2O + Cl^2 = 2HCl + H^3PO^4$$

Phosphorous acid contains three atoms of hydrogen, two of which are replaceable by an equivalent quantity of a metal. It is hence called a dibasic acid.

The composition of the neutral phosphites is expressed by the general formula

$$R'^2HPO^3,$$

in which R′ represents a monatomic metal like potassium or sodium.

PHOSPHORIC OXIDE, OR PHOSPHORUS PENTOXIDE.

(PHOSPHORIC ANHYDRIDE.)

P^2O^5

This compound may be obtained by burning phosphorus in a large globe filled with dry air. A dense white smoke is produced, and condenses upon the walls of the vessel in flakes like snow. This body is the anhydride of phosphoric acid. When exposed to the air, it absorbs moisture and is converted into metaphosphoric acid.

$$P^2O^5 + H^2O = 2HPO^3$$

When thrown into water it dissolves with a hissing noise, such as is produced by a red-hot iron.

Phosphoric oxide volatilizes at a dull-red heat; it is undecomposable by heat. It yields the oxychloride when distilled with phosphorus pentachloride.

$$P^2O^5 + 3PCl^5 = 5POCl^3$$

Phosphorus pentoxide is much used in the laboratory for drying gases, and as a dehydrating agent.

PHOSPHORIC ACID.

(ORTHOPHOSPHORIC ACID.)

H^3PO^4

Preparation.—1. This acid may be prepared by boiling phosphorus with nitric acid. On account of the violence of the reaction the operation is difficult to regulate, and even dangerous when ordinary phosphorus is employed, but it succeeds very well with powdered amorphous phosphorus. This is heated with tolerably concentrated nitric acid in a retort, fitted with a receiver, and, when the whole of the phosphorus has disappeared, a little nitric acid is added to the contents of the retort, and the liquid is concentrated in a platinum capsule. When the last portions of nitric acid have been driven out, a small quantity of water is added, and the syrupy liquid is placed in a bell-jar over a dish containing concentrated sulphuric acid. At the end of some time, the phosphoric acid is deposited in the form of hard, transparent, prismatic crystals.

2. A current of chlorine may be passed through warm water under which is a layer of melted phosphorus. Phosphoric acid and hydrochloric acid are formed.

$$PCl^5 + 4H^2O = H^3PO^4 + 5HCl$$

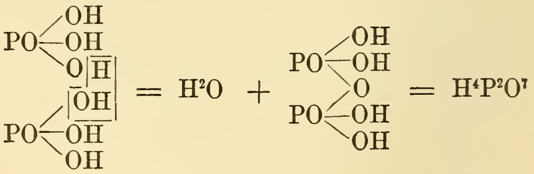
As soon as all of the phosphorus has disappeared the solution is evaporated, and the hydrochloric acid is driven out by heating the residue to 200°. The residue is dissolved in water and forms a solution which will deposit the acid in crystals when concentrated as indicated above.

Properties.—When exposed to the air, these crystals attract moisture and deliquesce. Their solution is very acid. It does not coagulate white of egg, and it produces no cloud in a solution of barium chloride, but it forms a white precipitate of ammonio-magnesium phosphate in a solution of magnesium sulphate on the addition of ammonia. With silver nitrate to which ammonia has been added, it gives a yellow precipitate of trisilver phosphate, Ag^3PO^4. Orthophosphoric acid contains three atoms of hydrogen, each of which is replaceable by an equivalent quantity of metal.

PYROPHOSPHORIC ACID.

$H^4P^2O^7$

When orthophosphoric acid is heated for a long time to 213° it loses water and is converted into a new acid, which is called pyrophosphoric. Two molecules of phosphoric acid lose one molecule of water, and then unite to form a single molecule of pyrophosphoric acid.



The residue constitutes an opaque, semi-crystalline mass, composed almost entirely of pyrophosphoric acid.

Its aqueous solution forms a white precipitate of silver pyrophosphate in solutions of silver nitrate.

$$H^4P^2O^7 + 4AgNO^3 = Ag^4P^2O^7 + 4HNO^3$$

When heated with water, pyrophosphoric acid again combines with one molecule of that liquid, and is converted into phosphoric acid by a reaction the inverse of that by which it is formed.

METAPHOSPHORIC ACID.

HPO^3

Preparation.—When phosphoric acid is heated to redness in a platinum crucible, a hard, transparent, vitreous mass is obtained on cooling; this is metaphosphoric acid.

It is formed by the abstraction of one molecule of water from phosphoric acid.

$$H^3PO^4 - H^2O = HPO^3$$

It may also be obtained directly from calcium acid phosphate, the preparation of which from bone-ash has already been described. A slight excess of dilute sulphuric acid is added to the concentrated solution of this salt, and the insoluble calcium sulphate formed is separated by filtration. Since, however, the calcium sulphate is not entirely insoluble in water, the solution is concentrated, and alcohol added, which completely precipitates the sulphate. The liquid is again filtered, the alcohol driven off by evaporation, and the residue heated to a temperature near redness to remove the excess of sulphuric acid.

On cooling, a vitreous mass of metaphosphoric acid is obtained.

An aqueous solution of metaphosphoric acid instantly produces a precipitate of silver metaphosphate in a solution of silver nitrate.

$$HPO^3 + AgNO^3 = AgPO^3 + HNO^3$$

A few drops of the acid solution added to white of egg suspended in water produces an abundant white precipitate.

The same metaphosphoric acid is formed when phosphoric oxide is thrown into a large quantity of cold water, or when it is allowed to deliquesce in the air. Under these circumstances, one molecule of phosphoric oxide combines with only one molecule of water.

$$P^2O^5 + H^2O = 2HPO^3$$

The preceding considerations establish the existence of three phosphoric acids, which differ both in composition and properties. To these three acids correspond three salts of silver, and it will be seen that the latter differ from the acids only by containing silver instead of hydrogen, a substitution which takes place atom for atom.

ACIDS.	SILVER SALTS.
H^3PO^4 phosphoric acid (orthophosphoric).	Ag^3PO^4 trisilver phosphate (orthophosphate).
$H^4P^2O^7$ pyrophosphoric acid.	$Ag^4P^2O^7$ silver pyrophosphate.
HPO^3 metaphosphoric acid.	$AgPO^3$ silver metaphosphate.

It may be added that, independently of the acids and salts of which the composition and nomenclature have just been considered, others have been described, the most interesting of which are related to the metaphosphates, of which they constitute polymeric modifications. That is, two, three, four, or more molecules of metaphosphoric acid are condensed in a single molecule, forming more complicated acids.

COMPOUNDS OF PHOSPHORUS AND SULPHUR.

When phosphorus is heated with dry sulphur, or when a mixture of the two bodies is melted under water, they combine with a vivid combustion which is sometimes accompanied by dangerous explosions. The action is less violent with amorphous phosphorus. According to the proportions of these bodies which are brought into contact, several combinations of phosphorus and sulphur may be obtained, among which the trisulphide, P^2S^3, and the pentasulphide, P^2S^5, correspond to phosphorous and phosphoric oxides. The pentasulphide may be obtained in pale yellow crystals.

ARSENIC.

Vapor density compared to air	10.37
Vapor density compared to hydrogen	150.
Atomic weight As	= 74.45

Arsenic was discovered by A. Schroeder in 1694.

Natural State and Extraction.—There exists in nature a common and abundant mineral which contains iron, sulphur, and arsenic, and which is called *mispickel;* it is a sulpharsenide of iron. When it is strongly heated, the arsenic is volatilized and a residue of iron sulphide remains.

$$\underset{\text{Mispickel.}}{FeSAs} = \underset{\text{Iron sulphide.}}{FeS} + As$$

The operation is conducted on the large scale in earthenware cylinders placed horizontally in a furnace. The arsenic sublimes into sheet-iron pipes fitted to the open extremity of the cylinders which extend beyond the furnace. The volatilization of the arsenic is facilitated by the addition of a certain quantity of metallic iron.

The arsenic of commerce may be purified by distilling it with charcoal in a stoneware retort.

Properties.—Recently-sublimed arsenic presents the appearance of a steel-gray, crystalline mass, having a metallic lustre. Its crystalline form is an acute rhombohedron. Its density is about 5.7.

Arsenic volatilizes without melting at a temperature below dull redness. **Its vapor is yellow.** When it is heated under strong pressure it melts to a transparent liquid. On exposure to the air it loses its lustre and assumes a black-gray color; in this case its surface becomes covered with a thin layer of a brown-black pulverulent substance, regarded by some chemists as a suboxide of arsenic.

Arsenic oxidizes when it is heated in the air or in oxygen.

If a small quantity of arsenic be thrown upon a red-hot coal, white vapors are produced, and an alliaceous odor is perceptible.

A fragment of arsenic may be strongly heated in the horizontal branch of a tube containing oxygen (Fig. 71); the metal takes fire and burns with bluish flame, producing white vapors of arsenious oxide.

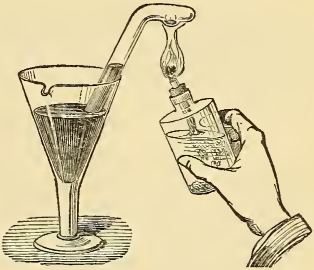


FIG. 71.

If arsenic be preserved from the air under a layer of water, in which it is insoluble, it oxidizes slowly, in such a manner as to form a small quantity of arsenious acid, which dissolves in the water. This property explains the efficacy of powdered arsenic (commercial *cobalt*) for poisoning flies.

Powdered arsenic sprinkled into dry chlorine burns with bright scintillations into the trichloride $AsCl^3$. Arsenic also combines directly with bromine, with iodine, and with sulphur.

Arsenic is used to alloy the lead used for the manufacture of shot, which are thereby rendered more spherical in form, and so hardened that they will not foul the gun.

HYDROGEN ARSENIDE (ARSINE).

Density compared to hydrogen 39
Molecular weight AsH^3 . . . . $= 78$

Preparation.—This gas may be prepared by the action of hydrochloric acid upon zinc arsenide.

$$\underset{\text{Zinc arsenide.}}{Zn^3As^2} + 6HCl = 2AsH^3 + \underset{\text{Zinc chloride.}}{3ZnCl^2}$$

It must be handled with prudence, as it is extremely poisonous.

Properties.—Hydrogen arsenide is colorless; its odor is penetrating and garlicky. At a red heat it is decomposed into arsenic and hydrogen. On the application of flame, it burns in the air with a bluish light, producing fumes of arsenious oxide. If the supply of air be insufficient, arsenic is deposited. With one and a half times its volume of oxygen, hydrogen arsenide forms an explosive mixture, the products of the combination being water and arsenious oxide.

$$4AsH^3 + 6O^2 = As^4O^6 + 6H^2O$$

Chlorine decomposes hydrogen arsenide with a flash of light and formation of hydrochloric acid. An excess of chlorine yields arsenic trichloride, but in the presence of water, arsenious oxide is formed.

$$4AsH^3 + 12Cl^2 + 6H^2O = As^4O^6 + 24HCl$$

Water dissolves about one-fifth of its volume of hydrogen arsenide. When this gas is agitated with a solution of cupric sulphate, it disappears entirely if the gas be pure, and leaves a residue of hydrogen should that gas have been present in the free state in the mixture (Dumas).

$$\underset{\text{Cupric sulphate.}}{3CuSO^4} + 2AsH^3 = \underset{\text{Copper arsenide.}}{Cu^3As^2} + 3H^2SO^4$$

Silver nitrate solution decomposes hydrogen arsenide; silver is precipitated, and arsenious acid formed.

$$AsH^3 + 6AgNO^3 + 3H^2O = H^3AsO^3 + 6HNO^3 + 6Ag$$

ARSENIC CHLORIDE.

$AsCl^3$

Preparation.—1. When dry chlorine is passed over powdered arsenic, arsenic chloride distils and condenses as a yellow liquid, containing an excess of chlorine, from which it may be freed by distillation over arsenic (Dumas).

2. A mixture of arsenious oxide and sulphuric acid is gently heated in a retort, and fragments of fused sodium chloride gradually added; arsenic chloride distils and condenses in the receiver.

$$6H^2SO^4 + \underset{\text{Sodium chloride.}}{12NaCl} + As^4O^6 = \underset{\text{Sodium sulphate.}}{6Na^2SO^4} + 4AsCl^3 + 6H^2O$$

Properties.—Arsenic chloride is a colorless, oily, and very dense liquid. It boils at 134°. Its density at 0° is 2.205. It gives off white fumes in the air, and is very poisonous.

An excess of water instantly decomposes it into hydrochloric acid and arsenious oxide, which, being but slightly soluble, is precipitated.

$$4AsCl^3 + 6H^2O = As^4O^6 + 12HCl$$

Arsenic bromide and *iodide* are formed in an analogous manner. A *fluoride*, AsF^3, is also known, and may be prepared by distilling a mixture of arsenious oxide, fluor spar, and sulphuric acid in a lead retort. It is a colorless liquid.

ARSENIOUS OXIDE.

As^4O^6

Preparation.—This dangerous poison is obtained in the arts by roasting arseniferous minerals, particularly mispickel. Roasting is an operation which consists in heating a mineral in contact with air, by which the oxidizable elements present are oxidized. When arseniferous minerals are roasted, arsenious oxide is formed among other products, and volatilizes, and is condensed either in wide horizontal chimneys or in a large building divided into numerous communicating compartments, through which the vapor is led consecutively. It is collected in the form of a powder, and is resublimed in cast-iron pots surmounted by sheet-iron cylinders, in which it condenses.

Properties.—Recently-sublimed arsenious oxide occurs as vitreous masses; but it soon loses its transparency and becomes milk-white, presenting the appearance of porcelain. When a large piece of the opaque oxide is broken, the interior is usually found to be still transparent and vitreous.

Arsenious oxide then exists in two forms: the vitreous variety is amorphous; the opaque is crystalline. The former variety changes into the latter by a molecular transformation which takes place in the midst of the amorphous vitreous mass.

Arsenious oxide crystallizes in regular octahedra or in tetrahedra; sometimes, but more rarely, in right-rhombic prisms. It is dimorphous.

It dissolves slowly in cold water, in which it is but slightly soluble, and in this respect there is a curious difference between the opaque and the vitreous varieties. The latter is three times more soluble than the former; while one part of the vitreous oxide dissolves in 108 parts of water at 15°, one part of the opaque variety requires 355 parts of water for its solution at the same temperature.

The aqueous solution of arsenious oxide feebly reddens blue litmus. It is almost tasteless. It may be regarded as containing normal arsenious acid, H^3AsO^3, corresponding to normal phosphorous acid, H^3PO^3; but this hydrate cannot be separated from the solution. On evaporation, the oxide As^4O^6 is always deposited.

$$4H^3AsO^3 = As^4O^6 + 6H^2O$$

The aqueous solution of arsenious oxide, neutralized with ammonia, gives a green precipitate with solution of cupric sulphate; this is copper arsenite, or Scheele's green. With silver nitrate it gives a canary-yellow precipitate of silver arsenite.

Arsenious oxide is more soluble in hydrochloric acid than in water. If a slip of clean copper be introduced into this solution, it becomes covered with a steel-gray or black coating of arsenic.

Reinsch's test for arsenic consists in boiling the suspected substance with dilute hydrochloric acid and bright metallic copper. The arsenic is deposited upon the copper, and by carefully heating the latter in a small tube the arsenic volatilizes and is converted into arsenious oxide, which condenses in the crystalline form, easily recognizable by aid of a microscope.

By the action of zinc the solution of As^4O^6 in hydrochloric acid disengages hydrogen arsenide; the zinc displaces the hydrogen of the hydrochloric acid, and, by the action of this nascent hydrogen upon the arsenious oxide, water and hydrogen arsenide are formed.

$$As^4O^6 + 12H^2 = 6H^2O + 4AsH^3$$

Marsh's Apparatus.—The reducing action of nascent hydrogen upon arsenious oxide is used for the detection of this substance by the aid of *Marsh's apparatus.*

This consists of an apparatus for the generation of hydrogen (Fig. 72); it contains pure zinc and dilute sulphuric acid, and the hydrogen burns at the drawn-out jet with an almost colorless flame. If, however, a few drops of a solution of arsenious oxide be introduced by the funnel-tube, the character of the flame is at once changed; it becomes bluish, elongated, and diffuses a white smoke, and if a white porcelain surface be depressed into it, large spots of a brownish color are produced. These are composed of arsenic, which is set free in the interior of the flame by the decomposition of the hydrogen arsenide by the heat.

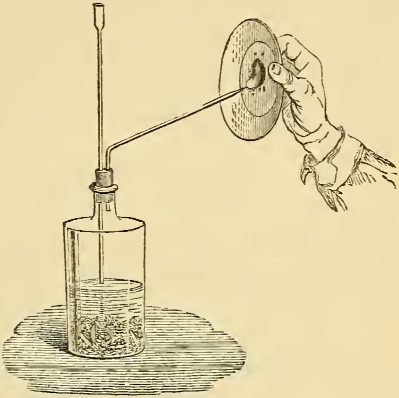


Fig. 72.

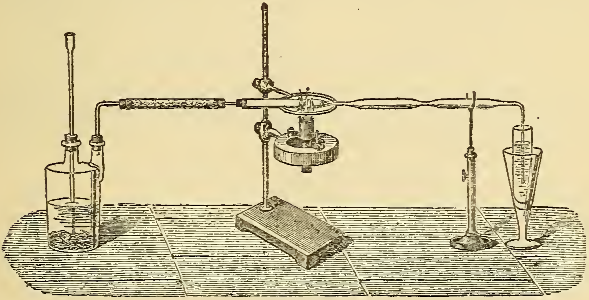


Fig. 73.

Fig. 73 represents a more perfect form of Marsh's apparatus. The hydrogen, mixed with the hydrogen arsenide, first traverses a tube filled with cotton, to arrest small drops of liquid which are carried with the gas; it then passes through a hard glass tube constricted at several points and heated near one of the constrictions. The hydrogen arsenide is decomposed and the arsenic deposited in the narrow and cooled portion of the tube. Lastly, the gas is passed through a solution of silver nitrate, which retains as arsenious acid any arsenic that might escape as undecomposed hydrogen arsenide (see page 188).

Marsh's apparatus permits the detection of the least trace of arsenious or arsenic acid in a liquid. It is of great value in medico-legal researches in cases of suspected poisoning by arsenic.

ARSENIC ACID

H^3AsO^4

Preparation.—When arsenious oxide is heated with nitric acid having a specific gravity of 1.35, red vapors are disengaged and the oxide is oxidized into arsenic acid, which may be obtained as a syrupy liquid by sufficient concentration. When left for a long time in a cool place it deposits colorless crystals, which constitute a hydrate $2H^3AsO^4 + H^2O$ (E. Kopp). These crystals are very deliquescent, and dissolve in water with the production of cold. They melt at 100°, losing their water of crystallization, and there remains a mass composed of fine needles of the normal acid H^3AsO^4.

When heated for some time to a temperature between 140 and 180°, this acid loses water, and is converted into *pyroarsenic acid*, $H^4As^2O^7$.

$$2H^3AsO^4 - H^2O = H^4As^2O^7$$

Between 200 and 206° another quantity of water is driven out, and on cooling there remains a pasty, pearly mass, which is *metarsenic acid*, $HAsO^3$.

$$H^3AsO^4 - H^2O = HAsO^3$$

It will be noticed that in their modes of formation and in their constitution, arsenic, pyro-arsenic and metarsenic acids are analogous to the corresponding acids of phosphorus.

When metarsenic acid is heated to dull redness, it loses all of its hydrogen in the form of water, and is converted into arsenic oxide, As^2O^5.

$$2HAsO^3 - H^2O = As^2O^5$$

At this temperature the oxide melts, and at a bright-red heat it is decomposed into arsenious oxide and oxygen.

$$2As^2O^5 = As^4O^6 + 2O^2$$

When exposed to the air it absorbs moisture, but very slowly, and even when treated with water it requires a certain time for solution.

Ordinary arsenic acid, which may be called ortharsenic, is very soluble in water; its solution strongly reddens blue litmus and possesses a very acid taste. It is reduced by nascent hydrogen, like the solution of arsenious oxide. When neutralized with ammonia, it forms a bluish-white precipitate with solution of cupric sulphate, and a red-brown precipitate with silver nitrate. Hydrogen sulphide produces no immediate precipitate.

A solution of sulphurous acid reduces arsenic acid to arsenious oxide, and then on the addition of hydrogen sulphide, a yellow precipitate of arsenic sulphide, As^2S^3, is formed.

COMPOUNDS OF SULPHUR AND ARSENIC.

Three sulphides of arsenic are known:

Arsenic disulphide, or realgar	As^2S^2
Arsenic trisulphide, or orpiment	As^2S^3
Arsenic pentasulphide	As^2S^5

Arsenic Disulphide, As^2S^2.—This body occurs in nature in the form of transparent red crystals, which belong to the type of the oblique rhombic prism.

It is obtained as a red mass having a conchoidal fracture by melting 75 parts of arsenic with 32 parts of sulphur. It is fusible, and may be crystallized by slow cooling. When strongly heated in closed vessels, it boils and distils without alteration, but when heated in the air, it burns into arsenious and sulphurous oxides. The alkaline sulphides and ammonium sulphide dissolve realgar, leaving a brown powder which has been considered as a subsulphide of arsenic. Boiling solution of potassium hydrate also dissolves realgar, forming a mixture of potassium arsenite and sulpharsenite; the latter is a soluble compound of arsenic trisulphide and potassium sulphide; a brown powder remains undissolved.

Arsenic Trisulphide, or Orpiment, As^2S^3.—When a solution of arsenious oxide is submitted to the action of hydrogen sulphide, the liquid assumes a yellow color without the formation of any precipitate, but if a drop of hydrochloric acid be added, a yellow, flocculent precipitate of arsenic trisulphide is formed at once.

$$As^4O^6 + 6H^2S = 2As^2S^3 + 6H^2O$$

The composition of arsenic trisulphide corresponds to that of arsenious oxide, and is the same as that of the orpiment found in nature.

It may also be obtained by fusing together arsenic and sulphur in the proper proportions, or even arsenious oxide and sulphur; in the latter case, sulphurous oxide is disengaged, and arsenic trisulphide sublimes. Thus prepared, orpiment occurs as crystalline masses of a yellow color, bordering upon orange, and a pearly aspect. Its density is 3.459. It is fusible and volatile.

Arsenic trisulphide obtained by precipitation is insoluble in cold water, and but slightly soluble in boiling water, but it is very soluble in ammonia. By continued boiling with water, it yields hydrogen sulphide and arsenious acid (de Clermont and Frommel). It is also dissolved by solutions of the alkaline sulphides with the formation of sulpharsenites, compounds of two sulphides, in which the alkaline sulphide plays the part of a base and the arsenic trisulphide the part of an acid. Orpiment also dissolves in solutions of the caustic alkalies with the formation of an arsenite and a sulpharsenite.

Arsenic Pentasulphide, As^2S^5.—When an excess of hydrogen sulphide is passed into solution of arsenic acid heated to 70°, arsenic pentasulphide is precipitated (Bunsen). Also when a sulpharsenate of an alkali is decomposed by a mineral acid.

$$2Na^3AsS^4 + 3H^2SO^4 = 3Na^2SO^4 + As^2S^5 + 3H^2S$$

It is a lemon-yellow powder, may be fused and distilled without alteration, and is insoluble in water.

The alkaline sulphides dissolve it with the formation of sulpharsenates. Among the latter there is one having the composition K^3AsS^4, and which corresponds to the arsenate K^3AsO^4. It is formed by the following reaction:

$$As^2S^5 + 3K^2S = 2(K^3AsS^4)$$

ANTIMONY.

$Sb = 119.5$

Antimony is generally classed with the metals. It indeed possesses the lustre of a metal, and it conducts heat and electricity; but in a true chemical classification these physical properties cannot overbalance the most striking chemical analogies. By its affinities, and by the nature and constitution of its compounds, antimony must find a place by the side of arsenic, which must itself be classed with phosphorus and nitrogen.

Metallurgy of Antimony.—The most common ore of antimony is *stibnite*, Sb^2S^3, and was known to the ancients. The metal is extracted from it by a very simple process. The sulphide is first separated by fusion from the earthy materials, called *gangue*, with which it is associated; it is then roasted or heated in contact with air. The sulphur is in great part expelled in the form of sulphurous oxide gas, and the antimony is converted into oxide, which still contains some undecomposed sulphide. The whole is then pulverized, and the powder mixed with pulverized charcoal impregnated with sodium hydrate. This mixture is calcined in crucibles, and the antimony oxide and a portion of the sulphide are reduced by the charcoal; sodium sulphide is also formed, and this dissolves a portion of the antimony sulphide, forming a flux which floats upon the molten antimony; after cooling, the latter is found at the bottom of the crucible as a button, easy to separate from the scoriæ.

By another process the antimony sulphide is fused with metallic iron. Iron sulphide and antimony are formed, and the latter collects at the bottom by reason of its greater density.

Perfectly pure antimony is prepared in the laboratory by reducing antimonous or antimonic oxide by charcoal.

Properties.—Antimony is a brilliant white metal, having a slightly bluish lustre; it is brittle, and has a laminated fracture. Its density is 6.715. It melts at about 630°, and sensibly vaporizes at a white heat.

Antimony may be crystallized by allowing large masses of the fused metal to cool slowly, and decanting the liquid portion. Small acute rhombohedra may be obtained in this manner.

When heated in contact with air, antimony is converted into antimonous oxide, Sb^4O^6. If the flame of a blow-pipe be directed upon a fragment of antimony in a cavity scraped in a piece of charcoal, the metal melts, becomes red-hot, and gives off white fumes. If now the molten globule be allowed to fall to the floor, it breaks up into a multitude of smaller globules, and each particle rebounds as a brilliant spark, leaving behind it a train of smoke.

Powdered antimony burns brilliantly in dry chlorine.

Type metal contains 20 per cent. antimony and 80 per cent. lead; the alloy is hard, and takes a sharp impression of the mould. Other useful alloys of antimony are Britannia metal and various antifriction metals.

HYDROGEN ANTIMONIDE (STIBINE).

There is a compound of hydrogen and antimony which cannot be obtained in the pure state at ordinary temperatures, but which is the body SbH^3. It is decomposed by heat, and the decomposition of the pure compound begins between —65 and —56°; it can be prepared largely diluted with hydrogen by the action of nascent hydrogen upon a solution containing antimony: when decomposed by heat it forms metallic rings and mirrors, which it is of importance to distinguish from those formed by arsenic. The following differences are sufficient for this purpose:

The antimony rings are not displaced when heated in a current of hydrogen; the arsenic rings are volatilized, and condense in a cooler portion of the tube.

The spots and rings of antimony are not dissolved by a solution of sodium hypochlorite (Labarraque's solution), which at once dissolves those of arsenic.

The antimony spots are readily dissolved by a drop of nitric acid, and the liquid leaves on evaporation a white residue, which is not colored by the addition of a drop of silver nitrate solution. Under the same circumstances, the arsenical spots leave a white residue, which assumes a brick-red color when moistened with a solution of silver nitrate, owing to the formation of silver arsenate.

COMPOUNDS OF ANTIMONY AND CHLORINE.

Antimony trichloride	$SbCl^3$
Antimony pentachloride	$SbCl^5$

Antimony Trichloride, $SbCl^3$.—This compound, formerly known as butter of antimony, is formed by the action of hydrochloric acid upon antimony sulphide. It is generally prepared in the laboratory from the residue from the preparation of hydrogen sulphide. This acid liquid is distilled in a retort provided with a receiver, which is changed as soon as the antimony chloride which distils over begins to crystallize in the neck of the retort.

This chloride is solid, transparent, and colorless. It melts at 73.2°, and boils at 230°. It dissolves in water charged with hydrochloric acid, forming a colorless solution, but when this liquid is diluted with water there is formed an abundant white precipitate, long known as *powder of Algaroth.* It is an oxychloride of which the composition does not appear constant. There is one which contains $SbOCl$, and which can be regarded as antimony trichloride, in which two atoms of chlorine have been replaced by one atom of oxygen.

Antimony Pentachloride, $SbCl^5$.—This is formed by the action of an excess of chlorine upon antimony or upon the trichloride. It is a yellow liquid, giving off white fumes in the air. It is volatile, but cannot be distilled without undergoing a partial decomposition into chlorine and antimony trichloride. When exposed to the air, it absorbs moisture and is converted into a crystalline mass, which is a hydrate of the pentachloride. When treated with a large excess of water, it is decomposed with production of heat, and formation of pyrantimonic and hydrochloric acids.

An antimonous bromide, $SbBr^3$, and an iodide, SbI^3, are known, and the fluorides, SbF^3 and SbF^5, have also been obtained.

COMPOUNDS OF OXYGEN AND ANTIMONY.

Two oxides of antimony are known, corresponding to those of phosphorus and arsenic:

Antimonous oxide	Sb^4O^6
Antimonic oxide	Sb^2O^5

Normal antimonic acid, H^3SbO^4, corresponding to phosphoric and arsenic acids, is not known in the free state, but a derivative of this acid exists and may be regarded as antimony antimonate. Its composition is Sb^2O^4, and it is derived from antimonic acid by the substitution of an atom of antimony for three atoms of hydrogen.

H^3SbO^4 antimonic acid.
$SbSbO^4$ antimony antimonate.

There is a pyrantimonic and also a metantimonic acid, analogous to the corresponding phosphorus acids:

$H^4Sb^2O^7$ pyrantimonic acid.
$HSbO^3$ metantimonic acid.

ANTIMONOUS OXIDE.

Sb^4O^6

This is obtained by oxidizing the metal in the air. The operation may be conducted in two crucibles placed one above the other, an opening being pierced in the upper one for the access of air. They are heated to redness in a furnace, and on cooling, the antimony is found to be partially converted into brilliant needles formerly known as silver flowers of antimony. The crystals are right rhombic prisms, mixed with regular octahedra, for antimonous oxide crystallizes in two forms, presenting the same character of dimorphism as arsenious oxide. The two compounds are hence said to be *isodimorphous.*

When solution of sodium hydrate, or better, sodium carbonate, is poured into solution of antimony trichloride, a white precipitate of antimonous hydrate is formed, and, in the latter case, carbonic acid gas is disengaged.

$$SbCl^3 + \underset{\text{Sodium hydrate.}}{3NaOH} = \underset{\text{Antimonous hydrate.}}{H^3SbO^3} + \underset{\text{Sodium chloride.}}{3NaCl}$$

This hydrate readily parts with a molecule of water, being converted into another hydrate, $HSbO^2$.

$$H^3SbO^3 - H^2O = HSbO^2$$

ANTIMONY ANTIMONATE.

Sb^2O^4

This compound is formed when antimonous oxide is heated for a long time in the air, oxygen being absorbed, or when antimonic oxide is strongly calcined, oxygen being then disengaged.

It is a white, infusible powder, undecomposable by heat and insoluble in water.

ANTIMONIC OXIDE AND ACIDS.

When powdered antimony is heated with concentrated nitric acid, a white powder is obtained, which is metantimonic acid. It contains one atom of hydrogen capable of being replaced by an equivalent quantity of metal, and thus corresponds to metaphosphoric acid.

HPO^3	$HSbO^3$	$KSbO^3$
Metaphosphoric acid.	Metantimonic acid.	Potassium metantimonate.

When it is heated to dull redness, it loses water and is converted into antimonic oxide.

$$2HSbO^3 - H^2O = Sb^2O^5$$

If antimony pentachloride be poured into an excess of water, a white precipitate of pyrantimonic acid is formed. It is the analogue of pyrophosphoric acid, and, like the latter, contains four atoms of hydrogen.

$H^4P^2O^7$	$H^4Sb^2O^7$	$K^4Sb^2O^7$
Pyrophosphoric acid.	Pyrantimonic acid.	Potassium pyrantimonate.

According to Fremy, potassium pyrantimonate may be obtained by heating metantimonic acid or potassium metantimonate with potassium hydroxide, in a silver crucible.

$$\underset{\substack{\text{Potassium}\\\text{metantimonate.}}}{2KSbO^3} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{2KOH} = \underset{\substack{\text{Potassium}\\\text{pyrantimonate.}}}{K^4Sb^2O^7} + H^2O$$

The metantimonate may be extracted by water, in which it is soluble, from the white mass, formerly designated *diaphoretic antimony*, which is obtained by deflagrating in a red-hot crucible a mixture of 2 parts of nitre (potassium nitrate) and 1 part of powdered antimony. Cold water first dissolves potassium nitrate from this mass, and then potassium metantimonate. The solution of the latter salt produces with hydrochloric acid a white precipitate of metantimonic acid.

SULPHIDES OF ANTIMONY.

Two sulphides of antimony are known :

Antimony trisulphide, or antimonous sulphide . .	Sb^2S^3
Antimony pentasulphide, or antimonic sulphide . .	Sb^2S^5

Antimonous Sulphide, Sb^2S^3.—This compound, ordinarily called sulphide of antimony, occurs both in the crystalline form and amorphous. Crystallized, it exists in nature and is the mineral commonly known as *stibnite.* It is separated from its gangue by fusion, and is thus obtained in gray masses composed of brilliant needles having a metallic lustre.

Amorphous, it constitutes the orange-colored precipitate formed by the action of hydrogen sulphide upon a solution of antimony chloride. The precipitate is insoluble in ammonia, but dissolves in ammonium sulphide and in the alkaline sulphides.

Antimony trisulphide is reduced by hydrogen at a high temperature; hydrogen sulphide is formed, and antimony remains.

When heated in the air, antimony sulphide is oxidized with formation of sulphur dioxide and antimonous oxide. The incompletely roasted residue melts at a red heat, and on cooling assumes the form of a brown vitreous mass called glass of antimony. It is an impure oxysulphide which appears to contain the compound $Sb^2S^2O = \left.\begin{matrix}SbS\\SbS\end{matrix}\right\}O$.

Antimony trisulphide is used in pyrotechny, adding to the brilliancy of colored fires.

Antimony Pentasulphide, Sb^2S^5, is obtained as an orange-red powder by passing hydrogen sulphide through a solution of the pentachloride in hydrochloric acid. It is more generally prepared as follows: Finely-pulverized antimony trisulphide is digested with sulphur and a solution of sodium hydrate, or a mixture of sulphur, sodium carbonate, and lime; the antimony sulphide gradually dissolves in the liquid, and the product of the reaction is a sulphantimonate of sodium, which is deposited in fine crystals from the concentrated liquid.

$$Sb^2S^5 + \underset{\text{Sodium sulphide.}}{3Na^2S} = \underset{\text{Sodium sulphantimonate.}}{2Na^3SbS^4}$$

It is soluble in water, and on the addition of hydrochloric acid to its solution, hydrogen sulphide is disengaged and antimony pentasulphide is precipitated.

$$2Na^3SbS^4 + 6HCl = 6NaCl + Sb^2S^5 + 3H^2S$$

General Considerations upon the Elements of the Nitrogen Group.—Nitrogen, phosphorus, arsenic, and antimony, and bismuth might be added, form a group of elements allied by the most striking analogies. This is made manifest by the atomic composition of their compounds, as will be seen in the following synopsis:

HYDROGEN COMPOUNDS.

NH_3 Ammonia.	PH_3 Hydrogen phosphide.	AsH_3 Hydrogen arsenide.	SbH_3 Hydrogen antimonide.

CHLORINE COMPOUNDS.

NCl_3 Nitrogen trichloride.	PCl_3 Phosphorus trichloride.	$AsCl_3$ Arsenic trichloride.	$SbCl_3$ Antimony trichloride.
—	PCl_5 Phosphorus pentachloride.	—	$SbCl_5$ Antimony pentachloride.

OXYGEN COMPOUNDS.

N_4O_6(?) Nitrogen trioxide.	P_4O_6 Phosphorous oxide.	As_4O_6 Arsenious oxide.	Sb_4O_6 Antimonous oxide.
N_2O_5 Nitrogen pentoxide.	P_2O_5 Phosphoric oxide.	As_2O_5 Arsenic oxide.	Sb_2O_5 Antimonic oxide.

—	H_3PO_3 Phosphorous acid.	H_3AsO_3 Arsenious acid.	H_3SbO_3 Antimonous acid.
HNO_2 Nitrous acid.	—	—	$HSbO_2$ Antimonyl hydrate.
—	H_3PO_4 Phosphoric acid.	H_3AsO_4 Arsenic acid.	—
—	$H_4P_2O_7$ Pyrophosphoric acid.	$H_4As_2O_7$ Pyro-arsenic acid.	$H_4Sb_2O_7$ Pyro-antimonic acid.
HNO_3 Nitric acid.	HPO_3 Metaphosphoric acid.	$HAsO_3$ Metarsenic acid.	$HSbO_3$ Metantimonic acid.

If the analogy between nitrogen and phosphorus were complete, there should be an orthonitric acid, $H_3NO_4 = HNO_3 + H_2O$, corresponding to ordinary or orthophosphoric acid. This acid is not known as a definite hydrate, but compounds exist which are derived from it. Thus, bismuth subnitrate, $BiNO_4$, can be regarded as a salt of orthonitric acid, in which three atoms of hydrogen are replaced by one atom of triatomic bismuth.

BORON.

B = 10.9

Boron is found in boric acid and in borates. Among the more important of the latter are sodium borate or *borax*, calcium borates or *borocalcite* and *colemanite*, and calcium sodium borate, known as *boronatrocalcite*. The element was first isolated by Gay-Lussac and Thenard in 1808, by fusing boric oxide with potassium. It occurs in several modifications.

Preparation.—*Amorphous boron* is obtained by reducing boric oxide with sodium in an iron crucible.

$$\underset{\text{Boric oxide.}}{2B^2O^3} + Na^3 = \underset{\text{Sodium metaborate.}}{3NaBO^2} + B$$

A more convenient method consists in heating an intimate mixture of 100 parts anhydrous borax with 50 parts magnesium powder to redness in a well-covered crucible. The powdered mass is thoroughly washed, first with water then with hydrochloric acid, and dried at 100°.

Adamantine boron is prepared by fusing boric oxide with an excess of aluminium. The boron set free is dissolved by the aluminium, and on slow cooling separates in crystals, whose color varies from yellow to dark brown, according to the nature of the impurities, aluminium and carbon, one or both of which they invariably contain. These crystals may be isolated by treating the cold mass with hydrochloric acid.

Properties.—Amorphous boron is infusible, but may be volatilized by the intense heat of the electric furnace. When heated to 300° in the air, it burns into boric oxide. Its combustion in pure oxygen is very brilliant, and it possesses a singular affinity for nitrogen, with which it combines directly at a red heat, forming a nitride, BN. In an atmosphere of nitric oxide, it burns into a mixture of boric oxide and boron nitride (Wöhler and Deville).

Boron decomposes water at a red heat, and otherwise behaves as an energetic reducing agent.

Adamantine boron crystallizes in quadratic octahedra, having a density of 2.6, and a hardness and brilliancy next to diamond. It is infusible, and strongly resists the action of oxidizing agents and alkaline solutions. Hampe and Joly consider the crystals to be definite compounds of boron with aluminium and carbon.

BORON CHLORIDE.

BCl^3

Preparation.—This body may be prepared by heating crude amorphous boron in a current of chlorine, or by the action of chlorine on an incandescent mixture of boric oxide and charcoal.

$$\underset{\text{Boric oxide.}}{B^2O^3} + 3C + 3Cl^2 = \underset{\text{Boron chloride.}}{2BCl^3} + \underset{\text{Carbon monoxide.}}{3CO}$$

Properties.—In a state of purity, boron chloride is a colorless, mobile, and highly-refractive liquid, boiling at 17°. It fumes in the air, and is readily decomposed by water into boric and hydrochloric acids.

$$BCl^3 + 3H^2O = 3HCl + B(OH)^3$$

BORON FLUORIDE.

BF^3

Density compared to air	2.31
Density compared to hydrogen	34.

Preparation.—Boron fluoride was discovered by Gay-Lussac and Thenard in 1810. It is prepared by heating in a glass retort an intimate mixture of one part of boric oxide and two parts of powdered calcium fluoride with twelve parts of sulphuric acid. The gas disengaged is collected over mercury.

$$\underset{\text{Calcium fluoride.}}{3CaF^2} + \underset{\text{Boric oxide.}}{B^2O^3} + 3H^2SO^4 = \underset{\text{Calcium sulphate.}}{3CaSO^4} + 3H^2O + 2BF^3$$

Properties.—Boron fluoride is a colorless gas, having a suffocating odor. It produces abundant fumes in the air, and is very soluble in water, which dissolves about 800 times its volume of this gas. Its affinity for water is so great that it carbonizes paper and analogous organic substances, from which it removes the elements of water.

The solution of boron fluoride in water is accompanied by a chemical reaction; when the aqueous solution of this gas, saturated at the ordinary temperature, is cooled to 0°, crystals of boric acid are deposited, and a very acid liquid is obtained, known as hydrofluoboric acid; its composition is expressed by the formula:

$$BF^4H = BF^3.HF$$

BORIC ACID.

H^3BO^3

Preparation.—Boric acid was discovered by Homberg in 1702. It is found in the free state in the craters of certain volcanoes, and exists in solution in the *lagoni* of Monte-Rotondo, in Tuscany. These are muddy little lakes, through which arise the gaseous emanations from the fissures of a volcanic soil. The gases (*suffioni*) contain sensible traces of boric acid, which is dissolved by the water of the *lagoni*. On evaporation, this water furnishes the crude boric acid.

Large quantities of boric acid are also obtained from the native borates of sodium, calcium, and magnesium, which are decomposed by dissolving them in hot hydrochloric acid. The boric acid then separates upon cooling.

In the laboratory, boric acid is prepared by decomposing a boiling saturated solution of borax or sodium borate with dilute sulphuric acid. The latter is added in small portions until the liquid strongly reddens litmus-paper; the solution is then allowed to cool, and the boric acid separates in the crystalline form.

Properties.—Pure boric acid crystallizes in pearly scales, somewhat greasy to the touch. It dissolves in 25 parts of water at 18°, and is much more soluble in boiling water. The solution is feebly acid, and changes blue litmus solution to a wine color. Boric acid dissolves in alcohol, and the solution burns with a green flame.

When heated to 100° it loses one molecule of water, and is converted into *metaboric* acid, HBO^2. If the latter be maintained for a time at a temperature of 140°, it is converted into *tetraboric* acid, $H^2B^4O^7$.

$$4HBO^2 = H^2B^4O^7 + H^2O$$

When boric acid is heated in a platinum crucible to a temperature near redness, it loses all of its water, melts, and solidifies to a transparent glass on cooling. This is boric oxide.

$$2H^3BO^3 = B^2O^3 + 3H^2O$$

At a red heat this body dissolves a great number of solid substances, particularly the metallic oxides; it then yields variously colored glasses on cooling.

Boric oxide is not decomposed by charcoal at a red heat, but is converted into boron chloride by the simultaneous action of chlorine and charcoal.

SILICON.

$Si = 28.2$

Like boron, silicon exists amorphous and in the crystalline form. It was discovered by Berzelius in 1825.

Preparation. 1. *Amorphous Silicon.*—Dry sodium silico-fluoride is heated with half its weight of metallic sodium: sodium fluoride is formed and silicon is set free.

$$\underset{\text{Sodium silico-fluoride.}}{Na^2F^2.SiF^4} + 2Na^2 = \underset{\text{Sodium fluoride.}}{6NaF} + Si$$

On cooling, the mass is exhausted, first with cold, and then with hot, water; a brown powder of amorphous silicon remains.

Impure silicon is readily prepared by heating to redness a mixture of fine quartz sand and magnesium powder in a test-tube.

$$SiO^2 + 2Mg = 2MgO + Si$$

2. *Crystallized Silicon.*—Deville and Caron obtained crystallized silicon by projecting a mixture of 3 parts of potassium and silicon double fluoride, 4 parts of zinc, and 1 part of sodium into a red-hot crucible. Fluoride of sodium is formed, and the silicon set free dissolves in the zinc and separates in the crystalline form on cooling; it is isolated from the zinc by dissolving the button in hydrochloric acid; the silicon remains in the form of brilliant laminæ or needles. Crystallized silicon is most conveniently prepared by reducing the oxide SiO^2 by charcoal in the electric furnace (Moissan).

Properties.—Amorphous silicon is a brown powder, more dense than water, in which it is insoluble, and producing dark stains on the fingers. When heated in the air, it takes fire and burns with a bright light into silicic oxide, SiO^2.

Crystallized silicon has a density of 2.49. It may be heated to redness in oxygen without taking fire, but when it is calcined with potassium carbonate the latter is decomposed with a vivid emission of light, potassium silicate being formed and carbon being set free. Crystallized silicon resists the oxidizing action of both potassium nitrate and potassium chlorate, but it dissolves slowly in a boiling solution of potassium hydrate, hydrogen being disengaged and potassium silicate being formed. It burns when heated to redness in an atmosphere of chlorine, and takes fire spontaneously in fluorine.

HYDROGEN SILICIDE.

Probable formula SiH^4

Preparation.—This compound was discovered by Wöhler and Buff in 1857. Magnesium silicide* is introduced into a

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* This is most readily prepared by heating one part finely pulverized quartz sand with one and a half parts magnesium powder.

two-necked bottle, which is then entirely filled with water that has been recently boiled. To one of the necks of the bottle is fitted a funnel-tube which passes to the bottom of the bottle; to the other, a delivery-tube leading to the pneumatic trough; this tube also is completely filled with water so that there is no air in the whole apparatus. Concentrated hydrochloric acid is then introduced by the funnel-tube, and immediately reacts with the magnesium silicide, forming magnesium chloride, which dissolves, and gaseous hydrogen silicide, which must be collected in jars filled with recently boiled water.

Properties.—The gas thus obtained is not pure hydrogen silicide; it contains an excess of hydrogen. It is colorless and insoluble in water: water containing air in solution oxidizes it.

If bubbles of the gas be allowed to escape through the water of the trough, each bubble takes fire on coming to the surface, producing a bright light and a smoke of silicic oxide, which forms rings like those produced by hydrogen phosphide under similar circumstances, but often colored brown by a portion of silicon set free.

SILICON CHLORIDE.

$SiCl^4$

This compound is formed when silicon is heated to dull redness in a current of chlorine, or when the latter gas is passed over an incandescent mixture of charcoal and silica.

$$SiO^2 + C^2 + Cl^4 = SiCl^4 + 2CO$$

Preparation.—Precipitated silica, lamp-black, and oil are intimately mixed into a stiff paste. This paste is made into little balls, which are put into a crucible, the cover of which is then luted on, and the whole is heated to redness in a furnace. When cool, the balls are introduced into a porcelain tube or a clay retort (Fig. 74), which is then heated to bright redness, while a current of carefully-dried chlorine is passed through. The silicon chloride and the carbon monoxide formed are passed through two U tubes surrounded by a mixture of ice and salt. The silicon chloride is thus condensed.

An easier method of preparation consists in gently heating in a current of chlorine the crude product obtained by reducing silica with magnesium. Silicon chloride distils, and is condensed in a freezing mixture (Gattermann).

Properties.—Silicon chloride is a volatile, colorless liquid, of an irritating odor. It fumes in the air. Its density is 1.52, and it boils at 59°.

It is instantly decomposed by water, silicic and hydrochloric acids being formed. A part of the silicic acid is precipitated in the form of a jelly, while another part remains in solution. The latter is perhaps a hydrate corresponding to the chloride.

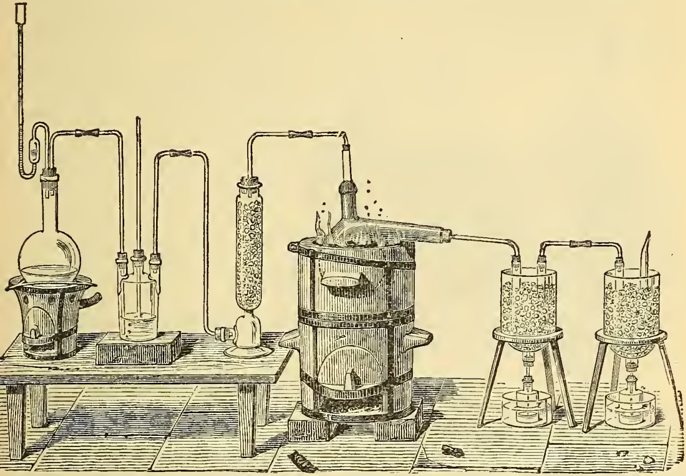


FIG. 74.

$$SiCl^4 + 4H^2O = 4HCl + Si(OH)^4$$

There exist a tetrabromide of silicon, $SiBr^4$, and a tetraiodide, SiI^4, both corresponding to the chloride just described.

Besides these compounds there are also known the tri-halides, Si^2Cl^6, Si^2Br^6, and Si^2I^6, as well as *silicon chloroform*, $SiHCl^3$, and the analogous compounds of bromine and iodine.

SILICON FLUORIDE.

SiF^4

Density compared to air	3.6
Density compared to hydrogen	52.

Preparation.—An intimate mixture of silicious sand and finely-powdered calcium fluoride, or fluor spar, is introduced into a glass flask (Fig. 75), and a sufficient quantity of sulphuric acid is added to reduce the whole to a creamy consistence. A gentle heat is applied, and the gas disengaged may be collected over mercury.

$$\underset{\text{Calcium fluoride.}}{2CaF^2} + 2H^2SO^4 + \underset{\text{Silicic oxide.}}{SiO^2} = \underset{\text{Calcium sulphate.}}{2CaSO^4} + SiF^4 + 2H^2O$$

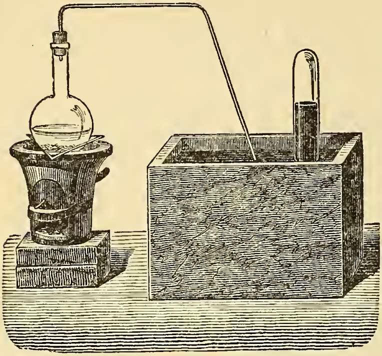


Fig. 75.

Properties.—Silicon fluoride is a colorless, suffocating gas, producing white fumes when allowed to escape into the air. It may be liquefied by a low temperature and a strong pressure. On contact with water it is decomposed, silicic hydrate separating in gelatinous flakes, and hydrofluosilicic acid being formed.

$$3SiF^4 + 4H^2O = \underset{\text{Hydrofluosilicic acid.}}{2(H^2F^2.SiF^4)} + H^2SiO^3$$

Hydrofluosilicic Acid.—A saturated, aqueous solution of this acid is a highly acid liquid, fuming in the air, and evaporating slowly at 40° from a platinum-dish, leaving no residue.

It is prepared by passing gaseous silicon fluoride into water under which is a layer of mercury. The delivery-tube must dip beneath the surface of the mercury, so that the silicon fluoride can only come in contact with the water after passing through the metal; otherwise the delivery-tube would become obstructed by the deposit of gelatinous silica.

Hydrofluosilicic acid is employed as a reagent in the laboratory. It precipitates the salts of potassium and sodium, forming insoluble fluosilicates, $R^2F^2.SiF^4$.

SILICA.

SiO^2

Native State.—Silicic oxide is widely diffused in nature. It occurs crystallized in the various *quartzes*, and as *tridymite;* cryptocrystalline, as *agate*, *chalcedony*, *carnelian*, *flint*, etc.; granulated, it is found in sandstones and the sand produced by their disaggregation; in this case it is often mixed with variable quantities of alumina and oxide of iron.

Rock-crystal is pure silicic oxide. It occurs as six-sided prisms, terminated by pyramids of six faces (Fig. 76).

Amorphous silica exists in various minerals, such as *opal* and *hydrophane*. It is also found in the form of pulverulent deposits and in solution in many running waters, in large proportion in the hot waters of the geysers in Iceland.

Properties.—Quartz is colorless when pure; its density is 2.69, and it is No. 7 in the scale of hardness (page 789). It is very refractory: in the oxyhydrogen flame it undergoes a viscous fusion, but can be melted to a clear liquid, and even volatilized, by means of the electric furnace (page 210). It forms a bluish vapor. It is not attacked by acids, with the exception of hydrofluoric acid. Boiling alkaline solutions scarcely affect it, but the amorphous varieties of silica, such as flint, as well as opal and the other hydrates, dissolve more readily in boiling solutions of the alkaline hydroxides.

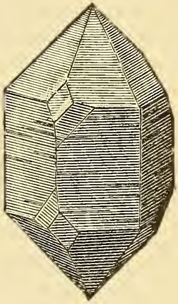


FIG. 76.

All of the varieties of silica, when heated to redness with the alkalies or alkaline carbonates, combine with the bases, forming silicates which enter into fusion at a high temperature and solidify to a vitreous mass on cooling. Potassium silicate, or *soluble glass*, is a transparent mass, soluble in water. When hydrochloric acid is added to this solution, potassium chloride is formed and silicic acid is precipitated as a gelatinous mass, which is not insoluble in water. An aqueous solution of silicic acid may be obtained.

If hydrochloric acid be added to a dilute solution of potassium silicate, the liquid remains transparent although it contains silicic acid. It may be poured into a dialyser, composed of a piece of parchment-paper stretched over a wooden or glass ring, and floated on the surface of pure water contained in another vessel. The potassium chloride gradually passes through the membrane, as would any crystallizable body, and the silicic acid remains alone dissolved in the water in the dialyser, as all other amorphous bodies which are soluble in water would do. Graham gave the name *dialysis* to this separation of crystallizable bodies, which he named *crystalloids*, from uncrystallizable bodies, which he named *colloids*, by means of certain membranes. The former bodies pass through the membranes, which are, however, impermeable to the colloids.

The silicic acid which remains in solution probably constitutes normal or ortho-silicic acid, $Si(OH)^4$. By the loss of a molecule of water, this tetrabasic acid would be converted into dibasic metasilicic acid, $SiO(OH)^2$. Many of the natural silicates represent salts of these acids: *olivine*, Mg^2SiO^4, and *garnet*, $Al^2Ca^3(SiO^4)^3$, are orthosilicates, while *Wollastonite*, $CaSiO^3$, and *enstatite*, $MgSiO^3$, are metasilicates. A numerous class of minerals correspond to more complex acids resulting from the condensation of two or more molecules of ortho- and meta-silicic acids. *Felspar*, for example, has the composition $AlKSi^3O^8$, and must be regarded as a salt of the polysilicic acid, $H^4Si^3O^8$.

Glass is a mixture of potassium or sodium silicate with calcium silicate, and generally contains aluminium silicate. It is made by the prolonged fusion of potassium or sodium carbonate with pure quartz sand and lime. Flint glass contains lead, introduced in the form of red lead. Colored glasses are obtained by adding metallic oxides to the above ingredients. Cuprous oxide gives red glass; cupric oxide, green; cobalt oxide, blue, etc. Soda glass is more fusible than potash glass.

The Electric Furnace.—The highest temperatures which were formerly employed in chemical operations were those produced by the oxyhydrogen blow-pipe. This has been recently supplanted by a device known as the electric furnace, in which the energy of powerful electric currents is converted into heat. The temperatures which can be thus reached and maintained far exceed 3000°. Nearly all those bodies which were formerly regarded infusible and non-volatile have been melted and vaporized in the electric furnace, and many new products have been obtained by its means.

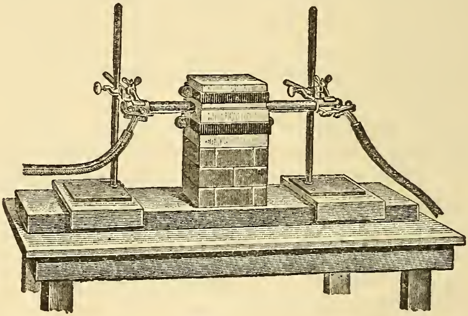


Fig. 77.

A simple form of electric furnace, constructed by Moissan, is shown in Fig. 77. It consists of a block of lime, cut in two, hollowed out at the centre, and perforated to permit the introduction of the carbon electrodes. The arc formed between these plays upon the substance in the cavity, and is regulated by moving the carbons; its position is controlled by a powerful magnet.

CARBON.

$C = 11.97$

Natural State and Varieties.—The carbon of chemists is pure charcoal. This substance is known to all; black, friable, light, absolutely fixed, inalterable by the air at ordinary temperatures, but combustible when heated in the air, it results from the calcination of organic matters, and particularly wood, in closed vessels. But carbon by no means always reveals these same properties. It occurs in nature under forms so different that it is impossible to apply a general description to all of its known varieties. What could be more different, as far as physical properties are concerned, from the soot deposited by a smoky flame, or the light, porous, and opaque charcoal, than the hard, dense, and transparent substance found in nature in the form of diamond? Nevertheless, these bodies are composed of one and the same substance, carbon; alike, they all burn in oxygen at a high temperature, producing carbon dioxide.

Among the various forms which carbon assumes, and which constitute one of the most curious examples of dimorphism, the following may be described:

Diamond.—This is the hardest of all bodies; it scratches all others, and can only be trimmed by grinding with its own dust. It is found crystallized in the form of the regular octahedron and various forms derived from it, such as the rhombic dodecahedron, trisoctahedron, and hexoctahedron. The faces are generally convexly curved (Fig. 78).

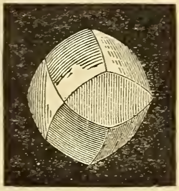


FIG. 78.

Moissan has succeeded in obtaining the diamond artificially. He dissolved carbon in molten iron, the temperature being raised to 3000°. Upon chilling the mass, a portion of the carbon crystallized out, and though exceedingly small, the crystals showed all the characteristics of the diamond.

The density of the diamond is between 3.50 and 3.55. It is a bad conductor of heat and electricity; it strongly refracts and disperses light. From this latter fact Newton first divined its combustible nature, which was proved, in 1694, by the Florentine academicians of *del Cimento*, who burned a diamond in the focus of a concave mirror. Lavoisier and Davy repeated this celebrated experiment, and proved that the sole product of the combustion is carbon dioxide. At the temperature of the electric arc the diamond swells up and blackens, being converted into graphite.

Graphite, or Plumbago.—This is a crystalline variety of carbon, which is found in primitive rocks in brilliant steel-gray foliated masses. It sometimes occurs in hexagonal laminæ. It can be scratched with the finger-nail, and leaves a black trace when drawn over paper. Its density is 2.2, and it conducts heat and electricity. It burns only at very high temperatures; ordinarily, it contains from one to two per cent. of foreign matters.

It has been obtained artificially. Molten iron possesses the property of dissolving carbon at a very high temperature, and depositing it on solidifying in hexagonal scales of graphite.

Graphite is converted into a yellow substance known as *graphitic acid* when treated with a mixture of nitric acid and potassium chlorate. The diamond is not attacked by this mixture.

Plumbago is used for the manufacture of lead-pencils and crucibles, and as a lubricant, and is sometimes called black lead.

There are other natural substances popularly regarded as varieties of carbon, but they are very impure. Their carbon is combined with more or less hydrogen, and they are in fact mixtures of complex hydrocarbons. They are:

Anthracite, a hard and compact variety of carbon containing from 8 to 10 per cent. of earthy matters.

Bituminous coal, a brilliant, black variety, strongly impregnated with bituminous and earthy matters. It has been produced by the slow decomposition of vegetable matters buried in the earth in the early geological ages. This origin is indicated by the impressions of leaves, stems, and fruits, which are evident in certain specimens of this coal. It contains only from 75 to 88 per cent. of carbon. When it is calcined in closed vessels, it disengages combustible gases and products which may be condensed in the liquid form and then separate into two layers. One is aqueous and ammoniacal, while the other is composed of tar. The residue of the distillation of bituminous coal is *coke*. The interior walls of the cast-iron vessels in which coal is distilled become covered with a compact layer of a gray, dense, hard and sonorous carbon, which is a good conductor of heat and electricity. This is the *carbon of gas-retorts*, and is produced by the igneous decomposition of hydrocarbons rich in carbon, which are disengaged during the calcination of the coal.

Fat coals are those which burn with a long flame, softening in burning; *dry coals* burn with a short flame which produces less heat than the preceding.

Lignite is a combustible mineral containing less carbon, and more impure than bituminous coal; it is found in the lower tertiary formations. *Natural jet*, which is employed for the manufacture of ornaments, is a variety of lignite.

Among the artificial carbons, independently of coke, may be mentioned wood charcoal, lamp-black, and animal charcoal.

Wood Charcoal.—When wood is calcined in closed vessels it leaves a residue which is ordinary charcoal. It is prepared on the large scale by two processes, carbonization in stacks, which is carried on in the forests, and distillation in closed vessels. Charcoal is amorphous, brittle, and sonorous, a bad conductor of heat and electricity. Its density does not exceed 1.57. The lighter varieties are the more combustible. Its combustion leaves a residue of one or two per cent. of ash, formed principally of mineral salts, among which the most abundant are the carbonates of calcium and potassium.

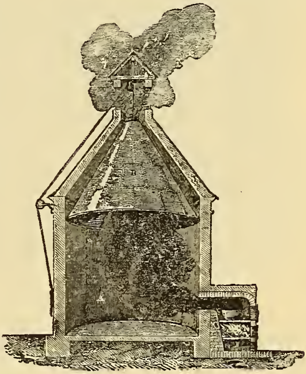


Fig. 79.

Lamp-black is produced by the incomplete combustion of organic substances rich in carbon. When rosin or tallow is burned, a dense smoke is produced which is composed of particles of carbon that have escaped combustion. In the arts, lamp-black is procured by burning rosin in cast-iron pots, C (Fig. 79), heated by a fire, F. The vapors given off are ignited, and the smoke is conducted into a chamber, A, the walls of which are hung with canvas. On this the lamp-black is deposited, and is detached by lowering the cone B, which acts as a scraper. Lamp-black is not pure carbon. It contains tarry and oily matters, from which it may be freed by calcination in a covered crucible. It is used for the manufacture of printing-inks.

Animal charcoal is produced by calcining animal matters, such as blood, the débris of skin, horn, bone, etc., in closed vessels. Bone-black or ivory-black contains the calcareous salts, calcium phosphate and carbonate, which form the base of the osseous tissue. The carbon is consequently disseminated through a porous mass. These salts may be extracted by treating the bone-black with dilute hydrochloric acid, by which they are dissolved. The residue, washed with water and dried, is known as washed or purified animal charcoal.

Absorbent Properties of Charcoal.—The amorphous and porous varieties of carbon, of which several forms have been described, possess the property of absorbing and retaining in their pores, gases, liquid and solid bodies. It is to this absorptive faculty that are due the decolorizing and disinfecting properties of charcoal, which are made use of to a large extent in the arts.

If a piece of incandescent charcoal be plunged into mercury that it may cool out of contact with the air, and then be introduced into a small jar filled with ammonia or hydrochloric acid over the mercury-trough, the gas is at once absorbed and the mercury rises in the jar.

The following table, by Th. de Saussure, indicates the quantities of several gases which are absorbed by one volume of charcoal:

1 volume of	charcoal absorbs	90	volumes of	ammonia.
“	“	85	“	hydrochloric acid.
“	“	65	“	sulphur dioxide.
“	“	55	“	hydrogen sulphide.
“	“	40	“	nitrous oxide.
“	“	35	“	carbon dioxide.
“	“	9.42	“	carbon monoxide.
“	“	9.25	“	oxygen.
“	“	7.50	“	nitrogen.
“	“	1.75	“	hydrogen.

Charcoal increases in weight when exposed to the air, for it absorbs and condenses the atmospheric moisture. When plunged into water charged with a small quantity of hydrogen sulphide, it absorbs that gas and removes the odor of the water.

The disinfecting properties of charcoal are thus easily explained. It is well known that charcoal will remove the unpleasant odor of corrupted waters, of meats slightly spoiled, and in general of organic matters in a state of putrefaction. A layer of charcoal between two layers of sand is an excellent filter for the clarification of drinking waters.

The decolorizing properties of charcoal are another manifestation of this general faculty of absorption, which is possessed in the highest degree by animal charcoal. If litmus solution or red wine be agitated with a sufficient quantity of animal charcoal and subsequently filtered, the liquids pass through colorless.

This property of animal charcoal is largely applied in the arts, particularly for decolorizing sugars and syrups.

Chemical Properties —Carbon is distinguished by its powerful affinity for oxygen, an affinity which is not, however, exercised except at high temperatures. It only combines with oxygen at a red heat, and remains incandescent as long as combination goes on, the heat produced by the combination being sufficient to maintain the incandescence. In pure oxygen it burns with a brilliant light. The product of the combustion is carbonic acid gas.

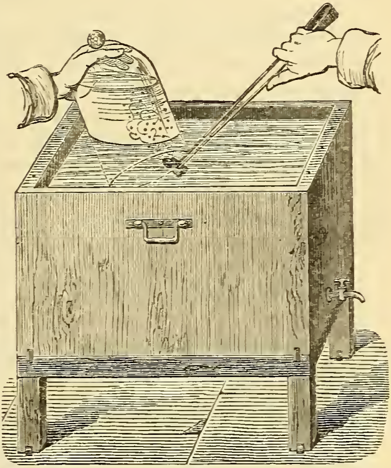


FIG. 80.

By the aid of heat, carbon decomposes a great number of oxygenized compounds, removing and combining with the whole or a part of their oxygen. This decomposition takes place at comparatively low temperatures when the oxygenized body does not strongly retain its oxygen; in this case, carbon dioxide is formed, and the reduction of cupric oxide by charcoal furnishes an example. In the contrary case, the reduction, that is, the decomposition of the oxidized body, requires a very high temperature; carbon monoxide is then formed. The reduction of zinc oxide by charcoal is an example.

If an incandescent charcoal be rapidly plunged under a bell-jar filled with water on the pneumatic trough, bubbles of gas arise and collect in the jar (Fig. 80). They are formed of a mixture of hydrogen, carbon monoxide, and a small quantity of carbon dioxide. These gases are produced by the decomposition of the water by the charcoal, which was red-hot at the moment of contact with the liquid.

$$C + H^2O = H^2 + CO \text{ carbon monoxide.}$$

Water gas, a mixture of hydrogen and carbon monoxide, is made, according to this reaction, by passing steam over highly-heated coal, coke, or other form of carbon.

Carbon combines directly with sulphur at a high temperature, forming carbon disulphide.

Carborundum, CSi.—At the high temperature of the electric furnace and under the influence of the current, carbon reduces silica; the product of the reaction is a transparent greenish or yellowish mass of crystals having a hardness but little below that of the diamond, and used as a substitute for diamond for cutting and polishing under the name carborundum. It is unaffected by acids, even by hydrofluoric acid, but is decomposed by fusion with alkalies. This substance is a definite compound of carbon and silicon, as indicated by the formula.

CARBIDES OF BORON.—Boric oxide, like silica, is reduced by carbon in the electric furnace, the boron combining with the excess of carbon to form carbides of definite composition. One of these, B^2C^2, resembles graphite, but is fusible at very high temperatures. Another carbide, CB^6, is said to be harder even than the diamond (Moissan).

COMPOUNDS OF CARBON AND OXYGEN.

Two compounds of carbon and oxygen are known:

Carbon monoxide	CO
Carbon dioxide, or carbonic acid gas	CO^2

The latter body, which has long been known as carbonic acid, is the oxide corresponding to the true carbonic acid, which would be

$$CO^2 + H^2O = H^2CO^3$$

This normal carbonic acid is as yet unknown: it is doubtless too unstable to exist in the free state. However, its existence may be admitted, for a corresponding compound is known in sulphocarbonic acid H^2CS^3.

CARBON MONOXIDE.

Density compared to air	0.967
Density compared to hydrogen	13.9
Molecular weight CO	= 27.78

Preparation.—1. An intimate mixture of zinc oxide and charcoal may be calcined in a clay retort.

$$ZnO + C = CO + Zn$$

2. A convenient method of preparing carbon monoxide consists in heating oxalic acid with an excess of sulphuric acid in a glass flask. The oxalic acid loses the elements of water, which it yields to the sulphuric acid, and breaks up into carbon dioxide and carbon monoxide.

$$\underset{\text{Oxalic acid.}}{C^2H^2O^4} = \underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Carbon dioxide.}}{CO^2} + H^2O$$

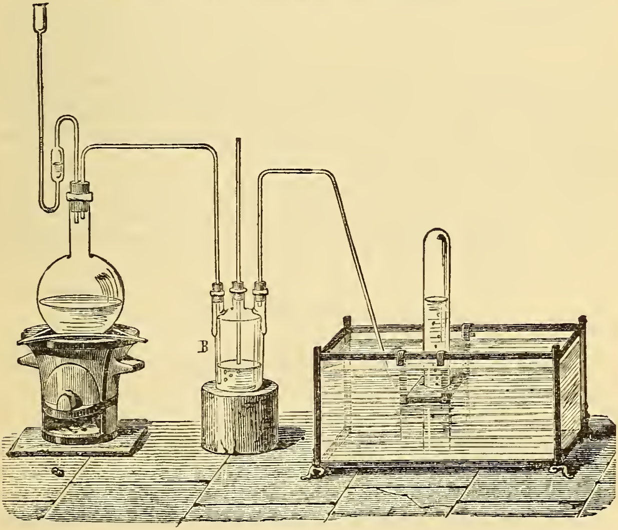


Fig. 81.

The mixture of the two gases is passed through a wash-bottle, B (Fig. 81), containing a solution of potassium hydroxide, by which the carbon dioxide is absorbed, potassium carbonate being formed. The carbon monoxide may then be collected over water.

Another excellent method consists in heating a mixture of one part of powdered potassium ferrocyanide with ten parts of concentrated sulphuric acid. The carbon monoxide evolved is practically pure.

$$\underset{\text{Potassium ferrocyanide.}}{K^4Fe(CN)^6} + 6H^2SO^4 + 6H^2O = 2K^2SO^4 + \underset{\text{Ferrous sulphate.}}{FeSO^4} + 3(NH^4)^2SO^4 + 6CO$$

Properties.—Carbon monoxide is a colorless, odorless gas. Its critical conditions are —139.5° and 35.5 atmospheres; the liquid boils at —190° and freezes at —207°. Carbon monoxide is neutral, and does not cloud lime-water, which distinguishes it from carbon dioxide. It extinguishes burning bodies, but is combustible itself, burning in the air with a blue flame, and forming carbon dioxide. It is not only unfit for respiration, but is very poisonous, combining with and profoundly altering the red corpuscles of the blood.

Composition.—If two volumes of carbon monoxide be mixed with one volume of oxygen in an eudiometer, and a spark be passed, complete combustion takes place, and the three volumes of the mixture are reduced to two volumes of carbon dioxide. This can be verified by passing into the eudiometer a solution of potassium hydrate, which will completely absorb the new gas.

It hence follows that two volumes of carbon monoxide contain the same quantity of carbon as two volumes of carbon dioxide. Knowing from other circumstances that two volumes of carbon dioxide contain two volumes of oxygen, it follows that two volumes of carbon monoxide contain one volume of oxygen. Its molecular formula is therefore CO.

Carbon monoxide undergoes dissociation at a very high temperature, and may be resolved into carbon and oxygen.

It is almost insoluble in water, but is absorbed by a solution of cuprous chloride in hydrochloric acid (Doyère and F. Le Blanc). Advantage is taken of this property in volumetric analysis to separate carbon monoxide from certain other gases.

When heated for a long time to 100°, in sealed tubes with potassium hydroxide, it combines with the alkali, forming potassium formate (Berthelot).

$$CO + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium formate.}}{KCHO^2}$$

Action of Chlorine upon Carbon Monoxide.—Under the influence of sunlight, carbon monoxide combines directly with an equal volume of chlorine, forming a gas which is known as *carbonyl chloride*, or *phosgene*. The volume of the carbonyl chloride is one-half that of the sum of the combining gases, so that its formula is $COCl^2$.

Carbonyl chloride may be easily condensed to a colorless liquid, boiling at 8.2°. Its vapor is colorless, produces a suffocating sensation, and provokes tears. It is instantly decomposed by water, with the formation of carbon dioxide and hydrochloric acid.

$$COCl^2 + H^2O = 2HCl + CO^2$$

Its mode of formation, its composition, and its properties indicate its relations to carbon dioxide.

2 volumes CO absorb 2 volumes of chlorine to form 2 volumes $CO.Cl^2$
2 volumes CO absorb 1 volume of oxygen to form 2 volumes CO.O

Carbon monoxide thus plays the part of a radical; it combines directly with oxygen or with chlorine to form either oxide or chloride of carbonyl.

L. Mond has discovered a remarkable class of compounds of carbon monoxide with certain metals. *Nickel carbonyl*, $Ni(CO)^4$, may be considered as the type of these compounds; it is formed by passing carbon monoxide over finely divided nickel at a temperature of 100°. It condenses at low temperatures to a colorless, highly refracting liquid having a density of 1.35, and boiling at 43°. At a temperature below 200°, it decomposes into carbon monoxide and metallic nickel.

CARBON DIOXIDE.

Density compared to air	1.524
Density compared to hydrogen	21.83
Molecular weight CO^2	= 42.73

This gas was discovered by Black in 1757, and its composition was recognized by Lavoisier in 1776. It is one of the constituents of the atmosphere, and is the product of a great number of reactions which take place on the earth's surface, such as the combustion of carbon and organic matters, respiration, and the phenomena of putrefaction and fermentation. It issues from the soil of volcanic countries.

Preparation.—Fragments of marble, which is calcium carbonate, are introduced into a two-necked bottle fitted with a delivery-tube and a safety-tube (compare Fig. 11, page 60). The bottle is half-filled with water, and hydrochloric acid is gradually added by the funnel-tube. An effervescence immediately takes place, due to the disengagement of carbon dioxide.

$$\underset{\text{Calcium carbonate.}}{CaCO^3} + 2HCl = CO^2 + \underset{\text{Calcium chloride.}}{CaCl^2} + H^2O$$

The gas is most conveniently collected by dry downward displacement, like chlorine.

When it is desired to prepare large quantities of the gas, a self-regulating generator, such as that described on page 102, is advantageously used. Acid vapors and other impurities are removed by passing the gas through a saturated solution of potassium acid carbonate.

Very pure carbon dioxide is also obtained by heating the acid carbonates of the alkaline metals.

$$\underset{\text{Sodium acid carbonate.}}{2NaHCO^3} = CO^2 + \underset{\text{Sodium carbonate.}}{Na^2CO^3} + H^2O$$

On a large scale, the gas is manufactured by heating limestone or magnesite.

Composition.—1. If carbon be burned in oxygen, the latter is converted into carbon dioxide without changing its volume. Hence two volumes of carbon dioxide contain two volumes of oxygen. These two volumes of oxygen, which represent two atoms, are combined with one atom of carbon, and the composition of a molecule of carbon dioxide is hence expressed by the formula

$$CO^2 = 2 \text{ volumes.}$$

2. Dumas and Stas determined the centesimal composition of carbon dioxide by burning a known weight of diamond in oxygen, and carefully weighing the carbon dioxide produced. By subtracting the weight of the diamond burned from that of the carbon dioxide, the weight of the oxygen was determined. The apparatus employed is represented in Fig. 82.

The increase in weight of the tubes L, M, N, O, P indicates the quantity of carbon dioxide formed.

Dumas and Stas thus found that 100 parts of carbon dioxide contain

Carbon	27.27
Oxygen	72.73
	100.00

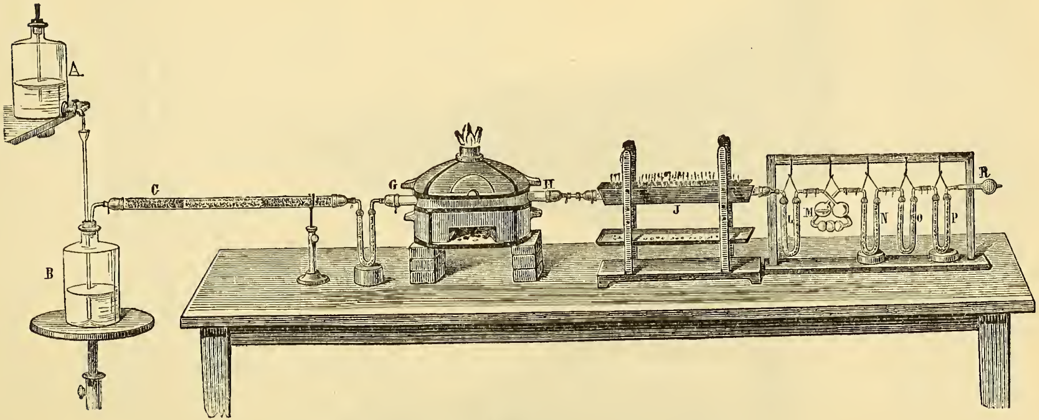


FIG. 82.

B, bottle filled with oxygen; the gas is displaced by water which flows from the bottle A.—C, tube filled with pumice-stone impregnated with sulphuric acid for drying the oxygen.—GH, reverberatory furnace, with its porcelain tube, in which the diamond or pure graphite is heated.—J, combustion furnace, containing a tube filled with oxide of copper; the object of this tube is that any traces of carbon monoxide which might be formed by the incomplete combustion of the diamond may be converted into carbon dioxide on contact with the heated cupric oxide.—L, M, tubes filled with solution of potassium hydrate to absorb the carbon dioxide.—N, O, P, tubes containing sulphuric acid and pumice-stone to absorb any vapor that might be carried from the potassium hydrate by the excess of oxygen as it leaves the apparatus.

a centesimal relation which corresponds to the proportion of one atom of carbon to two atoms of oxygen:

Carbon	11.97
Oxygen	31.76

Physical Properties.—Carbon dioxide is colorless; it has a feeble, somewhat pungent odor. A litre of this gas at 0°, and under the pressure of 760 millimetres, weighs 1.97 grammes.

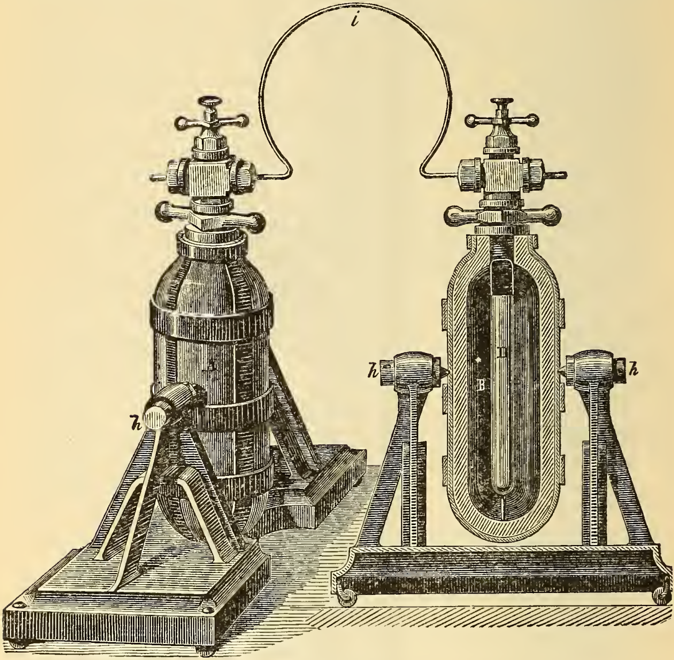


Fig. 83.

It was first liquefied by Faraday. At 0° it requires a pressure of 38.5 atmospheres, and at 31° (its critical temperature), 74 atmospheres. The apparatus which is now used for its liquefaction is represented in Fig. 83. It is composed of two reservoirs, A and B, communicating by the metallic tube *i*, furnished with a stop-cock at each end. The cylinders are made of heavy cast-iron, and are further strengthened by forged iron bands forced over their circumference. Each cylinder is movable on a horizontal axis, *h*. B is the generator; into it are introduced 1800 grammes of sodium dicarbonate, and a cylindrical copper tube, D, containing 1000 grammes of ordinary sulphuric acid. The cylinder is then closed by a strong screw plug, and a few oscillating movements are given to it in order that the sulphuric acid may gradually run out upon the sodium dicarbonate. Carbon dioxide is disengaged and is liquefied by its own pressure as it accumulates in the apparatus. By the effect of the chemical action the temperature is raised to 30 or 40°, and, communication being established between the two cylinders, the carbon dioxide distils rapidly into the receiver, the temperature of which is about 15°.

The operation is repeated several times, that one or two kilogrammes of the liquid may accumulate in the receiver. A tube passes to the bottom of this vessel, and on opening the stop-cock which closes the superior extremity of this tube, a jet of the liquid is thrown out with force; it is received tangentially in a metallic box, A, A′ (Fig. 84), having very thin sides. In this a portion of the oxide solidifies by reason of the great depression of temperature produced by the change of another portion into the gaseous state. A glittering-white, flaky mass collects in the receiver, having the appearance of snow. This is solid carbon dioxide. It is a bad conductor of heat and electricity, and can be exposed to the air for a few minutes before it disappears. In reassuming the gaseous form, it produces an intense cold. If it be mixed with ether, the mixture, which is less porous and a better conductor of heat, can produce a lowering of temperature as great as —90°. By pouring it upon mercury, large masses of that metal may be frozen.

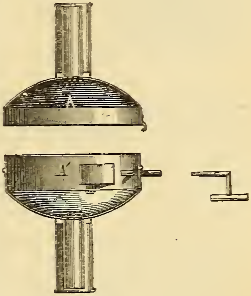


Fig. 84.

Liquid carbon dioxide is now manufactured on a commercial scale, and sold in strong steel cylinders. It is colorless and mobile; has a density of 0.72 at +27°, and 0.98 at —8°.

This considerable difference between the densities is due to the enormous dilatation which the liquid undergoes between these limits of temperature. Indeed, ten volumes of liquid carbon dioxide at 0° occupy fourteen volumes at 30°. Hence the coefficient of expansion of the liquid is superior to that of the gas.

Carbon dioxide is incombustible, and extinguishes burning bodies.

If carbon dioxide be poured from one vessel into another containing a lighted candle, it falls upon the flame like water, extinguishing it at once (Fig. 85).

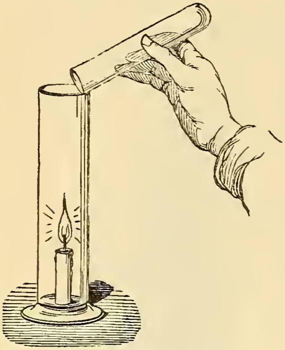


Fig. 85.

Lime-water poured into a jar of carbon dioxide becomes clouded, owing to the formation of insoluble calcium carbonate.

These experiments permit the easy recognition of carbon dioxide from carbon monoxide.

Carbon dioxide dissolves in its own volume of water at 15° under the normal pressure. If the pressure be increased, the solubility of the gas is increased in the same proportion. Thus, under a pressure of ten atmospheres one litre of water will dissolve ten litres of carbon dioxide; but it must be remembered that under a pressure of ten atmospheres these ten litres are reduced to one litre. Thus, one litre of water, which dissolves one litre of carbon dioxide at the ordinary pressure, dissolves also one litre under a pressure of ten atmospheres, and it may be said that water always dissolves its own volume of carbon dioxide, whatever may be the pressure. Water saturated with carbon dioxide under strong pressure, disengages a portion of the gas as soon as the pressure is removed. Such water is universally known and consumed in large quantities under the name of aerated water or soda water.

The solution of carbon dioxide exercises a much more energetic solvent action upon certain substances than pure water. It dissolves calcium carbonate, forming a soluble dicarbonate; it is even capable of dissolving calcium phosphate, transforming it into acid phosphate, which is soluble.

Carbon dioxide is more soluble in alcohol than in water.

It is undecomposable by heat alone, but may be decomposed or reduced at high temperatures by contact with bodies avid of oxygen. It is not reduced by hydrogen. With carbon the reduction takes place at a red heat, giving rise to the formation of carbon monoxide, the volume of which is double that of the carbon dioxide employed.

$$\underset{\text{Carbon dioxide (2 vols.).}}{CO^2} + C = \underset{\text{Carbon monoxide (4 vols.).}}{2CO}$$

CARBON DISULPHIDE.

CS^2

This body is prepared by passing sulphur vapor over incandescent charcoal. In the arts, the operation is conducted in cylindrical, cast-iron vessels, filled with charcoal and heated to redness, into which sulphur is introduced. The carbon disulphide distils, and is condensed in a suitable cooling apparatus.

Carbon disulphide is a colorless, very mobile, and highly-refracting liquid. Its odor is usually strong and unpleasant, but is rather agreeable when the compound is perfectly pure. Its density at 15° is 1.271, and it boils at 46°. It is very inflammable, and burns with a blue flame, producing sulphur dioxide and carbon dioxide.

$$CS^2 + 3O^2 = 2SO^2 + CO^2$$

Its vapor, mixed with oxygen, explodes when heated.

Carbon disulphide corresponds in composition to carbon dioxide.

CO^2 carbon dioxide.
CS^2 carbon disulphide.

It is also analogous to the latter body in its chemical functions. While carbon dioxide combines with metallic oxides, forming carbonates, carbon disulphide combines with metallic sulphides, forming *sulphocarbonates* or thiocarbonates.

$$CO^2 + \underset{\text{Sodium oxide.}}{Na^2O} = \underset{\text{Sodium carbonate.}}{Na^2CO^3} \text{ corresponding to } \underset{\substack{\text{Carbonic acid} \\ \text{(hypothetical).}}}{H^2CO^3}$$

$$CS^2 + \underset{\text{Sodium sulphide.}}{Na^2S} = \underset{\text{Sodium sulphocarbonate.}}{Na^2CS^3} \text{ corresponding to } \underset{\text{Sulphocarbonic acid.}}{H^2CS^3}$$

Sodium carbonate and sulphocarbonate possess the same constitution. By the action of strong acids they should give analogous products: the one, carbonic acid, H^2CO^3; the other, sulphocarbonic acid, H^2CS^3. The latter body is indeed formed under such circumstances, but normal carbonic acid, if it exist, possesses no stability, and at once decomposes into carbon dioxide and water.

Carbon disulphide is employed in the arts in the manufacture of vulcanized caoutchouc, and as a solvent for caoutchouc in the fabrication of goods impermeable to water by the deposit of a thin layer of that substance. It is also employed as a solvent for, and in the extraction of, fats and oils. In the laboratory it is useful as a solvent for sulphur, phosphorus, iodine, oils, fats, etc.

CARBON OXYSULPHIDE.

Density compared to air	2.1046
Density compared to hydrogen	30.4
Molecular weight CSO	=59.61

This body was discovered by von Than in 1867. It is intermediate between carbon dioxide and carbon disulphide.

COO carbon dioxide.
CSO carbon oxysulphide.
CSS carbon disulphide.

Preparation.—It is prepared by decomposing potassium sulphocyanate by dilute sulphuric acid. Potassium sulphate and sulphocyanic acid are formed, and the latter, in the presence of an excess of sulphuric acid and water, decomposes into ammonia and the gas carbon oxysulphide, which may be collected over mercury; the ammonia remains combined with the sulphuric acid in the form of sulphate.

$$\underset{\text{Sulphocyanic acid.}}{CSNH} + H^2O = NH^3 + \underset{\text{Carbon oxysulphide.}}{CSO}$$

Properties.—Carbon oxysulphide is a colorless gas, having an odor like that of carbon disulphide, but also recalling that of hydrogen sulphide.

On contact with an incandescent body, even a match presenting a spark of fire, it takes fire, burning with a blue flame, and depositing sulphur if the supply of air be insufficient. With one and a half times its volume of oxygen it constitutes an explosive mixture.

2 volumes of carbon oxysulphide . . = CSO mixed with
3 volumes of oxygen . . . . = O^3 yield
2 volumes of carbon dioxide . . . . = CO^2 and
2 volumes of sulphur dioxide . . . . = SO^2

Water dissolves about its own volume of carbon oxysulphide, but the solution decomposes in a few hours, with the formation of hydrogen sulphide and carbon dioxide.

$$CSO + H^2O = CO^2 + H^2S$$

Carbon oxysulphide is absorbed completely, but more slowly than carbon dioxide, by solutions of the alkaline hydroxides; by a reaction analogous to the preceding, a sulphide and a carbonate are formed.

COMPOUNDS OF CARBON AND HYDROGEN.

These compounds are numerous and important. Carbon unites with hydrogen in different proportions, and the atoms of carbon and hydrogen may accumulate in considerable numbers in the molecules of their compounds. These combinations are called hydrocarbons or carbides of hydrogen. Hydrogen monocarbide, or marsh gas, contains only one atom of carbon combined with four atoms of hydrogen; its molecule is therefore represented by the formula CH^4. In olefiant gas, or ethylene, two atoms of carbon are united with four atoms of hydrogen; in the volatile liquid known as benzene or benzol, which is obtained in large quantities from coal-tar, six atoms of carbon are combined with six atoms of hydrogen. Lastly, the molecule of oil of turpentine contains ten atoms of carbon and sixteen of hydrogen.

Hence these substances give us the following formulæ:

CH^4 methane, or marsh gas.
C^2H^4 ethylene, or olefiant gas.
C^6H^6 benzene.
$C^{10}H^{16}$ turpentine.

These examples, which might be indefinitely multiplied, show: 1st. That the atoms of carbon unite in various proportions with the atoms of hydrogen to constitute the molecules of the hydrocarbons. 2d. That they accumulate in greater or less numbers to form molecules more and more complex, that is, containing an increasing number of atoms of carbon and hydrogen.

All of these bodies must be considered among the organic compounds; indeed, the latter are nothing more than the compounds of carbon, and carbon monoxide and dioxide may also be properly considered as the most simple organic combinations.

Hence if the most strictly rigorous method were adhered to, the description of the compounds of carbon and oxygen would be followed by that of all the other compounds of this element, that is, of all the organic compounds. However, for the purposes of study it is advantageous to treat the latter bodies separately, and they will be so considered in this work. The following experiments will expose some of the general properties of the hydrocarbons which have been mentioned:

1. If a lighted taper be applied to a jar of methane, which is also called marsh gas, because it is disengaged from the muddy bottoms of marshes, the gas takes fire and burns with a faintly luminous flame.

2. If the same experiment be repeated with ethylene gas, which contains for the same proportion of hydrogen twice as much carbon as marsh gas, a highly luminous flame results.

3. It is well known that benzene and turpentine take fire when lighted, and burn with bright flames; but it is also known that their flames are smoky.

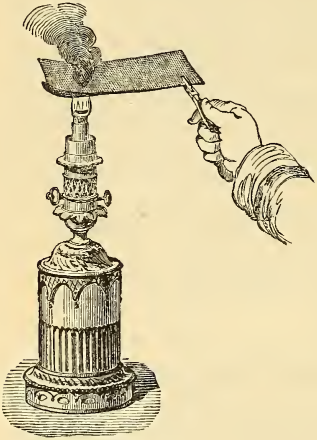


Fig. 86.

The hydrocarbons are then combustible; and how could they be otherwise, since they contain only two combustible elements, carbon and hydrogen? The products of the combustion are water and carbon dioxide, and the formation of the latter gas may be proved by agitating the contents of the jars in which the combustion has taken place with lime-water; the latter immediately becomes milky by the precipitation of calcium carbonate.

This combustion is more or less complete; when the gas or vapor which burns contains a large amount of combustible elements, the oxygen of the air may not be present in sufficient quantity to burn them all, that is, to oxidize them completely. Under these conditions it is the hydrogen which is burned by preference, and the carbon partly escapes combustion.

A flame is a gas or vapor in combustion. This combustion is an oxidation, and it is the oxygen of the air which is the agent. In order that it may take place, it is generally necessary that the combustible gas shall be brought to a high temperature; but once commenced, the combustion continues of itself, because the heat disengaged by the oxidation is sufficient to maintain the phenomenon. But if a flame be suddenly cooled, the combustion is at once arrested.

A flame may be cooled by depressing into it a piece of fine wire gauze. The incandescent gases cannot pass through the meshes of the gauze without being cooled by contact with the metal, which is a good conductor of heat. For this reason, no combustion takes place above the gauze (Fig. 86).

If a piece of wire gauze be held over an escaping jet of gas, the latter may be ignited above the gauze, and will burn without the combustion being propagated to the gas below; the gauze acts as a screen, separating the jet into two portions, the lower cold and invisible, the upper in combustion and luminous.

Sir Humphry Davy made a happy application of these facts in the construction of the miner's safety-lamp. This is an ordinary lamp surrounded by a cylinder of wire gauze (Fig. 87).

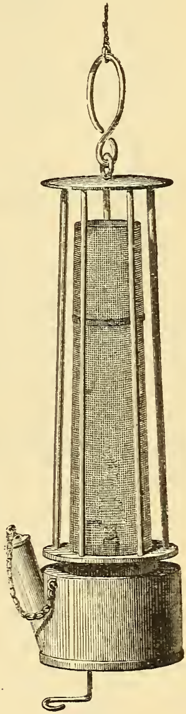


FIG. 87.

Such a lamp gives less light than one not protected by an envelope, but it removes the danger of explosions of fire-damp, for when an explosive mixture is formed in the galleries of a mine, the gas may penetrate to the interior of the lamp and take fire there, but the flame cannot pass through the cooling envelope of wire gauze. The safety-lamps are now constructed with the lower part of the cylinder of glass, so that there is no diminution in the amount of light given.

As the oxidation of combustible elements is the source of heat, it is evident that the different parts of a flame cannot be uniformly hot, for the oxygen of the surrounding air cannot equally attain all portions. The exterior borders are the most intensely heated; they are surrounded by air, and constitute the seat of combustion. From them the heat is radiated not only externally, but also to the interior of the flame, where it produces interesting phenomena.

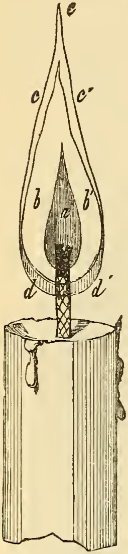


Fig. 88.

These may be studied by analyzing a flame, that is, considering separately the different parts of which it is composed. If the flame of a candle be examined, it will be found to present three distinct layers, or cones (Fig. 88).

1. A dark central part, *a*, which surrounds the wick. This is known as the obscure cone, or cone of generation; its temperature is not high.

2. A luminous part, *bb′*, surrounding the obscure cone. This is the centre from which the light is emitted. It is known as the luminous cone, or cone of decomposition.

3. An exterior envelope, *cc′*, thin, and producing but little light, yellow towards the summit, *e*, and bluish towards the base, *dd′*. It is the cone of complete combustion, and its temperature is the highest.

It is easy to account for these phenomena. The material of the candle is melted by the heat of the flame, the liquid is drawn up into the wick by capillarity, and arrives at the incandescent summit. There it is decomposed, producing gases and vapors rich in carbon and hydrogen, and which rise around the wick, forming an irregular cone. The gaseous products constituting this cone do not present the same composition throughout. They have been analyzed by H. Sainte-Claire Deville, by the aid of very ingenious processes.

The obscure cone is formed of gaseous products holding in suspension finely-divided carbon, which has not yet arrived at incandescence.

These products become heated on reaching the more central portions of the flame. Then the carbon, which is set free by the decomposition of gases rich in carbon, is brought to bright incandescence, but it is completely burned only when it reaches the exterior envelope, where the oxygen is in excess. A simple experiments will demonstrate that the most luminous portion of the flame holds in suspension finely-divided and incandescent carbon. If a porcelain saucer be depressed into this portion, the carbon will be deposited on the vessel as soot.

It is this solid and incandescent carbon which causes the luminosity of the flame. The flame of hydrogen, which contains only gaseous products, is pale. In the calcium or Drummond light it produces great brilliancy because a solid body, lime, is heated to bright incandescence. When the carbon suspended in a flame is in excess in proportion to the supply of oxygen, it is incompletely burned, and is carried into the air. The flame then smokes.

At the base of the cone, carbon monoxide and methane, the first products of the decomposition of the candle, burn on contact with the air at *dd'* with a bluish flame.

The luminosity of a flame is not necessarily due to the presence in it of solid matter. It depends very largely upon the temperature and the density of the burning gas. The flame of hydrogen, according to Frankland, is luminous when that gas is burned under strong pressure, and the flame of illuminating gas may be rendered non-luminous by diluting with an indifferent gas, such as nitrogen, and thus reducing the temperature.

Illuminating gas is a mixture of hydrogen with various gaseous hydrocarbons and a small proportion of carbon monoxide. It is manufactured by the destructive distillation of bituminous coal. The aqueous products containing ammonia, and the tarry matters formed during the distillation are condensed, and the gas is purified by washing with water and passage over slaked lime to remove sulphur and other impurities.

Illuminating gas forms an explosive mixture with air, but if the mixture be burned as it is formed, the resulting flame will be almost colorless and will deposit no soot, the whole of the carbon coming in contact with sufficient oxygen for its complete combustion. These conditions are fulfilled in the Bunsen burner (Fig. 89). In this burner, the force of the escaping gas-jet draws in air through holes near the jet in a wider tube, at the end of which the mixture is burned.

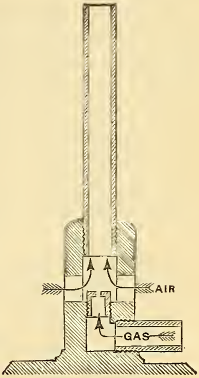


FIG. 89.

GENERAL NOTIONS UPON THE NON-METALS.

THEORY OF ATOMICITY.

From a consideration of the facts acquired in the study of the elements known as non-metals, we may deduce certain general consequences, and while looking back on the field over which we have passed, we may at the same time fix certain landmarks for the remainder of our course.

The elements which we have studied are not alike in their aptitude to enter into combination, nor in the general characters of their compounds. In this respect, analogies and differences have been established between them, and these have become the basis of a rational classification. Following the example of Dumas, we may arrange these elements in groups or families, uniting in the same group those which are related by their chemical functions.

HYDROGEN.
FLUORINE.
CHLORINE.
BROMINE.
IODINE.

OXYGEN.
SULPHUR.
SELENIUM.
TELLURIUM.

NITROGEN.
PHOSPHORUS.
ARSENIC.
ANTIMONY.
BORON.

SILICON.
CARBON.

HELIUM.
NEON.
ARGON.
METARGON.
XENON.

The elements of the last group, which includes argon and helium, are characterized by their inability to form chemical compounds.

In order to account for the chemical functions of the other non-metals—that is, for the parts which they play in their combinations—we must first consider their hydrogen compounds. These constitute the following series

HH Hydrogen.	H^2O Water.	H^3N Ammonia.	H^4Si Hydrogen silicide.
HCl Hydrochloric acid.	H^2S Hydrogen sulphide.	H^3P Hydrogen phosphide.	H^4C Hydrogen carbide.
HBr Hydrobromic acid.	H^2Se Hydrogen selenide.	H^3As Hydrogen arsenide.	
HI Hydriodic acid.	H^2Te Hydrogen telluride.	H^3Sb Hydrogen antimonide.	
HF Hydrofluoric acid.		H^3B Hydrogen boride.	

It is seen that the first four groups are characterized by the composition of their hydrogen compounds. While the bodies of the first group combine with hydrogen atom for atom, those of the second group require two atoms of hydrogen, those of the third three, and those of the fourth four, to form hydrogen compounds. Hence we may draw the conclusion that the atoms of these non-metals are far from being equivalent in their power of combination with hydrogen.

The atoms of chlorine, bromine, and iodine are equivalent to each other in this respect, for each requires but one atom of hydrogen.

The atoms of oxygen, sulphur, etc., are equivalent to each other, for each combines with two atoms of hydrogen.

The atoms of nitrogen, phosphorus, arsenic, antimony, and boron are equivalent to each other, for each of them unites with three atoms of hydrogen.

Lastly, the atoms of carbon and silicon are equivalent, for each can unite with four atoms of hydrogen.

But, on the other hand, it is evident that the atoms of chlorine, oxygen, nitrogen and carbon are not equivalent to each other, as regards their power of combination with hydrogen, since each of them unites with a different number of atoms of that body.

In this respect it may be said that

1 atom of chlorine	is equivalent to	1 atom	of hydrogen.
1 atom of oxygen	"	2 atoms	"
1 atom of nitrogen	"	3 atoms	"
1 atom of carbon	"	4 atoms	"

It is evident that the capacity of combination which resides in the atoms of simple bodies and by which they attract the atoms of hydrogen, is unequal. Leaving aside its intensity, this force is exerted in different degrees, for it determines the union of 1 atom of chlorine, oxygen, nitrogen, or carbon, with 1, 2, 3, or 4 atoms of hydrogen.

This number of hydrogen atoms is the measure of the degree of force which resides in the atoms,—of the capacity of combination which they possess for each other.

Hence we conclude that

The atoms of chlorine	and its associates are	*monatomic* or *univalent.*
The atoms of oxygen	" "	*diatomic* or *bivalent.*
The atoms of nitrogen	" "	*triatomic* or *trivalent.*
The atoms of carbon	" "	*tetratomic* or *quadrivalent.*

The capacity of combination which resides in the atoms, and which is exerted in such different manners according to the nature of the atoms, is called *atomicity.* Atomicity is the relative *equivalence* of the atoms; it is simple or multiple, and if we consider it in its first degree, we may say that the atoms of chlorine and the atoms of hydrogen are so constituted that a single atom of one attracts a single atom of the other. When they combine, they exchange in some manner a unit of saturation, and in the combination of chlorine and hydrogen two of these units of force are neutralized; two units of saturation or two atomicities are exchanged: the atoms of chlorine and of hydrogen are univalent.

The force which resides in an atom of oxygen is more complex. It attracts two atoms of hydrogen, and represents the second degree of capacity of combination, and we may say that in each atom of oxygen reside two atomicities, which are satisfied and exchanged when this atom combines with two atoms of hydrogen. Hence, four atomicities are satisfied by the combination.

Following the same reasoning, we consider that a triple capacity of combination is active in an atom of nitrogen when this atom unites with three atoms of hydrogen; and that six atomicities are satisfied by the combination.

Lastly, tetratomic carbon is provided with four atomicities, which are satisfied by the four atomicities which reside in four atoms of hydrogen.

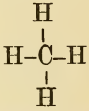
If this neutralization or exchange of two units of saturation be represented by a hyphen, we will have the following formulæ:

$H-Cl$
Hydrochloric acid.

$H-O-H$
Water.

$$\begin{array}{c} H \\ | \\ N \\ \wedge \\ H\quad H \end{array}$$

Ammonia.



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

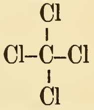
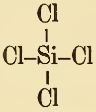
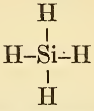
Hydrogen monocarbide.

It is seen that in the formulæ for water, ammonia and hydrogen monocarbide, the polyatomic elements, oxygen, nitrogen and carbon, constitute, as it were, the nuclei around which the other atoms are symmetrically grouped.

A great many other bodies present the same constitutions as the preceding; it is evident that a given element in any compound may be replaced by another element having the same atomicity, without disturbing the equilibrium of the atomicities, Indeed, if we suppose the chlorine, oxygen, nitrogen, and carbon to be replaced by elements of corresponding atomicities, we will have the series of hydrogen compounds already considered. All of the bodies which are classed together in the series belong to the *same type*. Each contains an equal number of atomicities for the same number of atoms.

According to the principle of substitution announced above, it is evident that the hydrogen in each of the hydrogen compounds under consideration may be replaced by another monatomic element, and the compounds thus formed will still belong to the primitive types.

So considered, a great number of compounds possess the same constitution,—that is, the same molecular structure,—as hydrochloric acid, water, ammonia, and methane or hydrogen monocarbide. Such are those arranged in vertical columns in the following table:

TYPE HCl	TYPE $H^{2}O$	TYPE NH^{3}	TYPE CH^{4}
Cl–Cl Free chlorine.	H–O–H Water.	 $\begin{array}{c}\mathrm{K}\\ \vert\\ \mathrm{N}\\ \diagup\ \diagdown\\ \mathrm{H\ \ H}\end{array}$ Potassium amide.	 $\begin{array}{c}\mathrm{Cl}\\ \vert\\ \mathrm{Cl{-}C{-}Cl}\\ \vert\\ \mathrm{Cl}\end{array}$ Carbon tetrachloride.
K–Cl Potassium chloride.	Cl–O–Cl Hypochlorous oxide.	 $\begin{array}{c}\mathrm{Cl}\\ \vert\\ \mathrm{P}\\ \diagup\ \diagdown\\ \mathrm{Cl\ \ Cl}\end{array}$ Phosphorus trichloride.	 $\begin{array}{c}\mathrm{Cl}\\ \vert\\ \mathrm{Cl{-}Si{-}Cl}\\ \vert\\ \mathrm{Cl}\end{array}$ Silicon tetrachloride.
K–I Potassium iodide.	H–O–K Potassium hydroxide.	 $\begin{array}{c}\mathrm{Cl}\\ \vert\\ \mathrm{Sb}\\ \diagup\ \diagdown\\ \mathrm{Cl\ \ Cl}\end{array}$ Antimony trichloride.	 $\begin{array}{c}\mathrm{H}\\ \vert\\ \mathrm{H{-}Si{-}H}\\ \vert\\ \mathrm{H}\end{array}$ Hydrogen silicide.
Ag–I Silver iodide.	Ag–O–Ag Silver oxide.		

All of these bodies belong to the respective types HCl, $H^{2}O$, NH^{3}, CH^{4}, the first three of which were established by Gerhardt, and have their existence explained by the atomicity of the elements; that is, by the varying equivalence of their atoms, measured, in the present examples, by the number of hydrogen atoms with which they combine.

One atom of oxygen is equivalent to two atoms of hydrogen or two atoms of chlorine. Hence, in the preceding combinations, two atoms of chlorine may be replaced by one atom of oxygen without changing the equilibrium of the atomicities. Thus, the oxides SiO^2,CO^2, correspond to the chlorides $SiCl^4$, CCl^4, and belong to the same type. The four atomicities of an atom of silicon or carbon are saturated by the four atomicities of two atoms of oxygen.

The trichlorides of phosphorus and antimony, PCl^3 and $SbCl^3$, which will be found in the preceding table, require an important remark. They are not saturated with chlorine, and each may combine with two more atoms of that element, producing the compounds PCl^5 and $SbCl^5$.

Thus, while phosphorus exhausts its power of combination with hydrogen in uniting with three atoms of that element in PH^3, its capacity of combination with chlorine is only exhausted when it has combined with five atoms; while it plays the part of a triatomic element in hydrogen phosphide, it is pentatomic in phosphorus pentachloride.

From these facts it follows that it is often difficult to measure in an absolute manner the capacity of combination which resides in an atom; for that capacity varies according to the nature of the elements upon which it is exerted. Affinity is an elective force. A given element does not attract all of the other elements with equal facility; it selects certain ones by preference, and neglects the others. With one, it may form but a single compound; with another, it may form several.

The most important compound of nitrogen and hydrogen is ammonia, NH^3, which cannot fix any more atoms of hydrogen. Saturated with hydrogen in ammonia, nitrogen manifests in contact with that element but three atomicities. But let ammonia be brought in contact with a body other than hydrogen, hydrochloric acid, for example, and it will combine with it, forming ammonia hydrochloride, or ammonium chloride. If its capacity of combination is exhausted for hydrogen, HH, it is not exhausted for hydrogen combined with chlorine, HCl. Thus, an atom of nitrogen possesses other affinities than those which it manifests for hydrogen in ammonia. While nitrogen is triatomic in ammonia because it is united with three monatomic atoms, it behaves as a pentatomic element in ammonium chloride.

The parts which polyatomic elements play in their compounds may be expressed by accents marking the number of atomicities or the *quantivalence* of the element, as shown in the following formulæ:

$O''H^2$	$N'''H^3$	$N^{v}H^{4}Cl$	$P'''Cl^3$	$P^{v}Cl^5$	$C^{iv}O''^2$
Water.	Ammonia.	Ammonium chloride.	Phosphorus trichloride.	Phosphorus pentachloride.	Carbon dioxide.

In these compounds, as has been remarked before, the polyatomic elements form, as it were, the nuclei around which the other elements are grouped. This is an important idea, since it leads to the determination of the *constitution* of the molecules, that is, the arrangement of their atoms. The considerations just presented concerning the functions of the elements in compounds alone permit the resolution of this question; they alone lead to the discovery of the relations existing between the atoms in their combinations, and to the determination of their relative positions, in a word, to the revelation of the *molecular structure.*

The following developments will demonstrate this fact.

We will reconsider certain of the combinations above mentioned, which have been taken as types.

In water, an atom of diatomic oxygen fixes two atoms of hydrogen. One atom of oxygen can fix two atoms of any monatomic element, forming compounds belonging to the same type as water; but it cannot at the same time fix a monatomic element and a diatomic element. In other words, an atom of hydrogen in water may be replaced by an atom of chlorine, bromine, iodine, or potassium, but not by an atom of oxygen; and if a second atom of the latter element be joined to the oxygen of water, it will be seen that there remains a free affinity which may be satisfied by hydrogen. Hydrogen dioxide would result.

$H{-}O''{-}H$	$H{-}O''{-}O''{-}H$
Water.	Hydrogen dioxide.

Hence, we draw the conclusion that in hydrogen peroxide, the two atoms of oxygen are combined with each other, and that in uniting together each atom loses one atomicity, the two others being satisfied by hydrogen.

The same considerations are applicable to the compounds of chlorine and oxygen.

Hypochlorous acid may be regarded as composed of an atom of chlorine united to the group hydroxyl.

$$Cl{-}O''{-}H = Cl(OH)'$$

Hypochlorous acid.

In this compound the chlorine exchanges one unit of saturation with the oxygen of the group OH, just as it exchanges one with hydrogen in hydrochloric acid: it is monatomic or univalent. In chloric acid it is combined with two atoms of oxygen and one group, OH. It exchanges 4 atomicities with oxygen, and one with the group OH:

$$Cl^{v}O''^{2}(OH)'$$

Chloric acid.

Chlorine thus manifests 5 atomicities in chloric acid; but it has 7 in perchloric acid.

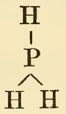
$$Cl^{vii}O^{3}(OH)'$$

Perchloric acid.

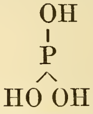
Without dwelling on these considerations, we will take one more example.

In hydrogen phosphide, one atom of phosphorus is combined with three atoms of hydrogen; it manifests but three atomicities, and these could not neutralize those which reside in three atoms of oxygen, since the latter possess six atomicities. If, then, three atoms of diatomic oxygen were united with one atom of triatomic phosphorus, it is clear that three affinities would remain free, one in each of the three atoms of oxygen. In phosphorous acid, these three affinities of the oxygen atoms are satisfied by three atoms of hydrogen. We may suppose that in the molecule of this compound, the phosphorus is the nucleus around which are grouped three atoms of oxygen, each of which is joined also to one atom of hydrogen.

This atomic grouping is indicated in the following formulæ:



Hydrogen phosphide.



Phosphorous acid.

This hydrogen, combined with the oxygen in all of the oxygen acids, plays invariably the same part: it saturates the one atomicity which remains free in one atom of oxygen. The oxygen thus combined with an atom of hydrogen, has lost one of its atomicities by the fact of this combination; it still retains one in the group OH, which represents, as it were, water less one atom of hydrogen.

$$HOH - H = (OH)'$$

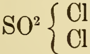
This group is named hydroxyl, and it is evident that, although it cannot exist by itself, it may play the part of a monatomic element, for it retains one free atomicity. It may then replace a monatomic element, such as hydrogen or chlorine. Indeed, it plays an important part in the constitution of acids.

If we consider the examples which have already been discussed, we will notice that it is this hydroxyl which, by combining with an element or group of elements capable of forming acids, confers upon them the characters of acids. So considered, hypochlorous acid is formed by the union of hydroxyl with an atom of chlorine.

$$Cl(OH)'$$

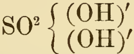
Hypochlorous acid.

Sulphuric acid is formed by the union of two hydroxyl groups with sulphurous oxide, and represents in a manner sulphuryl chloride in which the two atoms of chlorine are replaced by two hydroxyl groups.



$$SO^2\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right.$$

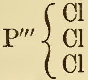
Sulphuryl chloride.



$$SO^2\left\{\begin{matrix} (OH)' \\ (OH)' \end{matrix}\right.$$

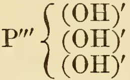
Sulphuric acid.

Phosphorous acid is formed by the union of three hydroxyl groups with one atom of phosphorus.



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

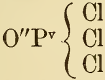
Phosphorus trichloride.



$$P'''\left\{\begin{matrix} (OH)' \\ (OH)' \\ (OH)' \end{matrix}\right.$$

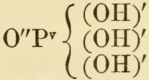
Phosphorous acid.

Lastly, phosphoric acid results from the union of three hydroxyl groups with one atom of phosphorus already combined with one atom of oxygen (phosphoryl).



$$O''P^{v}\left\{\begin{matrix} Cl \\ Cl \\ Cl \end{matrix}\right.$$

Phosphoryl trichloride.



$$O''P^{v}\left\{\begin{matrix} (OH)' \\ (OH)' \\ (OH)' \end{matrix}\right.$$

Phosphoric acid.

Such, according to the theory of atomicity, are the relations existing between the atoms of certain acids; such, in other words, is the constitution of these acids. It would be easy to extend these considerations to other bodies, but the examples we have chosen are sufficient to indicate the importance of the idea of atomicity, when it is applied to the discovery and definition of the part played by each element in a given compound. By supposing the capacities of combination of chlorine, oxygen, sulphur, and phosphorus to be known, we have been able to follow these bodies in their most important combinations, we have seen how they attract and group around themselves other elements. We have thus been able to penetrate the atomic structure of the molecules, and have built up as it were the molecular edifice. It must be remembered, however, that the preceding formulæ do not in any manner represent the real positions of the atoms in space. Their sole object is to indicate the points of attachment of the affinities, and consequently the mutual relations between the atoms.

CHEMICAL ENERGY—THERMO-CHEMISTRY.

The study of the elements and compounds already described has shown that combination is usually accompanied by a more or less intense development of energy, while in some cases energy is developed by decomposition. We have seen that many compounds are dissociated or separated into their elements by temperatures more or less elevated, and it is not difficult to understand that the amount of energy developed or absorbed in the formation of a compound, is the exact measure of the energy required or developed in its decomposition.

The determination of the precise amount of energy developed or absorbed in any chemical reaction is the object of thermo-chemistry. In order to simplify and harmonize results for comparison, the kilogramme degree is selected as the unit of energy, representing the quantity of heat necessary to raise the temperature of one kilogramme of water through one degree centigrade. This unit is termed a *calorie*, and the heat of formation or decomposition of a compound is expressed by the number of calories produced by the formation or decomposition of one molecule of the substance, the atom of hydrogen being supposed to weigh one gramme. Thus the heat of formation of carbon dioxide will be the number of calories produced by the perfect combustion of twelve grammes of carbon. When practicable, the heat of formation is determined by the energy of combustion. As a general formula, we may consider that the combining atoms possess a quantity of energy in some form, chemical or physical, which quantity we may call m. The product of the reaction will possess $m \pm n$ energy, $\pm n$ being the quantity of energy disengaged by the reaction.

It has been found that the amount of energy developed by the formation of any compound from its elements is precisely the same whether the body is formed at once or by several stages (Hess). Thus, the heat of formation of CO^2 is the same whether it be formed by

$$C + O^2 = CO^2, \text{ or by } C + O = CO \text{ and } CO + O = CO^2$$

In the oxidation of a combustible compound which has been formed with disengagement of energy, less heat should be produced than by the direct oxidation of the constituent elements, since part of their atomic energy has already been disengaged by their combination. Thus, the energy of formation of CH^4 should be represented by the difference between the heat produced by the combustion of CH^4, and that produced by the combustion of C plus that of H^4 ($H = 1$ gramme). The energy of formation of CO will be the difference between the energy of combustion of C and that of CO.

Direct and indirect methods of reasoning of this kind have enabled the calculation of the energy of formation of a large number of compounds.

The physical state of the reacting bodies and of the product is necessarily an important factor in thermo-chemical considerations. If the product be gaseous while the reacting bodies be liquid or solid, a certain amount of energy will be required to maintain the matter in the gaseous form, and this quantity must be calculated and added to that actually resulting from the reaction. If, on the contrary, the bodies entering into combination be liquid or gaseous while the result is solid, the direct energy of combination will be lower than the heat developed by the reaction.

While the laws governing chemical energy are as yet undeveloped, it is not difficult to understand the cause of the phenomena in which heat is disengaged or absorbed. We must believe that the atoms of any element are endowed with motion, and chemical energy then becomes atomic motion. If the atomic motion be arrested, the energy appears as heat, molecular motion, or in some other form. When two elements manifest energetic affinities for each other, it is because their atoms are moving in such a manner that a portion of the atomic motion may be mutually arrested; this atomic energy is then transformed into heat energy or molecular motion.

While all chemical action must be referred to atomic motion, the manner of that motion cannot at present be fully understood. Atomic energy, that is, affinity, must be a function of temperature, since the atomic vibrations of the elements may be so varied by an absorption of energy from external sources that, on one hand, the motions of atoms manifesting little affinity for each other may be so harmonized that combination must take place, and, on the other, the harmonious movements of unlike atoms may be rendered so incompatible that those atoms will separate, finding conditions of more stable equilibrium in molecules of the elementary substances.

In this manner we can readily interpret those cases in which decomposition is attended by a development of energy, as with hydrogen dioxide, nitrogen iodide, and many other compounds. In the formation of nitrogen iodide by the action of ammonia on iodine (page 155), ammonium iodide also is formed.

$$4NH^3 + 3I^2 = NI^3 + 3NH^4I$$

Ammonium iodide is formed with disengagement of energy, but in the above reaction that energy does not become apparent; the liquid does not become warm; the energy which disappears from the atoms in the ammonium iodide is transferred to the atoms of nitrogen and iodine, and enables them to combine, forming nitrogen iodide. These atoms then possess greater energy than when in molecules of nitrogen and iodine, and on the least disturbance of the unstable equilibrium the nitrogen iodide is decomposed; the atoms of nitrogen combine, forming molecules of nitrogen, and the atoms of iodine form molecules of iodine. The energy furnished by the formation of ammonium iodide then becomes external explosively.

A compound which is formed from its elements with liberation of energy is called an *exothermic* compound, while one which is similarly formed with absorption or disappearance of energy is called an *endothermic* compound. All explosive compounds are endothermic.

As a general rule, in any chemical equation the sum of the energies developed in the formation of the compounds produced must be greater than the sum of the energies developed in the formation of the substances reacting. Unless energy be supplied the reaction is otherwise impossible (Berthelot).

METALS.

The metals are elements which are good conductors of heat and electricity, and are endowed with a peculiar lustre, which is called the metallic lustre. This definition, it will be observed, is founded upon certain physical characters rather than upon chemical properties. It is unsatisfactory and wanting in exactness, for it is applicable to bodies which are properly considered as metalloids. Such is antimony, which has already been described, and bismuth, which should be placed beside antimony. Indeed, the distinction between the metals and non-metals is not so well marked that a line which shall separate these two classes of simple bodies may be sharply drawn.

Physical Properties of the Metals.—These will be found in the table on page 244, but the indications there given may be completed by certain other developments.

The metals are opaque, but their opacity is not absolute. A sheet of gold-leaf pressed out between two plates of glass allows the passage of a green light.

Gold possesses a brilliant lustre and a yellow color, but it loses this lustre when it is reduced to very fine powder. When, however, this powder is rubbed with a hard body, when, for example, it is triturated in an agate mortar, or passed under the burnisher, it acquires a certain degree of cohesion, and again assumes its lustre.

It is thus with all the metals. They lose their metallic lustre when finely divided and reassume it on burnishing.

The yellow color of gold is not its true color; the rays which reach the eye are the result of but one reflection, but if light be successively reflected from ten surfaces of gold, the metal will appear of a bright-red color. Under the same circumstances, copper will appear scarlet, zinc indigo, iron violet, and silver pure yellow (B. Prevost).

Most of the metals may be crystallized. Bismuth is the most striking example. If a few kilogrammes of pure bismuth be fused, and the liquid mass be allowed to cool slowly, the

Density.		Fusing Points. (Centigrade.)		Conductivity for Heat.		Specific Heats.		Order of Malleability.	Order of Ductility.	Tenacity expressed in the Number of Kilogrammes necessary to break a Wire 2 Millimetres in Diameter.		Hardness. [The hardness of the metals is greatly modified by very small quantities of impurities. Thus pure chromium is as soft as iron. The following table applies to the metals as usually found in commerce.]	
Platinum rolled	21.70	Mercury	−39°	Silver	1000	Potassium	0.1691	Gold.	Gold.	Iron	249.659	Manganese Chromium	scratch glass.
Platinum cast	21.15	Potassium	+ 62°5	Copper	736	Iron	0.1138	Silver.	Silver.	Copper	137.399		
Osmium	21.40	Sodium	95°6	Gold	532	Nickel	0.1086	Aluminium.	Platinum.	Platinum	124.690		
Gold (cast)	19.35	Tin	229°	Zinc	193	Cobalt	0.1070	Copper.	Aluminium.	Silver	85.062	Nickel Cobalt Iron Antimony Zinc	scratched by glass.
Mercury sol. at −42°	14.40	Bismuth	264°	Tin	145	Zinc	0.0955	Tin.	Iron.	Gold	68.216		
Mercury liq. at 0°	13.59	Lead	335°	Iron	119	Copper	0.0951	Platinum.	Nickel.	Zinc	49.790		
Palladium	11.80	Cadmium	360°	Lead	85	Palladium	0.0593	Lead.	Copper.	Nickel	47.676		
Lead (cast)	11.33	Zinc	410°	Platinum	84	Cadmium	0.0562	Zinc.	Zinc.	Tin	15.740		
Silver (cast)	10.57	Antimony	450°	Bismuth	18	Tin	0.0562	Iron.	Tin.	Lead	9.555		
Bismuth (cast)	9.82	Aluminium, about	750°	Conductivity for Electricity.		Silver	0.0570	Nickel.	Lead.			Palladium Platinum Copper Gold Silver Bismuth Cadmium Tin	scratched by carbonate of lime.
Nickel	8.82	Silver (high red)	1000°	Silver	100	Antimony	0.0508						
Copper (cast)	8.79	Copper	1100°	Copper	96	Mercury	0.0333						
Cadmium	8.60	Gold, about	1250°	Gold	74	Gold	0.0324						
Cobalt (cast)	7.79	Iron cast	1250°	Zinc	30	Platinum	0.0324						
Iron malleable	7.79	Iron soft (white heat)	1500°	Tin	18	Lead	0.0314						
Iron cast	7.25	Nickel and cobalt, about	1600°	Iron	16								
Tin (cast)	7.29	Platinum, about	2000°	Lead	8								
Manganese	7.20	Iridium, about	2500°	Platinum	8								
Chromium	7.01			Mercury	1.6							Lead, scratched by the nail.	
Zinc (cast)	6.86												
Antimony	6.71											Potassium Sodium	soft at ordinary temperatures.
Aluminium	2.56												
Sodium	0.97											Mercury, liquid at ordinary temperatures.	
Potassium	0.865												
Lithium	0.59												

metal will solidify first next to the walls of the vessel and on the surface, where it is most cooled. If, in a little while, the crust which covers the still liquid metal be pierced, and the latter be poured out, the whole of the interior of the vessel will be found covered with magnificent crystals, arranged in hopper-like pyramids, and presenting brilliant, rainbow-like colors.

Other metals, such as copper, lead, antimony, tin, silver, and gold, may be crystallized under certain conditions. Some of the metals are found crystallized in nature.

Those metals which may be beaten or rolled into thin laminæ are said to be *malleable*. AA (Fig. 90) represent two steel rollers capable of moving on their axes in opposite directions. A plate of metal engaged between them will be drawn in, and the rolled sheet will pass out on the other side with a uniform thickness equal to the distance between the two rollers. By diminishing this distance more and more by means of the screws BB, the sheet may gradually be reduced in thickness.

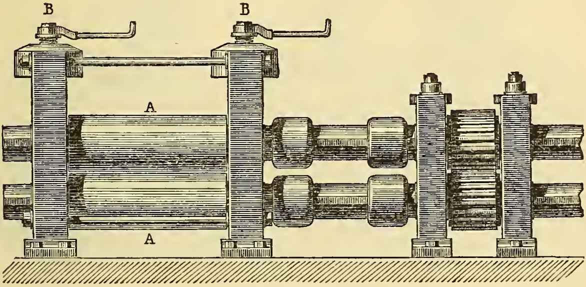


FIG. 90.

Metals which may be drawn out into wires are said to be *ductile*. The wire-drawing machine is represented in Fig. 91. It consists of a steel plate, *ff*, firmly fixed in the uprights CC, which are themselves solidly attached to a bench. The plate is pierced with a series of holes regularly decreasing in diameter. The wire is drawn from the bobbin A, through the holes and around the cylinder B, which is moved by power.

That a metal may be drawn into fine wires, it is necessary that it shall offer a certain resistance to rupture. This is called the *tenacity* of the metal. It is measured by suspending weights at the extremities of wires of the same diameter. The metals exhibit every degree of fusibility. Mercury is liquid at ordinary temperatures, while osmium cannot be melted in the oxyhydrogen flame. Some metals, such as mercury, potassium, zinc, are readily distilled; others are scarcely volatilized at the highest attainable temperatures.

Chemical Properties of the Metals.—The metals combine with each other and with the metalloids, the energy with which these combinations take place being very variable. In general, the metals having the strongest affinities are those known as the alkaline metals, because they are obtained from the alkalies. Such are potassium and sodium.

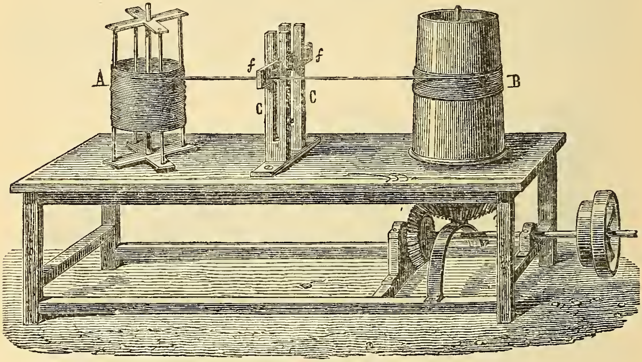


Fig. 91.

All the metals combine directly with chlorine. The chlorides thus formed do not all possess analogous compositions; they contain for one atom of metal a varying number of chlorine atoms.

A similar remark applies to the oxides and sulphides formed by the union of oxygen and sulphur with the metals. The power of combination of the latter with chlorine, sulphur, oxygen, etc., is far from being the same. In other words, the atoms of the metals combine unequally with the atoms of chlorine, oxygen, etc.; hence it follows that the atomic composition of the bodies thus formed is different. If the metals be compared together in this respect, analogies and differences will be established between them, which become the basis for a rational classification. Those metals which form compounds having analogous atomic constitutions are put into the same group. Such principles as these have guided us in the classification of the non-metals, and we will apply them to the metals as soon as we have acquired a general knowledge of their compounds.

Natural State and Extraction of the Metals.—Certain metals are found in nature free from all combination. It is thus that gold, silver, copper, bismuth, etc., are met with in the native state.

More often the metals are found combined with oxygen, sulphur, or other non-metals. The natural sulphides are numerous and abundant: those of silver, copper, mercury, lead, and zinc constitute the minerals from which these metals are ordinarily extracted.

Iron and tin are obtained from their oxides, which are found in nature.

The metals are often found in saline combinations, in the form of chlorides, carbonates, sulphates, phosphates, and silicates.

We can only indicate here in a very general manner the methods by the aid of which the metals are extracted from their combinations.

If a metal is to be obtained from its oxide, the latter is generally reduced by carbon at a high temperature. A number of oxides resist the reducing action of carbon at the highest temperatures attainable by the combustion of that element in the ordinary furnaces; with few exceptions, however, they will give up their oxygen to carbon when subjected to the intense heat of the arc in the electric furnace (see page 210). Some of the rarer metals have been obtained in this manner.

Certain oxides reducible by carbon do not yield pure metal by such reduction, as the metal combines with part of the carbon, forming a carbide from which removal of the carbon is difficult or even impossible. In such cases reduction of the oxide may be accomplished by a more oxidizable metal: thus manganese and chromium oxides may be reduced by aluminium or magnesium.

If the ore be a sulphide, it is first roasted, that is, heated in contact with the air. The oxygen of the air then acts upon the sulphur, which is disengaged in the form of sulphur dioxide, and upon the metal, which remains in the form of oxide; the latter is afterwards reduced by carbon.

The metals are sometimes obtained from their chlorides by heating the latter with sodium, magnesium, aluminium, or other metal which will combine with the chlorine, forming the corresponding chloride.

Electrolysis of salts, either in aqueous solution or in a state of fusion, is now advantageously employed for the extraction of metals like copper, nickel, aluminium, and magnesium.

ALLOYS.

The combinations of the metals with each other are called *alloys; amalgams* are the alloys formed by mercury.

If a small quantity of mercury be heated in a crucible or a capsule, and a morsel of sodium be thrown into it, the latter dissolves instantly; and by employing the proper proportions of mercury and sodium, the alloy may be obtained in crystals possessing a definite composition.

Crystalline combinations of zinc and antimony are known. The most interesting has the composition Sb^2Zn^3.

It is necessary to state that more generally the alloys do not present the characters of definite compounds. Many metals seem to alloy with each other in all proportions, forming mixtures which are more or less homogeneous; but this is only in appearance, and it must be admitted that one or more compounds exist in such a mixture, remaining dissolved in each other, or mixed with the excess of one of the metals. Such a mixture would form a sensibly homogeneous mass, especially when the molten mixture had been suddenly cooled. But if the cooling be slow, it may happen that the less fusible definite compounds separate from the mixture in the crystalline form, leaving the more fusible compounds which still remain liquid. Such a separation often takes place in large masses of melted alloys which are allowed to cool slowly. The process is called *liquation*, and it may be readily conceived that the alloys so cooled are far from homogeneous in composition after their solidification.

Conversely, when a mass composed of a mixture of metals and alloys is slowly heated, the more fusible assume the liquid state first, and separate from the others.

This difference between the fusing-points of the various definite compounds which may exist in an alloy is taken advantage of in the arts for their separation.

Alloys are generally more fusible than their component metals. Thus, there is an alloy which melts at about 66°, and contains bismuth, 4 parts; lead, 2 parts; tin and cadmium, each 1 part. It is known as Wood's fusible metal.

The following table gives the composition of some of the more important alloys:

Gold coin (United States, France, Germany)	Gold	900
	Copper	100
Gold coin (Great Britain)	Gold	916.6
	Copper	83.4
Gold jewelry[1]	Gold	750–920
	Copper	250–80
Silver coin (United States)	Silver	900
	Copper	100
Silver coin (Great Britain)	Silver	925
	Copper	75
Silverware (sterling silver)	Silver	925
	Copper	75
Bronze medals	Copper	93.5–95
	Tin	6–4
	Zinc	0.5–1
Gun-metal	Copper	100
	Tin	10
Bell-metal	Copper	78
	Tin	22
Speculum-metal	Copper	67
	Tin	33
Aluminium bronze	Copper	90–95
	Aluminium	10–5
Manganese bronze	Copper	90
	Manganese	10
Red brass	Copper	90
	Zinc	10
White brass	Copper	65
	Zinc	35
German silver	Copper	50
	Zinc	25
	Nickel	25
Type-metal	Lead	80
	Antimony	20
Britannia-metal	Tin	100
	Antimony	8
	Bismuth	1
	Copper	4
Hard pewter	Tin	92
	Lead	8
Soft pewter	Tin	82
	Lead	18
Plumbers' solder	Tin	66
	Lead	33

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[1] The proportion of gold in jewelry is expressed in carats, which signifies twenty-fourths. Thus, pure gold is twenty-four carats fine, while eighteen-carat gold contains eighteen twenty-fourths gold and six twenty-fourths of baser alloy.

METALLIC OXIDES AND HYDROXIDES.

Formation of Metallic Oxides.—The metals absorb oxygen with very unequal energy. Many of them become oxidized when exposed to the air at temperatures more or less elevated. In this respect it is important to distinguish the action of dry air from that of moist air.

Potassium is the only metal that absorbs dry oxygen at ordinary temperatures. All of the other metals, with the exception of silver, gold, and platinum, only become oxidized in the air at very high temperatures. Melted lead absorbs oxygen. Mercury becomes oxidized at about 350°; copper at a dull-red heat.

The combination often takes place with the production of luminous heat. Iron burns in oxygen, but it is necessary that the metal be first heated to bright redness that the combustion may take place.

However, the finely-divided iron that is obtained by reducing oxide of iron in a current of hydrogen at a comparatively low temperature, will take fire when exposed to the air at ordinary temperatures. It is pyrophoric, and the fine state of division of the metal favors the oxidation. If the powder be projected into the air, each particle takes fire and burns with a bright flash.

A bright sheet of iron will indefinitely preserve its brilliant surface in dry air, but if a drop of water be placed upon it, or if it be exposed to the action of a moist atmosphere, rust makes its appearance in a short time. This rust is ferric hydrate, for the metal has at the same time absorbed oxygen and water.

It is generally admitted that it is the oxygen of the air dissolved in the water that first fixes upon the metal, and that the combination is favored by the presence of carbon dioxide. However it may be, the spot of rust once formed constitutes a Voltaic couple with the iron itself, and the current so established decomposes the water. The oxidation then proceeds rapidly, the oxygen of the decomposed water combining with the metal.

It is possible that hydrogen dioxide may play a part in oxidations; it may be formed as a secondary product during the decomposition of the water, and fix directly upon the metals, converting them into hydroxides (Weltzien).

$$\underset{\text{Iron.}}{2Fe} + \underset{\text{Hydrogen dioxide.}}{3H^2O^2} = \underset{\text{Ferric hydroxide.}}{2FeO^3H^3}$$

$$\underset{\text{Magnesium.}}{Mg} + H^2O^2 = \underset{\text{Magnesium hydroxide.}}{MgO^2H^2}$$

Indeed, the oxidation of metals in moist air always produces hydroxides, and not oxides.

Composition and Classification of the Oxides.—It has already been remarked that the metals differ as to the number of oxygen atoms with which they combine; besides this, the same metal may form several compounds with oxygen, constituting different degrees of oxidation. Hence the oxides present different compositions, and the differences exercise a marked influence upon the properties of the compounds.

1. Certain oxides present the same atomic constitution as water. Two atoms of metal are combined with one atom of oxygen.

Ag^2O silver oxide.
Cu^2O cuprous oxide.
Hg^2O mercurous oxide.
Au^2O aurous oxide.
Tl^2O thallous oxide.

2. One atom of certain metals can combine with one atom of oxygen; the oxides of the general formula MO result.

BaO barium oxide.
SrO strontium oxide.
CaO calcium oxide.
MgO magnesium oxide.
MnO manganous oxide.
FeO ferrous oxide.
ZnO zinc oxide.
PbO lead oxide.
CuO cupric oxide.
HgO mercuric oxide.
SnO stannous oxide.

The metallic oxides containing but one atom of oxygen are generally energetic bases; that is, they react energetically with the acids, forming salts.

3. The *sesquioxides* are those which contain two atoms of metal and three atoms of oxygen. Such is antimony oxide, that has already been studied; the oxides of bismuth, gold, etc., present an analogous composition.

Sb^2O^3 antimony sesquioxide.
Bi^2O^3 bismuth sesquioxide.
Au^2O^3 gold sesquioxide.

Fe^2O^3 ferric oxide.
Mn^2O^3 manganic oxide.
Cr^2O^3 chromic oxide.
Al^2O^3 aluminium oxide.

4. A large number of oxides contain two atoms of oxygen.

BaO^2 barium dioxide.
SrO^2 strontium dioxide.
MnO^2 manganese dioxide.
PbO^2 lead dioxide.

SnO^2 stannic oxide.

The first four are incapable of uniting with acids to form corresponding salts. With hydrochloric acid, they yield either hydrogen peroxide or chlorine.

$$BaO^2 + 2HCl = BaCl^2 + H^2O^2$$
$$MnO^2 + 4HCl = MnCl^2 + 2H^2O + Cl^2$$

When manganese dioxide is heated with sulphuric acid oxygen is disengaged, and manganous sulphate is formed.

$$\underset{\text{Sulphuric acid.}}{H^2SO^4} + \underset{\text{Manganese dioxide.}}{MnO^2} = \underset{\text{Manganous sulphate.}}{MnSO^4} + H^2O + O$$

As to stannic oxide, it is the anhydride of a metallic acid.

$$SnO^2 + H^2O = \underset{\text{Stannic acid.}}{H^2SnO^3}$$

5. The oxides which contain three atoms of oxygen possess acid characters still more marked than stannic oxide. Chromium trioxide, CrO^3, is well known, and manganic and ferric anhydrides would present analogous compositions.

6. There is a class of oxides still more complex than the preceding; they can be regarded as formed by the union of two oxides, and they have been named *saline oxides.* Such are

Ferroso-ferric oxide $Fe^3O^4 = FeO + Fe^2O^3$, or magnetic oxide of iron.
Manganoso-manganic oxide $Mn^3O^4 = Mn^2O^3 + MnO$, or red oxide of manganese.
Diplumboso-plumbic oxide $Pb^3O^4 = PbO^2 + 2PbO$, or red oxide of lead.

The first two contain one molecule of a sesquioxide, combined with one molecule of a monoxide; the last, one molecule of a dioxide and two molecules of a monoxide.

Chemical Properties of the Oxides.—Some of the oxides are fixed, that is, undecomposable by heat; others lose the whole or a part of their oxygen at temperatures more or less elevated. The oxides of the noble metals, such as silver, gold, and platinum, are decomposed by heat alone into metal and oxygen. We have seen that mercuric oxide is decomposed by a dull-red heat. Many of the oxides that contain two or three atoms of oxygen lose a part of the latter element when heated to redness. Such are the dioxides of manganese, lead, and barium.

The oxides containing but one atom of oxygen are among the most stable. Some of them absorb oxygen when they are heated in contact with air, forming higher oxides. Among these are the monoxides of manganese, iron, lead, and tin.

Hydrogen reduces the greater number of the oxides at temperatures more or less elevated; water is formed, and the metal is set at liberty.

If a current of dry hydrogen be passed over ferric oxide heated in a glass bulb (Fig. 92), the oxide is reduced, and a black powder is obtained which is finely divided and pyrophoric iron. Vapor of water escapes at the same time by the drawn-out point of the bulb.

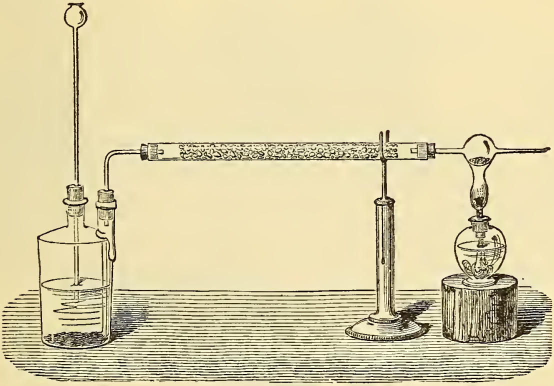

FIG. 92.

$$\underset{\text{Ferric oxide.}}{Fe^2O^3} + 3H^2 = 3H^2O + \underset{\text{Iron.}}{2Fe}$$

The ferric oxide may be replaced by cupric oxide, CuO. If this oxide be heated in a current of hydrogen, it is reduced, and the action is so energetic that it gives rise to the production of light and heat.

Carbon reduces the greater number of the oxides with formation of either carbon dioxide or monoxide. It is even more energetic in its action than hydrogen, for it decomposes oxides which are irreducible by the latter element, such as those of potassium and sodium. The various oxides require for their reduction more or less heat, according to the degree of energy with which they retain their oxygen. If the reduction be difficult, a high temperature is required, and carbon monoxide is formed; otherwise carbon dioxide is the product. The oxides of calcium, barium, strontium, and aluminium are not reducible by carbon, except at the high temperature of the electric arc.

A small quantity of cupric oxide may be reduced by charcoal by heating the mixture in a glass tube by the aid of a spirit-lamp (Fig. 93). Carbon dioxide is disengaged.

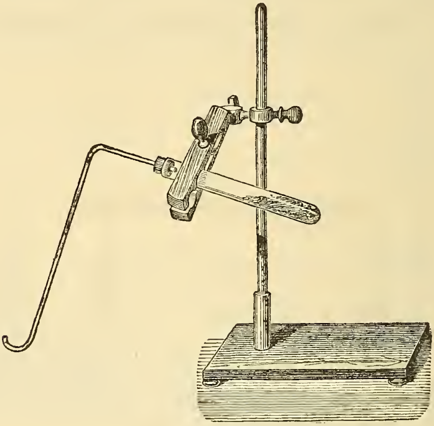

Fig. 93.

$$\underset{\text{Cupric oxide.}}{2CuO} + C = \underset{\text{Copper.}}{2Cu} + CO^2$$

But to reduce zinc oxide by charcoal, the mixture must be heated to bright redness in a clay or iron retort, and in this case carbon monoxide is evolved.

$$\underset{\text{Zinc oxide.}}{ZnO} + C = \underset{\text{Zinc.}}{Zn} + CO$$

Chlorine decomposes nearly all of the oxides at a high temperature. It drives out the oxygen and combines with the metal, forming a chloride. Some of the oxides are irreducible by carbon, and resist also the action of chlorine. Such an oxide is aluminium oxide, or alumina. But if these oxides be submitted to the simultaneous action of chlorine and carbon at a high temperature, they are converted into chlorides, and carbon monoxide is disengaged.

An intimate mixture of alumina and charcoal may be introduced into a porcelain tube, BB (Fig. 94), which is heated to bright redness, and a current of dry chlorine then passed through. In this case, carbon monoxide is disengaged, while aluminium chloride is formed and volatilizes and may be condensed in a cooled receiver.

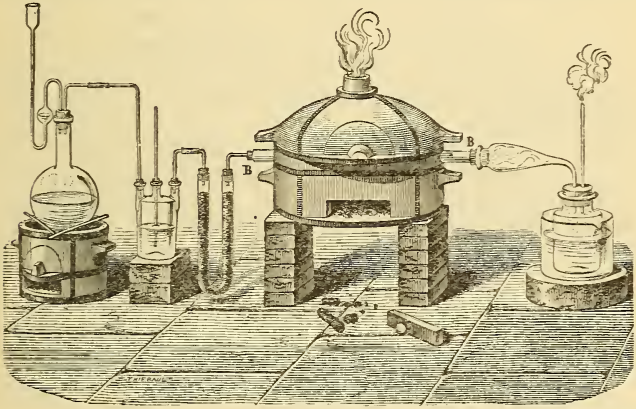

FIG. 94.

Sulphur decomposes all of the oxides except alumina and its analogues. The reaction takes place at a high temperature, and gives rise to the formation of a sulphide and sulphur dioxide, or a sulphide and a sulphate if the latter be not decomposable by heat.

If sulphur be heated with cupric oxide, cupric sulphide is formed and sulphur dioxide is evolved.

$$\underset{\text{Cupric oxide.}}{2CuO} + 3S = \underset{\text{Cupric sulphide.}}{2CuS} + SO^2$$

However, if calcium oxide (lime) or lead oxide, PbO, be heated with sulphur, a sulphate and a sulphide are formed.

$$\underset{\text{Calcium oxide.}}{4CaO} + 2S^2 = \underset{\text{Calcium sulphide.}}{3CaS} + \underset{\text{Calcium sulphate.}}{CaSO^4}$$

Action of Water upon the Oxides—Metallic Hydroxides and Acids.—If some fragments of barium oxide (baryta) be sprinkled with cold water, an energetic reaction immediately takes place. The water unites with the metallic oxide with so much energy that the heat disengaged is sufficient to convert a portion of the water into vapor. The barium oxide is converted into hydroxide.

$$\underset{\text{Barium oxide.}}{BaO} + H^2O = \underset{\text{Barium hydroxide.}}{Ba(OH)^2}$$

In the same manner, the oxides of potassium and sodium energetically absorb the elements of water, being converted into hydroxides.

$$\underset{\text{Potassium oxide.}}{K^2O} + H^2O = \underset{\text{Potassium hydroxide.}}{2KOH}$$

The hydroxides of potassium and sodium are soluble in water, and their solutions are caustic, changing tincture of violet to a green color and restoring the blue color to reddened litmus solution. These hydroxides constitute the *alkalies.*

The hydroxides of barium, strontium, and calcium are likewise soluble in water to a certain extent, and their solutions are also somewhat caustic.

Other hydroxides are insoluble; they may be obtained by double decomposition by precipitating the corresponding salts with an alkali.

If a solution of potassium hydroxide be poured into a solution of cupric sulphate, a light-blue precipitate of cupric hydroxide is formed.

$$\underset{\text{Cupric sulphate.}}{CuSO^4} + \underset{\text{Potassium hydroxide.}}{2KOH} = \underset{\text{Potassium sulphate.}}{K^2SO^4} + \underset{\text{Cupric hydroxide.}}{Cu(OH)^2}$$

But if this precipitate be heated, even in the liquid in which it was formed, it changes to brown, and is converted into oxide by losing its water.

$$Cu(OH)^2 - H^2O = CuO$$

A great number of metallic hydroxides undergo the same decomposition when they are heated.

There are true metallic acids which contain the elements of an oxide plus the elements of water. Such are

$$\underset{\text{Chromic acid.}}{H^2CrO^4} = \underset{\text{Chromium trioxide.}}{CrO^3} + H^2O$$

$$\underset{\text{Manganic acid.}}{H^2MnO^4} = \underset{\text{Manganese trioxide.}}{MnO^3} + H^2O$$

As far as their constitution is concerned, these metallic acids may be compared to sulphuric acid.

$$H^2SO^4 = SO^3 + H^2O$$

They also resemble sulphuric acid in their chemical functions; each contains two atoms of basic hydrogen, that is, two atoms of hydrogen which are replaceable by a metal.

SULPHIDES.

Sulphur has a great tendency to unite with the metals, and the union often takes place with a vivid evolution of heat. Copper-turnings and iron-filings burn in the vapor of sulphur. The phenomena which favor or determine, and those which accompany this combination, have already been indicated, and we have seen that the presence of a small quantity of water favors chemical union in a mixture of sulphur and iron-filings.

In composition the sulphides are analogous to the oxides.

The more important of the transformations which they may undergo are the following:

Oxygen decomposes all of the sulphides at a temperature more or less elevated.

Finely-divided potassium sulphide, obtained by calcining the sulphate with an excess of charcoal, is a black powder, but it becomes incandescent on contact with oxygen, and if thrown into the air it produces a shower of sparks. It is known as Gay-Lussac's pyrophorus. Its fine state of division favors the absorption of oxygen, and the latter converts it into sulphate.

$$\underset{\text{Potassium sulphide.}}{K^2S} + O^4 = \underset{\text{Potassium sulphate.}}{K^2SO^4}$$

Dry oxygen acts in the same manner upon all the sulphides when the corresponding sulphates are stable at high temperatures. In the contrary case, sulphur dioxide is formed, and a residue of oxide or even of metal is obtained, if the oxide be decomposable by heat.

If zinc sulphide be roasted, it is converted into zinc oxide, and sulphur dioxide is evolved; but if sulphide of mercury be heated in a current of air, metallic mercury is obtained.

$$\underset{\text{Mercuric sulphide.}}{HgS} + O^2 = \underset{\text{Mercury.}}{Hg} + SO^2$$

Moist oxygen acts upon the sulphides more readily than the dry gas. It unites with them at ordinary temperatures, forming sulphates.

$$\underset{\text{Sulphide of iron.}}{FeS} + O^4 = \underset{\text{Ferrous sulphate.}}{FeSO^4}$$

Chlorine attacks all of the sulphides, forming metallic chlorides and sulphur chloride, if the dry method be employed, or with deposition of sulphur if the reaction take place in presence of water.

Water dissolves the alkaline sulphides as well as those of calcium, barium, and strontium; the sulphides of the other metals are insoluble in water.

Hydrogen sulphide combines with certain sulphides, converting them into *hydrosulphides.* The analogy will be noticed between this reaction and that of water upon the oxides.

$$\underset{\text{Potassium sulphide.}}{K^2S} + H^2S = \underset{\text{Potassium hydrosulphide.}}{2KSH}$$

$$\underset{\text{Potassium oxide.}}{K^2O} + H^2O = \underset{\text{Potassium hydroxide.}}{2KOH}$$

CHLORIDES.

Chlorine, bromine, and iodine form with the metals compounds which possess the appearance and certain properties of salts. Indeed, common salt, or sodium chloride, has given the name to the entire class of saline compounds. Hence Berzelius named chlorine, bromine, and iodine the *halogen* bodies, and called their combinations with the metals the *haloid* salts. Thus he admitted the relation between these compounds and the true salts, while at the same time distinguishing them by a particular name, for while they resemble the salts in their properties, they differ from them in composition. This subject will be more fully considered farther on.

Composition.—The metals, as a rule, combine directly with chlorine, but the different metals do not combine with it in the same atomic proportions, and often the same metal forms several distinct combinations with this element. Hence the differences in the composition of the chlorides. They are formed by the union of an atom of metal with one, two, three, four, five, or six atoms of chlorine.

KCl Potassium chloride.	$CaCl^2$ Calcium chloride.	$SbCl^3$ Antimony trichloride.	$SnCl^4$ Tin tetrachloride.	$SbCl^5$ Antimony pentachloride.	$MoCl^6$ Molybdenum hexachloride.
$NaCl$ Sodium chloride.	$FeCl^2$ Ferrous chloride.	$BiCl^3$ Bismuth trichloride.	$TiCl^4$ Titanium tetrachloride.	WCl^5 Tungsten pentachloride.	WCl^6 Tungsten hexachloride.
$AgCl$ Silver chloride.	$ZnCl^2$ Zinc chloride.	$AuCl^3$ Gold trichloride.	$PtCl^4$ Platinum tetrachloride.		
$CuCl$ Cuprous chloride.	$CuCl^2$ Cupric chloride.	$AlCl^3$ Aluminium chloride.			
$HgCl$ Mercurous chloride.	$HgCl^2$ Mercuric chloride.	$CrCl^3$ Chromic chloride.			

It is seen that the same metal may form several combinations with chlorine.

> Mercury and copper combine with one or two atoms of chlorine.
> Iron combines with two or three atoms of chlorine.
> Tin and platinum combine with two or four atoms of chlorine.
> Tungsten combines with four, five, or six atoms of chlorine.

Owing partly to faulty determinations, and partly to anomalies in their vapor densities, some of the chlorides of the first and the third of the above series were for a long time regarded as consisting of two atoms of metal combined with two and with six atoms respectively of chlorine. Thus mercurous chloride was represented by the formula Hg^2Cl^2, and that of aluminium chloride was written Al^2Cl^6. In these, as well as in analogous cases, it has been shown that the vapor densities and other physical constants, when determined under the proper conditions, accord perfectly with the simpler formulæ given above.

Physical Properties of the Chlorides.—Most of the chlorides are solid and possess the aspect, color, and physical properties of the salts of the same metal. Nearly all are crystalline and soluble in water. Only the chloride of silver, mercurous and cuprous chlorides are insoluble; lead chloride and thallous chloride are but slightly soluble in water.

Certain metallic chlorides are liquid at ordinary temperatures. Such are the tetrachlorides of tin and titanium. Some, like the chlorides of zinc and bismuth, are solid, but fusible at low temperatures. These latter were formerly designated as *metallic butters.*

Most of the chlorides are fusible at high temperatures, and many of them are volatile and can be distilled without alteration. It is thus with the liquid chlorides, with the chlorides of zinc, bismuth, mercury, etc.

Chemical Properties.—As a rule, the chlorides are very stable. Only the chlorides of certain of the precious metals, as those of gold and platinum, are entirely decomposed by a high temperature. Some of the higher chlorides lose chlorine when calcined, and are converted into lower chlorides. Thus, cupric chloride is converted into cuprous chloride when heated out of contact with air.

A great number of the chlorides are reduced when they are heated in a current of hydrogen. In this case, hydrochloric acid is disengaged, and the metal remains. Thus, hydrogen removes the chlorine from the chlorides of silver and iron. These decompositions are determined by the powerful affinity of chlorine for hydrogen.

The action of the metals upon the chlorides gives rise to interesting phenomena which are worthy of study.

If corrosive sublimate, which is mercuric chloride, be mixed with powdered tin and the mixture be heated in a small glass retort provided with a receiver, a liquid will soon collect in the latter which diffuses thick vapors in the air. It is the tetrachloride of tin, which was formerly known as "fuming liquor of Libavius." It is formed by the decomposition of the mercuric chloride, which gives its chlorine to the tin, metallic mercury being at the same time set free.

Bismuth decomposes mercuric chloride in the same manner when the two substances are heated together. These experiments are conducted in the dry way. They may be modified by operating in the presence of water, in which we have remarked that most of the chlorides are soluble; it is thus with mercuric chloride.

If a plate of copper be plunged into a solution of this body, it at once becomes covered with a layer of metallic mercury.

That metal is displaced from its combination by the copper, which combines with the chlorine: cupric chloride is formed, and after the lapse of some time, the liquid will contain only that compound. It becomes green, and if a plate of zinc be plunged into it, the copper will be precipitated in its turn, and the zinc will combine with the chlorine and enter the solution; the liquid then contains zinc chloride.

Thus, the metals mutually displace each other from their solutions, according to the energy of their affinities. In this case it is the possession of the chlorine for which they antagonize each other, the stronger driving out the weaker. It must be remarked that in this respect the chlorides behave in the same manner as the oxygen salts.

This analogy is continued in innumerable reactions. Solutions of the chlorides enter into double decompositions like solutions of the true salts. If potassium hydroxide be added to a solution of either cupric sulphate or cupric chloride, in each case a light-blue precipitate of cupric hydroxide is obtained.

$$\underset{\text{Cupric sulphate.}}{CuSO^4} + \underset{\text{Potassium hydroxide.}}{2KOH} = \underset{\text{Potassium sulphate.}}{K^2SO^4} + \underset{\text{Cupric hydroxide.}}{Cu(OH)^2}$$

$$\underset{\text{Cupric chloride.}}{CuCl^2} + 2KOH = \underset{\text{Potassium chloride.}}{2KCl} + Cu(OH)^2$$

But cupric chloride resembles the sulphate in still another property. When perfectly pure it is yellowish. If it be moistened with water, it becomes heated and assumes a green color. It has combined with water, and will dissolve if enough of that liquid be added. A green liquor is thus obtained, which deposits, by spontaneous evaporation, magnificent green prisms. These crystals are hydrated cupric chloride. They contain water of crystallization, and can only exist on that condition. It is the same with the crystals of cupric sulphate.

Thus, certain chlorides are capable of taking water of crystallization like the true salts.

We may complete the analogy by one more characteristic.

1. If a solution of aluminium sulphate be added to a concentrated solution of potassium sulphate, and the mixture be agitated, an abundant crystalline deposit is obtained. This is a double salt,—potassium and aluminium sulphate, or alum.

2. If a solution of platinic chloride be added to a concentrated solution of potassium chloride, a yellow precipitate is

formed at once. It is the double chloride of potassium and platinum, which contains all of the elements of two molecules of potassium chloride and one molecule of platinic chloride. This example shows that the chlorides can combine together, forming double chlorides, just as the true salts may combine together to form double salts.

SALTS.

Definition.—The salts are formed by the substitution of metal for the hydrogen of the acids, and they result from the action of the acids upon the metallic oxides or hydroxides. The name acid applies to two classes of compounds: the first are formed by the union of hydrogen with a strongly electro-negative element, such as chlorine or bromine; these are the *hydracids.* Such are hydrochloric acid, HCl, and hydrobromic acid, HBr.

The acids of the other class are more complicated, containing hydrogen united with a strongly electro-negative oxidized group, that is, a group of atoms formed by oxygen and another element; these are the *oxyacids.* Such are nitric acid, HNO^3, and sulphuric acid, H^2SO^4.

These two classes of acids behave in the same manner in contact with bases, that is, with metallic oxides or hydroxides.

1. If hydrochloric acid be gradually added to a concentrated solution of potassium hydroxide, the liquid becomes heated, and, as it is neutralized by the acid, a white crystalline deposit separates and augments on cooling: it is potassium chloride.

2. If sulphuric acid diluted with its volume of water be cautiously and gradually added to a concentrated solution of potassium hydroxide, the liquid becomes heated, and, as it is neutralized by the acid, a white crystalline deposit separates and increases on cooling: it is potassium sulphate.

The analogy between the two reactions is marked. In each case a powerful base, potassium hydrate, has been neutralized by an energetic acid; the reaction has been accompanied by the production of heat, and has given rise to the formation of a saline matter which has been deposited. The part of the reaction which is invisible is the formation of water. This formation of water, which always accompanies the generation of a salt in the ordinary manner, is expressed in the following equations:

$$\underset{\text{Potassium hydroxide.}}{KOH} + HCl = \underset{\text{Potassium chloride.}}{KCl} + H^2O$$

$$2KOH + H^2SO^4 = \underset{\text{Potassium sulphate.}}{K^2SO^4} + 2H^2O$$

These reactions, it will be seen, consist in an interchange of elements, a double decomposition. The hydrogen of the acid is exchanged for the metal of the potassium hydroxide and by the exchange the potassium hydroxide is converted into water, while the acid, that is, the salt of hydrogen, is converted into a salt of potassium. All hydrogen compounds capable of thus exchanging their hydrogen for an equivalent quantity of metal, fill the functions of acids, and these acids become salts when their hydrogen is thus replaced by a metal. It may then be seen what an important part hydrogen plays in the formation of salts. Whence comes this property, this capacity for making such exchanges, and for replacement by metals? Without doubt from the element or group with which the hydrogen is united in the acids; and in this respect chlorine and sulphur play the same parts in hydrochloric and hydrosulphuric acids that the oxidized groups play in nitric, sulphuric, and phosphoric acids.

HCl Hydrochloric acid.	H^2S Sulphydric acid.	
$H(NO^3)$ Nitric acid.	$H^2(SO^3)$ Sulphurous acid.	$H^3(PO^3)$ Phosphorous acid.
$H(ClO^3)$ Chloric acid.	$H^2(SO^4)$ Sulphuric acid.	$H^3(PO^4)$ Phosphoric acid.

This property is characterized by saying that the elements or groups, to which the hydrogen is united, are strongly electro-negative, or *acid*, in opposition to the hydrogen, which is strongly electro-positive, or *basic*.

When such an acid reacts upon an oxide, or upon a hydroxide, an interchange of elements takes place, and a salt and water are formed; the latter is a constant product necessary to the reaction. Other examples may be added to those already given.

If a current of hydrogen sulphide be passed into a solution of potassium hydroxide until no more is absorbed, potassium hydrosulphide and water are formed.

$$H^2S + KOH = \underset{\text{Potassium hydrosulphide.}}{KSH} + H^2O$$

If an excess of dilute sulphuric acid be poured into a solution of potassium hydroxide, potassium acid sulphate and water are formed.

$$H^2SO^4 + KOH = \underset{\text{Potassium acid sulphate.}}{KHSO^4} + H^2O$$

Lastly, if cupric oxide be heated with dilute sulphuric acid, it dissolves, coloring the liquid blue. Cupric sulphate and water are formed.

$$H^2SO^4 + \underset{\text{Cupric oxide.}}{CuO} = \underset{\text{Cupric sulphate.}}{CuSO^4} + H^2O$$

Neutral, Acid, and Basic Salts.—If the salts result from the substitution of the metals for the basic hydrogen of acids, it is evident that their composition must be related to that of the acids from which they are derived. We know that the latter contain one, two, or three atoms of hydrogen, capable of being replaced by an equivalent quantity of metal: they are monobasic, dibasic, and tribasic. It is evident that the salts must present analogous differences in their composition, according as they are derived from a monobasic, a dibasic, or a tribasic acid.

A salt is *neutral* when the basic hydrogen has been entirely replaced by an equivalent quantity of metal. But the substitution may be only partial, for when an acid contains two atoms of basic hydrogen, only one of these atoms may be replaced by one atom of metal; there will then remain in the salt thus formed one atom of basic hydrogen.

When an acid contains three atoms of basic hydrogen, it may happen that only one is replaced by one atom of metal; there will then remain in the salt two atoms of basic hydrogen; or it may be that two atoms of hydrogen are replaced by an equivalent quantity of metal, and there will then remain in the salt a single atom of basic hydrogen.

Whenever basic hydrogen thus remains in a salt, the saturation of the acid is said to be incomplete. The salt formed ordinarily retains the characters of an acid; it is an *acid salt.* The following table indicates the possible cases of complete or incomplete saturation which may be presented by a monobasic, a dibasic, and a tribasic acid:

HNO^3	H^2SO^4	H^3PO^4
Nitric acid.	Sulphuric acid.	Phosphoric acid,

KNO^3

Potassium nitrate.

$\left.\begin{matrix}K\\H\end{matrix}\right\}SO^4$

Potassium acid sulphate.

$\left.\begin{matrix}K\\H^2\end{matrix}\right\}PO^4$

Monopotassium phosphate.

K^2SO^4

Potassium sulphate.

$\left.\begin{matrix}K^2\\H\end{matrix}\right\}PO^4$

Dipotassium phosphate.

K^3PO^4

Tripotassium phosphate.

Certain neutral salts possess the property of combining with the hydroxides or the oxides. The compounds so formed contain all the elements of the neutral salt plus those of the hydroxide or oxide; they are called *basic salts.* Thus, the oxides of lead and copper may combine with the various salts of lead and copper, forming basic salts of those metals.

Richter's Laws.—Towards the close of the last century fruitful investigation was made into the phenomena of neutralization or saturation of acids by bases. We know that a given weight of acid requires for its neutralization a fixed and absolutely invariable quantity of a given base. Thus, for the conversion of 1000 grammes of sulphuric acid into neutral potassium salt, a quantity of potassium hydrate corresponding to 961 grammes of potassium oxide, K^2O, is required. To saturate these 1000 grammes of sulphuric acid, it is necessary to take weights of the oxides which are invariable for each one separately, but which vary among themselves.

Thus, 1000 grammes of concentrated sulphuric acid are neutralized by the following quantities of the oxides named:

Potassium oxide	961	grammes.
Sodium oxide	632	“
Barium oxide	1561	“
Calcium oxide	571	“
Zinc oxide	866	“
Cupric oxide	811	“
Mercuric oxide	2204	“
Silver oxide	2367	“

Again, to neutralize 1000 grammes of the most concentrated nitric acid, the following quantities of the same oxides are required:

Potassium oxide	747	grammes.
Sodium oxide	492	“
Barium oxide	1214	“
Calcium oxide	444	“
Zinc oxide	651	“
Cupric oxide	631	“
Mercuric oxide	1714	“
Silver oxide	1841	“

Richter was the first to remark that these latter quantities are precisely in the same ratio to each other as the quantities of oxides which neutralize 1000 grammes of sulphuric acid. Thus,

$$\frac{961}{632} = \frac{747}{492}$$
$$\frac{961}{1561} = \frac{747}{1214}$$
$$\frac{961}{571} = \frac{747}{444}, \text{ etc.}$$

In other words, *the quantities of oxides which neutralize a given weight of one acid are proportional to the quantities of the same oxides which neutralize the same weight of another acid.* This law of the composition of salts was discovered, towards the close of the last century, by Richter, a chemist of Berlin. It is the law of relative combining proportions, applied to particular cases and the reactions of compounds, but soon afterwards to be generalized by Dalton and expressed as the fundamental law of chemical combination.

Richter also studied the phenomenon of the precipitation of metallic solutions by the metals. It is known that when a piece of iron is plunged into a solution of cupric sulphate, the iron dissolves, displacing a certain quantity of copper, without other change. Since the new salt formed, ferrous sulphate, exists in the solution in the same conditions of neutrality as the cupric sulphate, *the quantities of metal which thus displace each other are equivalent.* As neither oxygen nor acid is set at liberty, it must be admitted that the respective quantities of the metals, in the salts successively formed, are united to the same quantity of oxygen. It has even been supposed that in the salts which, like the sulphates, contain four atoms of oxygen, the metal is in intimate relation with one of these atoms, which is precisely sufficient to constitute the metal in the state of monoxide.

$$CuSO^4 = CuO,SO^3$$
$$FeSO^4 = FeO,SO^3$$

If this were so, it is evident that when cupric sulphate is decomposed by iron, the quantity of metal which enters into solution would combine or enter into relations with precisely the quantity of oxygen abandoned by the copper. This quantity of oxygen being constant, the quantities of the metals which combine successively with it, differ, but are equivalent to each other, and it is evident that the oxides thus formed would be more rich in oxygen as the weight of metal which enters into solution is less considerable; in other words, the richness of all these oxides in oxygen is inversely proportional to the weights of the metals which successively become dissolved; it was in this form that Richter announced the second law of the composition of salts. It will be seen that this law is implied in the first, and that both are but particular cases and natural consequences of the theory of equivalents, as it is understood at present and as it has already been explained (page 33).

General Properties of Salts.—The salts present very different colors. Those which are formed by an acid possessing a color are themselves colored; such are the chromates, manganates, and permanganates.

Most of the colored oxides form salts presenting various colors.

Ferrous salts are bluish-green.
Ferric salts are yellow or yellowish-brown.
Manganese salts are pink.
Chromium salts are dark green or red.
Nickel salts are green.
Cobalt salts are currant-red or blue.
Cupric salts are blue or green.
Gold salts are yellow.

It is to be remarked that these various colors are only developed, as a rule, when the salts are hydrated, that is, combined with water of crystallization. The taste of the salts depends upon their solubility; it is wanting altogether or but slightly marked in the insoluble salts; more or less pronounced and very diverse in the soluble salts. The salts of magnesium are bitter; the aluminium salts are astringent; those of iron astringent, with a metallic after-taste; the salts of lead are at the same time sweet and astringent; the salts of copper, antimony, and mercury have an acrid metallic taste, which is nauseous, and is called styptic.

The salts generally occur in crystalline form. Some of them may be obtained as amorphous precipitates, but if such salts be formed slowly under circumstances favoring crystallization, they also assume the form of crystals.

Isomorphism.—Certain salts which possess similar atomic compositions crystallize in identical or nearly identical forms; they are called *isomorphous*. It is thus with the double sulphates, which are called *alums*, and of which ordinary alum or aluminium and potassium sulphate is the type. These alums are formed by the union of a sulphate, $R^2(SO^4)^3$, with a sulphate, M^2SO^4, and they all contain 24 molecules of water of crystallization.

Thus, ordinary alum,

$$Al^2(SO^4)^3.K^2SO^4 \quad + \quad 24H^2O$$

Aluminium and potassium double sulphate.

is isomorphous with chrome alum and iron alum.

$$Cr^2(SO^4)^3.K^2SO^4 \quad + \quad 24H^2O$$

Chromium and potassium double sulphate.

$$Fe^2(SO^4)^3.K^2SO^4 \quad + \quad 24H^2O$$

Iron and potassium double sulphate.

All of these alums crystallize in regular octahedra. Further, a solution containing two alums, for example, aluminium and potassium sulphate and aluminium and ammonium sulphate, deposits on concentration crystals in which the two salts are mixed. Such is the character of isomorphous bodies; crystallizing in the same form, they may mix together and replace each other in all proportions in the same crystal. Many examples of isomorphism will be cited in the course of this work. It will now be sufficient to add that this idea of isomorphism has rendered valuable service to chemical theory by permitting the grouping together of bodies similar both in crystalline form and atomic constitution, and by furnishing in such cases useful indications for the determination of the atomic weights. It is evident that when two similar combinations, two sulphates, for example, are recognized to be isomorphous, it is necessary to represent their constitutions by analogous formulæ, and the latter can only be possible under the condition that the atomic weights of the metals contained in these sulphates have known values.

Action of Water upon the Salts.—If water be poured upon and agitated with powdered chalk, a white, cloudy liquid is obtained. The chalk is *suspended* in the water without being dissolved; it is simply held up in the form of minute particles, and if the liquid be allowed to stand, the precipitate is deposited, and clear water again appears above the deposit.

However, if saltpetre, or potassium nitrate, be agitated with water, a colorless, transparent liquid is obtained. The saltpetre is *dissolved* in the water; it has disappeared as a solid body.

It is melted by the water, as is commonly said, and is uniformly diffused through the liquid. It has itself become liquid, and this is the phenomenon of solution. It is accompanied by a production of cold, that is, an absorption of heat; for in assuming the liquid state and becoming diffused throughout the water, the saltpetre must absorb heat.

If the introduction of powdered nitre into the solution be continued, the solid still disappears, but a time arrives when the salt introduced ceases to dissolve; for water at a given temperature can only dissolve a fixed quantity of a salt, and when this limit is attained, the solvent force of the water upon the saltpetre is exhausted. The water is then said to be *saturated* with the salt, and any excess of the latter remains in the solid state.

But if now the solution be heated, this excess is in its turn dissolved, for the solubility augments with the temperature, and as the latter is raised, a larger quantity of the salt is dissolved. When the liquid begins to boil, the temperature and the solubility of the salt have reached their extreme limit.

If the boiling saturated solution be allowed to cool, it deposits a large portion of the salt in the form of crystals. In this manner voluminous, colorless, and transparent prisms are obtained which fill the vessel, and which are surrounded by a solution of saltpetre, saturated at the temperature to which the liquid has been cooled. This liquid is called the mother-liquor of the crystals. It is thus that soluble salts are crystallized by cooling their hot saturated solutions.

Generally the same facts are observed for other soluble salts. Their solubility increases with the temperature; there are, however, some exceptions to this rule. Sodium chloride is but slightly more soluble in hot than in cold water, and gypsum, or calcium sulphate, is sensibly more soluble in cold than in hot water; for, while 500 parts of boiling water are requisite to dissolve one part of gypsum, only 460 parts of cold water are necessary to dissolve the same quantity. The maximum solubility of sodium sulphate is between 32 and 33°.

Crystals of nitre may be obtained by another process. We may expose the cold saturated solution to the air at the ordinary temperature, or, better still, place it in a bell-jar over a vessel containing sulphuric acid. The water of the solution slowly disappears, and, as it is dissipated in vapor, a portion of the dissolved salt separates in the solid form. The crystals thus formed by *spontaneous evaporation* are generally very regular.

But water exerts another and a different action upon the salts.

Perfectly dry cupric sulphate, $CuSO^4$, is a white powder. If water be poured upon it, it becomes blue and dissolves, communicating to the liquid a blue color and notably raising its temperature. On evaporation, this liquid deposits crystals of blue vitriol, and if these be compared with the dry white powder with which we started, they will be found to differ from it by the water they contain. We have employed the anhydrous salt, and have hydrated it. In fact, the sulphate, $CuSO^4$, has absorbed five molecules of water, with which it has combined, and this combination, like all others, has taken place with the production of heat. The water which is thus absorbed by certain salts, and which combines with them in definite proportions, is necessary to the formation of their crystals; it is called *water of crystallization.*

It is not necessary to the constitution of the salts themselves; they can exist without it, and generally lose it when they are heated to a temperature more or less elevated, without undergoing any other decomposition. Certain salts abandon their water of crystallization with such facility that they give it up to the surrounding air when the latter is not saturated with moisture. They then become opaque and lose their forms, for crystals cease to exist when their water of crystallization is disengaged. These salts become covered with a dry powder in the air and are called *efflorescent salts.*

It is seen by the example just cited that the phenomenon of solution of salts in water, which depends upon a physical action, upon a change of state, is often complicated with a true combination of the salt with water, that is, a chemical action which disengages heat. The latter is generally more energetic than the physical action, and the difference between the two effects is then manifested by an elevation of temperature.

But the physical phenomenon is produced alone when the salt which dissolves is incapable of combining with water of crystallization. A depression of temperature is then observed, as we have seen in the case of nitre, the crystals of which are anhydrous; but another example will more clearly illustrate this important phenomenon.

If water be poured upon recently fused and powdered calcium chloride, the salt dissolves with production of heat. It changes not only its state but its composition; it combines energetically with the water, and this combination produces more heat than is absorbed by the change of state. Hence there is an elevation of temperature.

If calcium chloride, combined with its water of crystallization, be rapidly mixed with snow, the salt is so soluble in water that it causes the snow to melt at the same time that it becomes liquid itself. Here there is no combination, no chemical action, and no heat is disengaged. It is a double physical phenomenon,—fusion of the snow and fusion of the calcium chloride,—and neither of these bodies can undergo a change of state without absorbing heat. Hence there is a depression of temperature which may reach —40°.

A mixture of snow and calcium chloride is a *freezing mixture*. A mixture of equal parts of common salt and broken ice or snow is frequently used for the production of cold.

The phenomenon of the solution of salts in water presents none of the characteristics of a chemical action; it does not take place in definite proportions.

In fact, a soluble salt requires for its complete solution a quantity of water, which is always the same for a certain weight of the salt at a given temperature; but there exists no atomic relation between this quantity of water and the weight of the salt which is dissolved.

Further, although the solubility of a salt presents for each temperature a maximum limit, that is, although a given weight of a salt requires for its solution a quantity of water which is invariable and which cannot be diminished, when the solution has been accomplished an indefinite quantity of water may be added, and the liquid will still remain perfectly homogeneous.

Supersaturation.—We have seen that a saturated solution of a salt at a given temperature generally deposits a part of that salt on cooling. This is not always the case; it sometimes happens, if the cooling take place under certain conditions, that a portion of the salt, which the difference in temperature should reduce to the solid state, still remains in solution. The solution is then said to be *supersaturated*. Sodium sulphate and alum have a great tendency to form such solutions.

A hot, saturated solution of sodium sulphate is contained in the tube A (Fig. 95). It is heated to boiling, so that the vapor escapes by the drawn-out extremity. By the aid of a blowpipe, the tube is then sealed at C, before the vapor can condense, and is then allowed to cool. A vacuum is formed above the solution, for the air has been driven out by the vapor. The cold liquid remains limpid; it deposits no crystals. But the instant the drawn-out point of the tube is broken off, the air enters and crystallization at once commences at the surface and proceeds throughout the entire mass, which becomes solid; at the same time an elevation of temperature may be observed.

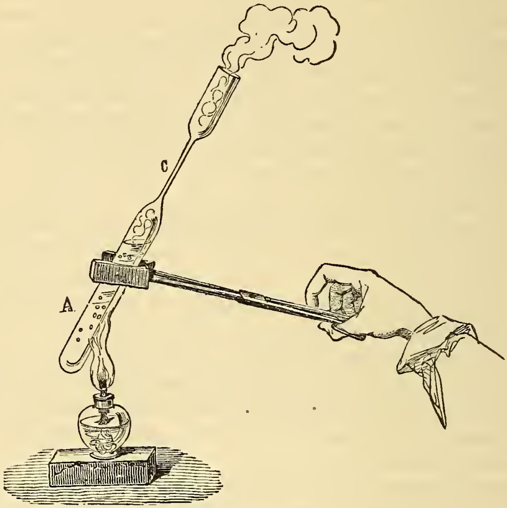

FIG. 95.

100 grammes of water and 200 grammes of crystallized sodium sulphate may be heated to ebullition in a narrow-necked flask, and as soon as vapor begins to issue from the mouth, the latter may be covered with a watch-glass and the whole allowed to cool tranquilly. The salt remains dissolved, and the solution contained in the flask is supersaturated; but as soon as the watch-glass is removed the liquid becomes a solid mass of crystals (Loewel).

In the first experiment it is the sudden entry of the air which determines the crystallization; in the second, it is the free access of air, and it may be admitted that in each case the air acts by the corpuscles which it holds in suspension, and which, falling into the solution, determine the crystallization. Indeed, Loewel has shown that air which has been filtered through cotton-wool has lost the property of causing supersaturated solutions to crystallize.

But what is the nature of these particles which by falling upon the surface of supersaturated solutions occasion crystallization? The researches of Gernez have thrown great light upon this question. According to him, they are saline particles similar to the salt dissolved. The sodium sulphate is deposited in the preceding experiments because the entry of the air has allowed an imperceptible particle of sodium sulphate to fall upon the surface of the liquid, and around this particle the crystallization begins immediately and is propagated throughout the entire mass of the supersaturated liquid. The air then contains a trace of sodium sulphate, as it contains a trace of common salt and of carbonate and sulphate of calcium. These particles are suspended in the air in a state of extreme division, and are carried from great distances by the winds.

A boiling saturated solution of sodium hyposulphite may be allowed to cool in a carefully-corked flask. When cold, it is so concentrated that it possesses an oily consistency. The flask may be carefully uncorked and the surface of the liquid touched with a rod to the end of which a small particle of sodium hyposulphite has been made to adhere. Crystallization at once commences at the spot where the rod touches the liquid, and in a few seconds the whole mass becomes solid. There is at the same time a notable disengagement of heat (Gernez).

The crystallization will also take place if a particle of sodium sulphate be allowed to fall into the solution, for the latter salt possesses the same crystalline form as sodium hyposulphite, and an analogous constitution.

Ebullition of Saline Solutions.—Aqueous solutions of the salts generally possess a boiling-point higher than that of water. Thus, a saturated solution of common salt boils at 108.4°; a saturated solution of potassium nitrate boils at 115.9°; and a saturated solution of calcium chloride boils only at 179.5°.

Action of Heat upon the Salts.—The hydrated salts lose their water when they are heated. Ordinarily, a temperature of 100° is sufficient to expel the water of crystallization. Certain salts melt in this water before losing it; they are so soluble in hot water that they dissolve in the water which at a lower temperature constitutes them in the crystalline state. This is called *aqueous fusion.* A great number of anhydrous salts melt when they are exposed to intense heat; this is called *igneous fusion.*

Heat exerts a decomposing action upon many salts. Upon this point it is difficult to give general laws. It can only be said that the stability of a salt depends upon three conditions, namely, the fixedness of the corresponding acid, the stability of the corresponding oxide, and the energy of the affinity with which the two react together to form the salt.

Thus the salts of acids decomposable by heat are themselves decomposed at an elevated temperature. It is thus with the chlorates, the perchlorates, and the nitrates. Among the sulphates, some are decomposable, others are fixed. The latter are those of potassium, sodium, barium, strontium, calcium, magnesium, lead, etc. The corresponding oxides of potassium, sodium, barium, etc., are fixed bases, and possess a powerful affinity for sulphuric acid. Hence their sulphates are stable.

Most of the carbonates are decomposable by heat; indeed, the affinity of carbonic acid for the bases is as a rule feeble. It is exceptionally strong for the alkaline bases; hence the alkaline carbonates resist the action of heat.

Action of Electricity upon the Salts.—When an electric current traverses the aqueous solution of a salt, the latter is decomposed. The metal separates at the negative pole, and the other element of the salt at the positive pole. This other element may be an electro-negative element, such as chlorine, or an oxidized group, that is, a group of atoms, one or more of which is oxygen.

The electrolysis of a salt may be effected as follows: An U tube (Fig. 96) contains a solution of cupric chloride. In each branch a plate of platinum dips into the liquid, and these plates, connected by conducting wires with the two poles of a battery, constitute the positive and negative electrodes. As soon as the current

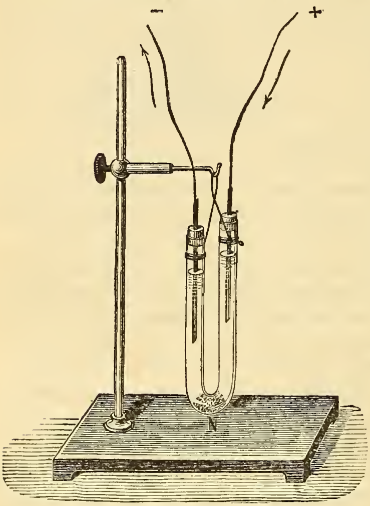

Fig. 96.

passes, the electro-positive element of the salt, the copper, is deposited upon the electro-negative electrode, and the chlorine, which is electro-negative, is disengaged at the positive electrode. A part of this chlorine combines with the platinum electrode by a secondary reaction, forming platinum chloride, but the principal action, that is, the decomposition of cupric chloride by electrolysis, is represented by the following equation:

$$\underset{\text{Cupric chloride.}}{CuCl^2} = \underset{\text{Copper.}}{\overset{+}{Cu}} + \underset{\text{Chlorine.}}{\overset{-}{Cl^2}}$$

If the cupric chloride be replaced by cupric sulphate, the current will decompose this salt into copper, which deposits upon the negative electrode, and into SO^4, which possesses no stability, and consequently breaks up at the positive electrode into SO^3, which combines with the water to form sulphuric acid, and O, which is disengaged at the positive electrode.

The decomposition of the SO^4 is a secondary action. The principal action accomplished by the work of the current is expressed by the following equation:

$$\underset{\text{Cupric sulphate.}}{CuSO^4} = \underset{\text{Copper.}}{\overset{+}{Cu}} + \underset{\text{Oxidized group.}}{\overset{-}{SO^4}}$$

The secondary reactions are as follows:

$$SO^4 = SO^3 + O$$
$$SO^3 + H^2O = H^2SO^4$$

The experiment may be repeated upon potassium sulphate, and a solution of this salt colored by the syrup of violets is introduced in the U tube. As soon as the current passes, bubbles of gas are seen to arise from each electrode. Free oxygen appears at the positive electrode, as in the preceding case, and at the same time the liquid filling this branch of the tube assumes a red color. This is the evidence of the presence of sulphuric acid formed at the positive electrode.

The gas disengaged at the negative electrode is hydrogen, which is produced by a secondary action of the water upon the potassium which is removed from the salt at the negative pole. Potassium hydroxide is thus formed, and the syrup of violets in this branch of the tube is colored green. The principal action accomplished by the current is expressed, as in the preceding cases, by the equation

$$\underset{\text{Potassium sulphate.}}{K^2SO^4} = \underset{\text{Potassium.}}{2K} + \underset{\text{Oxidized group.}}{SO^4}$$

The appearance of hydrogen and potassium hydroxide at one pole, and the disengagement of oxygen and formation of sulphuric acid at the other, are due to secondary reactions independent of the current, as has been explained.

The positive pole is called the *anode*, and the negative pole the *cathode*, and the elements or groups which separate are distinguished as *anions* and *cathions*, according to the poles at which they are set free. The groups into which a compound is separated by the electric current are called the *ions*.

According to a theory proposed by Arrhenius, a salt in dilute solution exists as such only in small proportion, the larger proportion being dissociated into the ions. Although it would at first seem improbable that a compound like sodium chloride would thus exist in solution as free chlorine atoms and free sodium atoms, it can be conceived that neither of them would manifest active properties in presence of the other. We have analogous cases in the vapors of certain substances: that of ammonium chloride, for instance, is dissociated into free ammonia and hydrochloric acid, each of which masks the reactions of the other. Phosphorus pentachloride vapor is in like manner dissociated into phosphorus trichloride and chlorine. The theory is supported by many facts which cannot be given here. The conduction of the current is effected by the ions, which are thus continually united and dissociated through the mass of the liquid while those at the poles are set free.

Faraday discovered the law expressing the relative quantities of the ions of different electrolytes that would be set free by a given current: it is, that a current of the same strength will set free quantities of the ions that are exactly proportional to their chemical equivalents. Referred to the elements, these quantities will be in the ratio of the atomic weights divided by the quantivalence.

Action of the Metals upon the Salts.—The metals may displace each other in their saline solutions.

If a plate of copper be plunged into a solution of silver nitrate, the copper enters into solution in the form of cupric nitrate, displacing and precipitating the silver.

$$Cu + \underset{\text{Silver nitrate.}}{2AgNO^3} = \underset{\text{Cupric nitrate.}}{Cu(NO^3)^2} + 2Ag$$

If a piece of iron be introduced into a solution of cupric sulphate, the iron instantly becomes covered with a layer of metallic copper, precipitated by a portion of the iron which enters the solution.

$$\underset{}{Fe} + \underset{\text{Cupric sulphate.}}{CuSO^4} = Cu + \underset{\text{Ferrous sulphate.}}{FeSO^4}$$

If a strip of zinc around which some brass wires have been twisted be suspended in a dilute solution of plumbic acetate, the zinc will slowly displace the lead, which will be deposited in brilliant scales upon the brass wires. The latter gradually assume the appearance of fern-leaves, and the experiment constitutes the formation of the lead-tree.

Richter, of Berlin, was the first to remark (1792) that the metals displace each other in their saline solutions without the neutrality of the latter being disturbed. When a neutral salt is precipitated by a metal, a new neutral salt results. The ferrous sulphate formed by the action of iron upon cupric sulphate is neutral like the latter.

It may be further stated that in this respect the chlorides behave like the oxygen salts. Iron displaces copper from cupric chloride as from the sulphate. In the first case it combines with Cl^2, in the second with SO^4, and in this circumstance again the latter group acts in the same manner as chlorine.

$$\underset{\text{Cupric chloride.}}{CuCl^2} + Fe = \underset{\text{Ferrous chloride.}}{FeCl^2} + Cu$$

$$\underset{\text{Cupric sulphate.}}{Cu(SO^4)} + Fe = \underset{\text{Ferrous sulphate.}}{Fe(SO^4)} + Cu$$

BERTHOLLET'S LAWS.

To conclude this general study of the salts, it only remains to indicate the actions exerted upon them by the acids and the bases, and the reciprocal actions of the salts themselves. These facts have been established and discussed principally by Berthollet, who demonstrated the influence of physical conditions, such as insolubility and volatility, upon the direction of chemical decompositions.

Action of Acids upon the Salts.—When an acid, that is, a salt of hydrogen, is added to a metallic salt, the former tends to exchange elements with the latter, in such a manner as to form a new salt and a new acid.

If sulphuric acid be added to powdered potassium nitrate, the latter partially dissolves without the aid of heat, and potassium acid sulphate and nitric acid are formed.

$$\underset{\text{Potassium nitrate.}}{KNO^3} + \underset{\text{Sulphuric acid.}}{H^2SO^4} = \underset{\text{Nitric acid.}}{HNO^3} + \underset{\text{Potassium acid sulphate.}}{KHSO^4}$$

But this reaction is by no means complete. Powerful as are its affinities, the sulphuric acid cannot decompose the whole of the potassium nitrate unaided by heat; a portion of the latter salt remains unaltered in presence of the excess of sulphuric acid, so that the resulting thick and fuming liquid really contains two acids and two salts, namely:

Sulphuric acid.
Nitric acid.
Potassium acid sulphate.
Potassium nitrate.

The reaction takes place as if two acids were in presence of a single base. There is a conflict between the acids, and they tend to divide the base, which is potassium, in such a manner that each acid may saturate a portion.

Hence the decomposition of potassium nitrate is not complete, and it is arrested as soon as the nitric acid set free can dispute with the sulphuric acid the possession of the base. There is then established a state of equilibrium between the two acids, both remaining in presence of the two salts.

But this equilibrium is unstable and may be deranged by various circumstances.

If the acid mixture be heated, abundant white vapors are disengaged. It is the nitric acid which volatilizes. But the sulphuric acid becomes thus preponderant in the liquid and decomposes another portion of potassium nitrate, and, if the volatilization of the nitric acid set free be not arrested by the removal of the heat, it is evident that nothing can prevent the complete decomposition of the potassium nitrate by the sulphuric acid. The nitric acid, which by its presence alone prevented this total decomposition, is rendered powerless.

Such is the influence of volatility or the gaseous state upon the progress of decompositions; it is manifested in the highest degree in acids more volatile than nitric acid, such as carbonic and sulphurous acids. We have already seen that the carbonates and sulphites are easily and entirely decomposed by the energetic acids.

While the volatility of acids favors the decomposition of their salts, *insolubility* may play an analogous part.

If hydrochloric acid be added to a solution of potassium silicate, a gelatinous precipitate of silicic acid is at once produced, and at the same time potassium chloride is formed. The decomposition is complete, for the silicic acid is insoluble.

If sulphuric acid be poured into a solution of barium nitrate, a precipitate of barium sulphate is immediately formed, while at the same time nitric acid is set free.

$$\underset{\text{Barium nitrate.}}{Ba(NO^3)^2} + \underset{\text{Sulphuric acid.}}{H^2SO^4} = \underset{\text{Nitric acid.}}{2HNO^3} + \underset{\text{Barium sulphate.}}{BaSO^4}$$

In this case also the decomposition is complete, for the barium sulphate is insoluble.

In these two reactions, the division of the base between the two acids cannot take place, since one of the products is immediately removed from the sphere of action by its insolubility. In the first case, it is the newly-formed acid which is precipitated; in the second, it is the newly-formed salt which is deposited in the insoluble state.

Influence of Mass.—One other circumstance can influence the extent of these decompositions: it is the relative *masses* of the bodies which are in presence of each other.

In the first experiment, it was supposed that an amount of sulphuric acid had been added to potassium nitrate sufficient to produce the double decomposition. If a large excess had been employed, it is evident that it would have become preponderant in the mixture, and that it would have displaced a more considerable portion of nitric acid.

The influence of mass is manifested in the case of very feeble acids, and permits them to displace stronger acids. If a small quantity of tricalcic phosphate be introduced into water charged with carbonic acid, the latter, compensating by its mass for its deficiency in energy, will remove from the phosphate a portion of its base. Calcium dicarbonate and calcium acid phosphate are formed, both of which are soluble.

Such, according to Berthollet, is the influence of insolubility and volatility upon the phenomena of double decomposition; such, on the other hand, is the influence of mass. The same conditions intervene, and in the same manner, in the reactions which we are about to study.

Action of Bases upon the Salts.—We will here consider only the action of the soluble bases, that is, the alkaline hydroxides.

If a solution of potassium hydroxide be poured into a solution of sodium sulphate, no apparent change takes place; but, according to the principle which has just been announced, it is probable that the potassium hydroxide has liberated a portion of sodium hydroxide.

$$\mathrm{Na^2SO^4} \;+\; \mathrm{2KOH} \;=\; \mathrm{K^2SO^4} \;+\; \mathrm{2NaOH}$$

Sodium sulphate. Potassium hydroxide. Potassium sulphate. Sodium hydroxide.

But this decomposition cannot be complete, and the liquid must contain four bodies, namely:

Sodium sulphate.
Potassium sulphate.
Sodium hydroxide.
Potassium hydroxide.

If potassium hydroxide be added to a solution of cupric sulphate, a light-blue precipitate of cupric hydroxide is obtained. In this case the decomposition is complete, owing to the insolubility of the cupric hydroxide, which cannot dispute with the potassium hydroxide the possession of the acid.

$$\mathrm{CuSO^4} \;+\; \mathrm{2KOH} \;=\; \mathrm{K^2SO^4} \;+\; \mathrm{Cu(OH)^2}$$

Cupric sulphate. Potassium hydroxide. Potassium sulphate. Cupric hydroxide.

If a solution of barium hydroxide be poured into a solution of potassium sulphate, a precipitate of barium sulphate is produced, and potassium hydroxide remains in solution. In this case again, the decomposition is complete, by reason of the insolubility of the barium sulphate. The potassium cannot divide the acid with the barium, for the latter escapes with all of it in the form of insoluble sulphate.

$$\mathrm{K^2SO^4} \;+\; \mathrm{Ba(OH)^2} \;=\; \mathrm{BaSO^4} \;+\; \mathrm{2KOH}$$

Potassium sulphate. Barium hydroxide. Barium sulphate. Potassium hydroxide.

Action of the Salts upon each other.—The action of salts upon each other is what would naturally follow from the principles exposed in treating of the action of acids upon salts. Indeed, the latter possess the same constitution as the acids, and in their reactions upon salts should give rise to phenomena of the same order. These are exchanges of elements, double decompositions, which take place and are more or less complete, according to the physical conditions of the bodies which are produced, and also according to the relative masses of the reacting bodies.

In the first place, we must consider the reciprocal actions of the soluble salts.

If a solution of cupric sulphate be treated with a solution of sodium chloride, no precipitate is formed, but the blue color of the liquid is changed to green. This color is that of cupric chloride, and it may be supposed that the latter salt is formed by the reciprocal action of the sodium chloride and cupric sulphate.

$$\underset{\text{Cupric sulphate.}}{CuSO^4} + \underset{\text{Sodium chloride.}}{2NaCl} = \underset{\text{Sodium sulphate.}}{Na^2SO^4} + \underset{\text{Cupric chloride.}}{CuCl^2}$$

But this interchange of elements between the cupric sulphate and the sodium chloride is arrested before the decomposition of the two salts is complete. A part of each remains unaltered in the presence of the other and of the two new salts which are formed. Consequently, the green liquor obtained in this experiment contains four salts, namely:

Cupric sulphate.
Sodium chloride.
Sodium sulphate.
Cupric chloride.

The respective proportions in which these salts exist in the mixture depend upon several circumstances. Malaguti has shown that in cases of this kind it is the energy of the affinity of the acids for the bases which governs the decomposition. The most energetic acid tends to combine with the most powerful base, and the proportion of the salt thus formed predominates in the mixture. Thus there is set up, as it were, between the elements in presence a sort of conflict, in which the stronger are victorious, while the weaker are not altogether annihilated. The result is a state of equilibrium which is only disturbed in case one of the products is by reason of its insolubility removed from the sphere of action of the other. The latter condition is realized in the following experiments.

When barium chloride is added to the blue solution of cupric sulphate, a precipitate of barium sulphate is immediately formed, and cupric chloride remains in solution, coloring the liquid green.

$$\underset{\text{Cupric sulphate.}}{CuSO^4} + \underset{\text{Barium chloride.}}{BaCl^2} = \underset{\text{Barium sulphate.}}{BaSO^4} + \underset{\text{Cupric chloride.}}{CuCl^2}$$

In this case the decomposition is complete, owing to the insolubility of the barium sulphate. That salt is removed by cohesion from the sphere of action of the compounds which remain in solution. The portions first formed, and thus withdrawn, are replaced by others, and the reaction once commenced is finished in the same manner, so that the whole of the cupric sulphate is converted into barium sulphate.

A concentrated solution of common salt produces no precipitate in a concentrated solution of magnesium sulphate. However, we must admit that there is an interchange of elements, and that the liquid contains four salts, namely:

Magnesium sulphate.
Sodium chloride.
Sodium sulphate.
Magnesium chloride.

If this solution be exposed to an intense cold, it deposits crystals of sodium sulphate, while magnesium chloride remains in solution (Balard). Of the four salts which are in presence of each other, the sodium sulphate is the least soluble; it is therefore deposited, and the double decomposition continues in the same manner until the greater part of the magnesium sulphate has been decomposed.

The subject could be further developed by other examples. Those which have been given are sufficient to expose the true principle of double decomposition.

We may add that if the operations be conducted in the dry way and at a high temperature, the volatility of the products which may be formed exerts an influence upon the reactions analogous to that which has been established for insolubility.

If an intimate mixture of mercuric sulphate and sodium chloride be heated in a glass matrass, a sublimate of mercuric chloride is formed.

$$\underset{\text{Mercuric sulphate.}}{HgSO^4} + \underset{\text{Sodium chloride.}}{2NaCl} = \underset{\text{Sodium sulphate.}}{Na^2SO^4} + \underset{\text{Mercuric chloride.}}{HgCl^2}$$

Action of Soluble Salts upon Insoluble Salts.—The study of double decomposition may be concluded by a summary exposition of the action of soluble salts upon insoluble salts. It is analogous to that which has just been studied, that is, it is characterized by a tendency to an interchange of elements. A single example will be sufficient.

If a solution of sodium carbonate be boiled for a long time with barium sulphate, it is found that the latter salt has undergone a partial decomposition. It is partially converted into barium carbonate, insoluble like the sulphate, and the liquid becomes charged with a certain quantity of sodium sulphate.

$$\underset{\text{Barium sulphate.}}{BaSO^4} + \underset{\text{Sodium carbonate.}}{Na^2CO^3} = \underset{\text{Sodium sulphate.}}{Na^2SO^4} + \underset{\text{Barium carbonate.}}{BaCO^3}$$

This decomposition is more complete as the proportion of sodium carbonate which reacts upon the barium sulphate is increased. Here, as in some of the preceding experiments, the influence exerted by the greater mass is very appreciable.

This study may be aptly terminated by summary indications upon the composition and properties of the more important classes of salts, which are the nitrates, sulphates, and carbonates.

NITRATES.

Composition.—Nitric acid containing HNO^3, the nitrates contain the group NO^3 combined with a metal which replaces the hydrogen of the acid. Consequently they contain one or more groups, NO^3, according to the nature of the metal which has neutralized the nitric acid. Thus,

$$1.\quad \underset{\text{Potassium hydroxide.}}{KOH} + \underset{\text{Nitric acid.}}{HNO^3} = \underset{\text{Potassium nitrate.}}{KNO^3} + H^2O$$

$$2.\quad \underset{\text{Plumbic oxide.}}{PbO} + 2HNO^3 = \underset{\text{Plumbic nitrate.}}{Pb(NO^3)^2} + H^2O$$

$$3.\quad \underset{\text{Bismuth hydroxide.}}{\left.\begin{matrix}Bi\\H^3\end{matrix}\right\}O^3} + 3HNO^3 = \underset{\text{Bismuth trinitrate.}}{Bi(NO^3)^3} + 3H^2O$$

With these few examples, we may conclude:

1. That potassium, which unites with one atom of chlorine to form potassium chloride, KCl, unites also with one group, NO^3, to form potassium nitrate.

2. That lead, which unites with two atoms of chlorine to form plumbic chloride, $PbCl^2$, unites also with two groups, NO^3, to form plumbic nitrate.

3. That bismuth, which unites with three atoms of chlorine to form bismuth trichloride, $BiCl^3$, unites also with three groups, NO^3, to form bismuth trinitrate.

In the chloride $K'Cl$ potassium is monatomic.
In the chloride $Pb''Cl^2$ lead is diatomic.
In the chloride $Bi'''Cl^3$ bismuth is triatomic.

In the nitrates, these three metals play the same parts as in the chlorides; and we may say, in a general manner, that the metallic nitrates contain a metal united with as many times NO^3 as the metal possesses atomicities.

In $K'(NO^3)$ monatomic potassium is united with NO^3
In $Pb''(NO^3)^2$ diatomic lead is united to $2NO^3$
In $Bi'''(NO^3)^3$ triatomic bismuth is united to $3NO^3$

Such is the law of the composition of the nitrates.

Properties.—All of the nitrates are soluble in water. Some of them are deposited from their solutions in the form of hydrated crystals. Such is cupric nitrate, which crystallizes with six molecules of water at a low temperature.

Others separate in anhydrous crystals. Such are the nitrates of potassium, sodium, silver, barium, and lead.

All of the nitrates are decomposable by heat, and the products of the decomposition vary with the nature of the nitrate and with the temperature. Thus, potassium nitrate is first converted into nitrite, and this is finally decomposed into nitrogen, oxygen, and potassium oxide. The nitrates of barium and lead yield nitrogen peroxide, oxygen, and a residue of oxide. Silver nitrate yields nitrogen peroxide, oxygen, and a residue of metal.

$$2AgNO^3 = 2NO^2 + O^2 + 2Ag$$

All of the nitrates liberate oxygen when they are heated; rich in oxygen, they constitute an abundant source of that element, and they are also easily reduced by bodies possessing a strong affinity for it.

Sulphur, charcoal, phosphorus, and certain metals are energetically oxidized when heated with the nitrates.

If sulphur be heated with potassium nitrate, potassium sulphate is formed, and sulphurous oxide and nitrogen are disengaged.

$$\underset{\text{Potassium nitrate.}}{2KNO^3} + S^2 = \underset{\text{Potassium sulphate.}}{K^2SO^4} + SO^2 + N^2$$

When powdered potassium nitrate is thrown upon burning charcoal, the salt melts and increases the combustion of the charcoal, producing a vivid deflagration. Potassium carbonate is formed and carbon dioxide and nitrogen are disengaged.

$$\underset{\text{Potassium nitrate.}}{4KNO^3} + 5C = \underset{\text{Potassium carbonate.}}{2K^2CO^3} + 3CO^2 + 2N^2$$

Distinctive Characters.—All of the nitrates deflagrate when thrown upon incandescent charcoal.

With concentrated sulphuric acid they evolve white vapors of nitric acid in the cold, and more abundantly when the reaction is aided by heat. When mixed with copper-filings and treated with concentrated sulphuric acid, they disengage red vapors.

When the solution of a nitrate is mixed with its own volume of concentrated sulphuric acid, and a crystal of ferrous sulphate is introduced into the liquid, the crystal very soon assumes a brown color, which is communicated to the liquid. In this very delicate reaction the nitric acid is reduced by the ferrous sulphate to nitric oxide, which colors the excess of ferrous sulphate brown (page 164).

The solution of a nitrate, when treated with sulphuric acid, will decolorize solution of sulphate of indigo when the liquid is heated to boiling.

SULPHATES.

Composition.—Sulphuric acid, H^2SO^4, contains two atoms of hydrogen capable of being replaced by a metal. When both are replaced by an equivalent quantity of metal, a neutral sulphate is formed. An acid sulphate is formed when a single one of these atoms of hydrogen is replaced by a single atom of metal. The hydrogen of the acid is removed by the oxygen of the metallic oxide or hydroxide which more or less completely saturates the sulphuric acid. Several cases may be presented.

$$1.\quad \underset{\text{Potassium hydrate.}}{K'OH} + H^2SO^4 = \underset{\text{Potassium acid sulphate.}}{\left.\begin{matrix}K'\\H\end{matrix}\right\}SO^4} + H^2O$$

$$2.\quad 2K'OH + H^2SO^4 = \underset{\text{Potassium sulphate.}}{K'^2SO^4} + 2H^2O$$

$$3.\quad \underset{\text{Plumbic oxide.}}{Pb''O} + H^2SO^4 = \underset{\text{Plumbic sulphate.}}{Pb''SO^4} + H^2O$$

$$4.\quad \underset{\text{Aluminium oxide.}}{(Al^2)^{vi}O^3} + \underset{\text{3 molecules.}}{\left\{\begin{matrix}H^2SO^4\\H^2SO^4\\H^2SO^4\end{matrix}\right.} = \underset{\text{Aluminium sulphate.}}{(Al^2)^{vi}\left\{\begin{matrix}SO^4\\SO^4\\SO^4\end{matrix}\right.} + 3H^2O$$

These examples show that all of the sulphates contain the group SO^4, which in sulphuric acid is united with two atoms of hydrogen. This group is diatomic; it is necessary, then, that in the sulphates it shall be united with a quantity of metal equivalent to two atoms of hydrogen.

1. In the acid sulphates it is united with an atom of hydrogen and an atom of a monatomic metal, $\left.\begin{matrix}R'\\H\end{matrix}\right\}SO^4$.

2. It is united with two atoms of a monatomic metal in the neutral sulphates R'^2SO^4.

3. With one atom of a diatomic metal in the neutral sulphates $M''SO^4$.

These cases are very simple. It is not so, however, with the fourth, in which we consider the saturation of sulphuric acid by an oxide R^2O^3, such as ferric oxide or aluminic oxide. Each of the three atoms of oxygen of the oxide R^2O^3 removes H^2 from a molecule of H^2SO^4, and it results that the metal which was combined with $3O''$, combines with $3(SO^4)''$. The two atoms of metal which are substituted for $3H^2$ in three molecules of H^2SO^4 are then equivalent to 6 atoms of hydrogen. They are hexatomic, as is marked by the index ^{vi}.

Properties.—The sulphates are nearly all soluble in water. Those of barium, strontium, and lead are insoluble. The sulphates of calcium and silver, and mercurous sulphate are but slightly soluble.

The alkaline sulphates, and those of calcium, barium, strontium, magnesium, and lead, are undecomposable by heat. The others are decomposed at a high temperature. A residue of oxide generally remains, while sulphur dioxide and oxygen are disengaged. The sulphates of zinc and copper are thus decomposed at a high red heat.

$$\underset{\text{Cupric sulphate.}}{CuSO^4} = SO^2 + O + \underset{\text{Cupric oxide.}}{CuO}$$

In case the oxide is reducible by heat, the residue consists of metal.

$$\underset{\text{Mercuric sulphate.}}{HgSO^4} = \underset{\text{Mercury.}}{Hg} + SO^2 + O^2$$

The sulphates $R^2(SO^4)^3$ are decomposed at a comparatively low temperature, disengaging vapor of sulphur trioxide and leaving a residue of sesquioxide.

$$\underset{\text{Ferric sulphate.}}{Fe^2(SO^4)^3} = \underset{\text{Ferric oxide.}}{Fe^2O^3} + \underset{\text{Sulphuric oxide.}}{3SO^3}$$

The sulphates are readily deoxidized by carbon and other reducing agents.

If an intimate mixture of potassium sulphate with an excess of charcoal be heated to bright redness, and allowed to cool out of contact with the air, a black powder is obtained, which produces a shower of sparks when projected into the air. It is the pyrophorus of Gay-Lussac. It owes its spontaneous inflammability on contact with the air to finely-divided potassium sulphide which it contains, and which attracts oxygen with great avidity. The sulphide is formed according to the following reaction:

$$\underset{\text{Potassium sulphate.}}{K^2SO^4} + 4C = 4CO + \underset{\text{Potassium sulphide.}}{K^2S}$$

In the same manner barium sulphate and calcium sulphate are converted into sulphides by the action of charcoal at a high temperature.

The other sulphates are also reduced under the same circumstances, but the products vary; carbon dioxide or carbon monoxide and sulphurous oxide are disengaged, and the residue consists of either oxide or metal.

Distinctive Characters.— When treated with sulphuric acid, the sulphates do not evolve any gas. They do not deflagrate when thrown upon burning charcoal. Their solutions give a white precipitate of barium sulphate with barium nitrate, which is insoluble in nitric acid. When this precipitate is washed, dried, and calcined with an excess of charcoal, it leaves a residue of barium sulphide, and when this is moistened with hydrochloric acid, it evolves hydrogen sulphide, which is easily recognized by its odor.

CARBONATES.

Composition.—Carbonic acid is dibasic, like sulphuric acid. It is not known in the state of hydrate, and the carbonates are formed by the direct union of carbon dioxide with the metallic oxides or hydroxides.

When freshly-burnt lime is exposed to the air, it attracts at the same time the moisture and the carbonic acid gas of the air, and is converted into carbonate.

$$CO^2 + \underset{\text{Calcium oxide.}}{CaO} = \underset{\text{Calcium carbonate.}}{CaCO^3}$$

The carbonates then contain the group CO^3 combined with a metal. In carbonic acid, this group would be united with two atoms of hydrogen. The composition of the more simple carbonates is expressed by the following formulæ:

H^2CO^3 carbonic acid (unknown).

$\left.\begin{matrix}R'\\H\end{matrix}\right\}CO^3$ acid carbonates (dicarbonates).

R'^2CO^3 neutral carbonates.

$M''CO^3$ neutral carbonates.

In these formulæ, R′ represents a monatomic metal, such as potassium, which is equivalent to one atom of hydrogen. M″ represents a diatomic metal, such as calcium, which is equivalent to two atoms of hydrogen.

Properties.—Only the alkaline carbonates are soluble in pure water. The others are insoluble, but they dissolve in water charged with carbonic acid.

The soluble carbonates possess an alkaline reaction. It is the same with the acid carbonates of the alkaline metals, which are ordinarily called bicarbonates, such as potassium acid carbonate or bicarbonate of potassium.

All of the carbonates except the alkaline carbonates are decomposable by heat. In this decomposition carbon dioxide is disengaged, and there remains a residue of oxide, or of metal in case the oxide be reducible by heat. Thus, the carbonates of magnesium, calcium, zinc, lead, and copper leave a residue of oxide after calcination; silver carbonate leaves a residue of metal.

Barium and strontium carbonates are but slowly decomposed at a white heat; their decomposition is facilitated by a current of steam, and easily effected in the electric furnace.

Reducing agents, such as carbon and metallic magnesium, act upon the carbonates as upon the corresponding oxides: if the base be reducible, the metal is formed.

If cupric carbonate be heated with charcoal, carbon dioxide is disengaged, and metallic copper remains.

$$\underset{\text{Cupric carbonate.}}{2CuCO^3} + C = 3CO^2 + \underset{\text{Copper.}}{2Cu}$$

In this experiment carbon dioxide is disengaged, for cupric oxide is easily reducible by charcoal. It is not the same with potassium oxide; hence potassium carbonate is only reduced by charcoal at a very high temperature with disengagement of carbon monoxide.

$$K^2CO^3 + 2C = 3CO + K^2$$

When magnesium is substituted for the charcoal in this experiment, less heat is required to bring about the reaction, and the carbon as well as the potassium of the carbonate is reduced to the elementary state.

$$K^2CO^3 + 3Mg = C + 2K + 3MgO$$

All the carbonates are decomposed by phosphorus.

A small piece of phosphorus may be placed at the bottom of a small test-tube, and the latter then nearly filled with well-dried sodium carbonate. The part of the tube containing the carbonate being heated to redness, the phosphorus may be heated so that its vapor will pass over the incandescent carbonate. The latter will be decomposed with the formation of sodium phosphate and a deposition of carbon. After cooling, the contents of the tube will be black.

The experiment may be repeated upon calcium carbonate. The phosphorus is placed in a small crucible, which is then introduced into a larger one. The calcium carbonate (chalk) is then placed upon the lid of the smaller crucible, which is pierced with holes. The arrangement is heated upon a double grate, so that when the chalk has been brought to incandescence, the vapor of phosphorus may be caused to pass through it by placing some hot coals upon the lower grate. The chalk is rapidly decomposed, carbon monoxide is disengaged, and a mixture of calcium phosphate and phosphide is formed. This mixture serves for the preparation of hydrogen phosphide.

Distinctive Characters.—When treated with sulphuric acid, the carbonates disengage a colorless, incombustible gas, which extinguishes burning bodies and produces a milkiness when agitated with lime-water.

CLASSIFICATION OF THE METALS.

In the preceding pages we have studied the composition and the general properties of metallic compounds. This study has revealed the fact that the metals possess very different aptitudes to form compounds, and various capacities of combination, which are manifested by the greater or less number of other atoms which the atoms of these metals can attract. In this respect, the differences existing between the metals are analogous to those which we have already remarked between the non-metals. On comparing the metals among themselves, some are discovered which resemble each other in the general structure of the compounds which they are capable of forming, and such can naturally be classed in the same group. On this plan the metals are divided into several families analogous to those first proposed by Dumas for the non-metals, and it will be seen that the general composition of the metallic compounds furnishes the elements for a natural classification of the metals. While this principle is excellent, its application is attended with some difficulties which chemistry has not yet been able to solve. Consequently, this chapter must be limited to summary indications upon the subject.

Some of the metals are incapable of combining with more than a single atom of chlorine, bromine, or iodine. The compounds thus formed correspond in their atomic constitution to hydrochloric, hydriodic, and hydrobromic acids. On comparing potassium chloride or silver chloride to hydrochloric acid, it will be seen that an atom of potassium or an atom of silver occupies in them the place occupied by the hydrogen of the acid. The atoms of potassium and of silver are therefore equivalent to the atoms of hydrogen as far as their capacity of combination is concerned. The other alkaline metals, such as sodium and lithium, are similar and belong to the same group. Their chlorides, bromides, and iodides, which are arranged in the following table, present analogous compositions:

MONATOMIC METALS.	MONATOMIC CHLORIDES.	MONATOMIC BROMIDES.	MONATOMIC IODIDES.
	$\underline{H'Cl}$	$\underline{HBr}$	$\underline{HI}$
Potassium K′	KCl	KBr	KI
Sodium Na′	$NaCl$	$NaBr$	NaI
Lithium Li′	$LiCl$	$LiBr$	LiI
Silver Ag′	$AgCl$	$AgBr$	AgI

These metals form hydroxides or oxides whose atomic constitutions correspond to that of water, one or both of the hydrogen atoms of the latter being replaced by an equivalent amount of metal. In the same manner the hydrosulphides and monosulphides of these metals are derived from hydrogen sulphide.

TYPE H^2O.		TYPE H^2S.	
OXIDES.	HYDROXIDES.	MONOSULPHIDES.	HYDROSULPHIDES.
K^2O ?*	KOH	K^2S	KSH
Na^2O ?*	$NaOH$	Na^2S	$NaSH$
Li^2O	$LiOH$	Li^2S	$LiSH$
Ag^2O		Ag^2S	

The same analogy is continued among the salts of these

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* The existence of these monoxides of potassium and sodium is rather doubtful. They are not obtainable from the hydroxides, carbonates, or nitrates by the action of heat, and the products resulting from the direct combination of the metals with oxygen appear to be very stable peroxides of the types RO^2 and RO.

metals, as will be seen from the nitrates and sulphates which we take as examples.

Nitric Acid, HNO^3.	Sulphuric Acid, H^2SO^4.	
Nitrates.	Sulphates.	Acid Sulphates.
KNO^3	K^2SO^4	$KHSO^4$
$NaNO^3$	Na^2SO^4	$NaHSO^4$
$AgNO^3$	Ag^2SO^4	

It is seen that in all of these compounds the metals under consideration replace hydrogen atom for atom; each of them possesses the same capacity of combination as that gas. They are said to be *monatomic.*

Certain other metals manifest a double capacity of combination; one atom of any of these is capable of replacing two atoms of hydrogen, consequently it can combine with two atoms of chlorine, bromine, or iodine, or with one atom of oxygen or sulphur. In the chlorides of these metals, the two atomicities of the metal are satisfied by the two atomicities of two atoms of chlorine. In their oxides, the two atomicities of the metal are satisfied by the two atomicities or bonds of affinity which reside in one atom of oxygen. These metals are then *diatomic.* They are quite numerous and can be divided into several groups, one of the most natural of which comprises barium, strontium, calcium, and lead. The following table shows the constitution of the principal compounds of these metals:

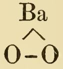
Diatomic Metals.	Chlorides.	Oxides.	Nitrates.	Sulphates.
	$2HCl$	H^2O	$2HNO^3$	H^2SO^4
Barium Ba'' .	$BaCl^2$	BaO	$Ba(NO^3)^2$	$BaSO^4$
Strontium Sr'' .	$SrCl^2$	SrO	$Sr(NO^3)^2$	$SrSO^4$
Calcium Ca'' .	$CaCl^2$	CaO	$Ca(NO^3)^2$	$CaSO^4$
Lead Pb'' . .	$PbCl^2$	PbO	$Pb(NO^3)^2$	$PbSO^4$

The metals of this group combine with oxygen in two proportions, forming not only the monoxides, RO, but also the dioxides, RO^2. They thus form two oxides, while they are capable of forming but one chloride, RCl^2. Thus, barium forms a monoxide, BaO, a dioxide, BaO^2, and a dichloride,

$BaCl^2$; but no tetrachloride of barium is known, and it is not probable that barium can act as a tetratomic element. How is it, then, that in the dioxide this metal can combine with two atoms of oxygen, while it cannot combine with four atoms of chlorine, which are equivalent to two atoms of oxygen? In other words, what is the atomicity of barium in the dioxide which would seem to correspond to a tetrachloride? It is undoubtedly diatomic in the dioxide as it is in the monoxide, and the constitution of barium dioxide is analogous to that of hydrogen dioxide, which has already been indicated. The two atoms of oxygen mutually satisfy two of their atomicities by combining together, and they retain two which are neutralized in combining with the diatomic atom of barium. Thus, in barium monoxide one atom of oxygen is joined to one atom of barium by both of its atomicities; in the dioxide two atoms of oxygen are united to one atom of barium, each by one atomicity. If we represent the saturation of two atomicities by a straight line, as has before been explained, we will have the following formulæ:

$$Ba{=}O$$

Barium monoxide.



$$\begin{array}{c} Ba \\ \wedge \\ O - O \end{array}$$

Barium dioxide.

In this manner, theory enables us to fix the relations existing between the atoms in a given body.

The comparison may be continued between the other diatomic metals. Magnesium, the radical of magnesia, somewhat resembles calcium in its relations, and forms, as it were, the centre of a group including magnesium, zinc, cobalt, and nickel, and which is called the magnesium group. Manganese and iron, on one hand, and copper, on the other, seem to join this group by certain of their characteristics. In their most stable and generally their most important compounds, these metals act as diatomic elements. All form the dichlorides RCl^2 and the oxides RO. But in other compounds, manganese and iron seem removed from the metals of this group, and resemble chromium and aluminium. Copper, which resembles magnesium in the series of cupric compounds, approaches mercury and silver in the cuprous series.

Bismuth, which might be classed with antimony, and gold are *triatomic* in their most important combinations. They form the chlorides $BiCl^3$ and $AuCl^3$.

A certain number of the metals may be grouped together as *tetratomic*, since they manifest four atomicities in their principal combinations. They are tin, titanium, and zirconium. They form the chlorides RCl^4 and the oxides RO^2. In stannic chloride, $SnCl^4$, the tin is saturated with chlorine, of which it cannot combine with more than four atoms; it is tetratomic in this saturated compound. But it may combine with only two atoms of chlorine, thus forming the chloride $SnCl^2$, which is not saturated, for it can still fix two more atoms of chlorine. Tin only manifests two atomicities in the dichloride.

In the same manner, ferrous chloride, $FeCl^2$, can absorb chlorine, becoming ferric chloride. Above 700° the latter contains one atom of iron and three of chlorine, but just above its temperature of volatilization it appears to contain two atoms of iron united with six of chlorine. The two iron atoms would constitute a hexatomic couple; the same peculiarity is presented by chromium and aluminium.

COMPOUNDS.	CHLORIDES.	OXIDES.	SULPHATES.
Ferric	$FeCl^3$ or Fe^2Cl^6	Fe^2O^3	$Fe^2(SO^4)^3$
Manganic	$MnCl^3$ or Mn^2Cl^6	Mn^2O^3	$Mn^2(SO^4)^3$
Chromic	$CrCl^3$ or Cr^2Cl^6	Cr^2O^3	$Cr^2(SO^4)^3$
Aluminic	$AlCl^3$ or Al^2Cl^6	Al^2O^3	$Al^2(SO^4)^3$

The following table gives a résumé of the constitution of the principal metallic combinations. The metals there chosen as examples have different atomicities.

METALS.	CHLORIDES.	OXIDES.	NITRATES.	SULPHATES.
Monatomic metal—Potassium K' .	KCl	K^2O	KNO^3	K^2SO^4
Diatomic metal—Barium Ba'' . . .	$BaCl^2$	BaO	$Ba(NO^3)^2$	$BaSO^4$
Triatomic metal—Bismuth Bi''' . .	$BiCl^3$	Bi^2O^3	$Bi(NO^3)^3$	$Bi^2(SO^4)^3$
Tetratomic metal—Tin Sn^{iv} . . .	$SnCl^4$	SnO^2		
Hexatomic group—$(Fe^2)^{vi}$	Fe^2Cl^6	Fe^2O^3	$Fe^2(NO^3)^6$	$Fe^2(SO^4)^3$

Such are the principles furnished by the theory of atomicity for a rational classification of the metals.

Mendelejeff's Theory.

Within recent years the labors of a Russian chemist, Mendelejeff, have developed interesting relations between the atomic weights and properties of the elements. He has shown that the properties are functions of the atomic weights, and that the functions are periodic. This relation is not applicable to a limited group of elements, but extends throughout the whole series, and consists not in certain analogies, but in the general physical and chemical properties taken together.

If the elements be arranged in the order of their atomic weights, it will be noticed that these latter increase gradually by only a few units, and also that the properties of the elements are gradually modified with the increase in atomic weights. The modifications are not, however, continuously progressive, but are developed in several series.

The differences between the atomic weights of neighboring elements are not equal, but are nearly so, and where these differences are excessive it is probably owing to the existence of undiscovered elements. Mendelejeff predicted the existence of several such elements, and at least three of the gaps have since been filled by the discovery of gallium, scandium, and germanium. The hypothesis is then certainly worthy of serious consideration in all attempts to classify the elements.

The theory may be best explained by considering an example of the periodicity on which it rests.

Let us study the first fourteen elements after hydrogen in the order of their atomic weights.

Li = 7. Gl = 9. B = 11. C = 12. N = 14. O = 16. F = 19.
Na = 23. Mg = 24. Al = 27. Si = 28. P = 31. S = 32. Cl = 35.5.

We have here two groups, in each of which the change in physical and chemical properties is markedly progressive with the increase in atomic weight. The densities gradually increase to the middle of each series, and then decrease to the end. The atomic volumes, which are the quotients of the atomic weights by the densities, gradually decrease to the middle of the series, and then augment. The volatility also diminishes from sodium to silicon, and again increases to the end of the series.

	Na.	Mg.	Al.	Si.	P.	S.	Cl.
Densities	0.97	1.75	2.67	2.49	1.84	2.06	1.38
Atomic volumes . . .	24	14	10	11	16	16	27

The atomicity, or combining capacity, as indicated by the number of atoms of hydrogen or chlorine with which one atom of the elements combines, displays a similar periodicity.

$LiCl$	$GlCl^2$	BCl^3	CH^4	NH^3	OH^2	FH
$NaCl$	$MgCl^2$	$AlCl^3$	$SiCl^4$	PH^3	SH^2	ClH

The oxygen compounds show a similar progression.

Li^2O	Gl^2O^2	B^2O^3	C^2O^4	N^2O^5	——	——
Na^2O	Mg^2O^2	Al^2O^3	Si^2O^4	P^2O^5	S^2O^6	Cl^2O^7

The number of oxygen atoms with which a constant number of atoms of elements of these series can combine, regularly increases, and the properties of the oxides undergo a gradual modification. Those at the beginning of the series form powerful bases; the intermediate oxides are indifferent, while the latter members form strong acids.

That which characterizes these variations is that they occur in the same manner in the two groups, so that the first member of the first series (Li) corresponds to the first member of the second. These two series form the first two *periods* of Mendelejeff, who has shown that these series or periods can be extended throughout the whole list of elements, and that *the properties of the elements are in periodic relations with their atomic weights.*

The arrangement of the elements in the periodic system is shown in the table on the following page. The horizontal rows, consisting when complete of seven elements, are called periods, while the vertical columns constitute the natural groups. The series are sub-classified according to the number of the line, as odd and even. The members of each group are related by their atomicities, as well as by the isomorphism and some other properties of their compounds, but differ very materially in other respects. The fourth, the sixth, and the tenth periods are each followed by three elements having nearly equal atomic weights, and these nine elements constitute the eighth or transitional group. Hydrogen stands alone. The empty spaces in the table are probably the positions of elements yet to be discovered. The positions of argon and helium are unknown.

MENDELEJEFF'S CLASSIFICATION OF THE ELEMENTS.

SERIES.	GROUP I. R^2O	GROUP II. RO	GROUP III. R^2O^3	GROUP IV. RH^4 RO^2	GROUP V. RH^3 R^2O^5	GROUP VI. RH^2 RO^3	GROUP VII. RH R^2O^7	GROUP VIII. RO^4
1	H = 1							
2	Li = 7.01	Gl = 9.08	B = 10.9	C = 11.97	N = 14.01	O = 15.88	F = 19.06	
3	Na = 23	Mg = 23.94	Al = 27.04	Si = 28	P = 30.96	S = 31.98	Cl = 35.37	
4	K = 39.03	Ca = 39.91	Sc = 43.97	Ti = 48	V = 51.1	Cr = 52	Mn = 54.8	Fe = 55.88, Ni = 58.71, Co = 58.55
5	Cu = 63.44	Zn = 65.1	Ga = 69.9	Ge = 72.3	As = 74.9	Se = 78.87	Br = 79.76	
6	Rb = 85.2	Sr = 87.3	Y = 89.6	Zr = 90.4	Nb = 93.7	Mo = 95.9	………	Ru = 101.4, Rh = 102.7, Pd = 106.91
7	Ag = 107.6	Cd = 111.7	In = 113 4	Sn = 118.8	Sb = 120	Te = 127.7	I = 126.54	
8	Cs = 132.7	Ba = 136.9	La = 138.5	Ce = 137	Di = 145	………	………	……… ……… ………
9	………	………	………	………	………	………	………	
10	………	………	Er = 166	… = 173	Ta = 182	W = 183.6	………	Os = 191, Ir = 192.5, Pt = 194.34
11	Au = 196.6	Hg = 199.8	Tl = 203.7	Pb = 206.39	Bi = 207.5	………	………	
12	………	………	………	Th = 231.96	………	U = 239.8		

The members of the same group possess similar properties, but are unlike the members of the other groups of the same or different series. The atomicity for oxygen increases up to the 8th group, but the equivalence for hydrogen increases up to the 4th, and then diminishes to the 8th. The metallic character is most marked in the first group. After a double series—fourteen elements—come three similar elements whose atomic weights are very close together.

POTASSIUM.

K = 38.82

Potassium was discovered by Sir Humphry Davy in 1807. It ordinarily occurs in commerce in gray, globular masses, readily indented by the finger-nail. It has a dull, tarnished appearance, but when freshly cut it exposes a brilliant surface.

Preparation and Properties.—Potassium is prepared by decomposing potassium carbonate by carbon at a high temperature.

$$\underset{\text{Potassium carbonate.}}{K^2CO^3} + 2C = \underset{\text{Carbon monoxide.}}{3CO} + K^2$$

The mixture is heated to whiteness in an iron retort and the vapors are passed into a copper receiver. The potassium distils and condenses in globules or irregular masses, still containing charcoal. It is purified by redistillation in an iron retort, and is condensed in a copper receiver filled with naphtha. The manufacture of potassium is a dangerous operation, owing to the formation of a very explosive compound of potassium and carbon monoxide, $C^6O^6K^6$ (see page 697). Winkler has proposed a method of preparing the metal which consists in heating a mixture of potassium hydroxide and magnesium.

$$2KOH + Mg = MgO + H^2 + 2K$$

The hydrogen disengaged in this reaction facilitates the distillation of the potassium.

Potassium melts at 62.5° (Bunsen). It boils at a red heat, and its vapor is green. When exposed to the air, it rapidly absorbs oxygen and at the same time decomposes the atmospheric moisture. It inflames at a temperature but slightly elevated and becomes converted into oxide.

If a fragment of this metal be thrown into water, it at once takes fire and rushes about on the surface of the liquid, burning with a violet flame. Finally, it disappears with a little explosion.

This brilliant phenomenon is due to the energy with which potassium decomposes water.

$$2H^2O + K^2 = 2KOH + H^2$$

The hydrogen which is disengaged is inflamed by the incandescent metal. The potassium hydrate formed ultimately dissolves in the water, but its temperature being very high at the moment of its solution, and its combination with the water also producing heat, there results a sudden formation of steam, which gives rise to the little explosion,

POTASSIUM OXIDES.

Potassium peroxide, KO^2 or K^2O^4, is formed when the metal is gently heated in a current of dry oxygen or air. It is an orange-colored substance which becomes darker on heating, and melts at about 280°, forming a dark-brown liquid. With water and with acids this peroxide reacts with violence, oxygen being disengaged, while hydrogen peroxide and potassium hydroxide or potassium salts are also formed.

Potassium monoxide, K_2O, is not known in the pure state. The product resulting from the combustion of the metal in air appears to be a mixture of this oxide and the peroxide.

POTASSIUM HYDROXIDE, OR CAUSTIC POTASH.

This important compound is prepared by boiling 1 part of potassium carbonate with 12 parts of water, and gradually adding milk of lime to the boiling liquid. The lime combines with the carbonic acid, forming an insoluble carbonate, while the potassium hydroxide remains in solution.

$$K^2CO^3 + \underset{\text{Calcium hydroxide.}}{Ca(OH)^2} = \underset{\text{Calcium carbonate.}}{CaCO^3} + 2KOH$$

When the decomposition is finished the liquid is allowed to settle, and the clear solution decanted and rapidly evaporated.

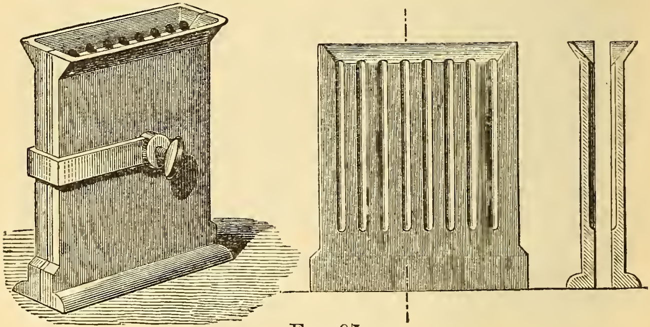


Fig. 97.

The residue is melted in a silver dish and poured out upon flat stone slabs or cast in cylindrical metallic moulds (Fig. 97).

This product is known as *potash by lime*. It is impure. By treating it with alcohol, which dissolves only the potassium hydrate, it may be purified from lime, and the salts of potassium it may contain, and especially the carbonate, which is formed by the absorption of carbonic acid gas from the air during the evaporation. The clear alcoholic solution is decanted, and after the alcohol has been expelled by distillation, the residue is evaporated to dryness and fused in a silver dish. It is known as *potash by alcohol.*

Perfectly pure potassium hydroxide, such as is frequently required in the laboratory, is prepared by double decomposition between potassium sulphate and barium hydroxide, the potassium hydroxide solution being separated by decantation from the insoluble barium sulphate.

$$K^2SO^4 + Ba(OH)^2 = BaSO^4 + 2KOH$$

Recently-fused potassium hydroxide occurs as opaque, white fragments having a short fibrous fracture and a density of 2.1. It melts at a red heat and volatilizes at whiteness; it is not decomposed by heat. When exposed to the air, it absorbs moisture and carbonic acid gas, and deliquesces. It is very soluble in water, and produces heat in dissolving. A hydrate, $KOH + 2H^2O$, is deposited from its hot and very concentrated solution in acute rhombohedra.

Potassium hydroxide is very caustic. It softens and destroys the skin, and for this purpose is employed in surgery as a caustic. It manifests the properties of an *alkali* in the highest degree; these are its solubility in water, its power to neutralize the acids and decompose a great number of metallic solutions, and its corrosive action on the tissues. This alkalinity may be shown by the energy with which the most feeble solutions of potash restore the blue color to reddened litmus, and change to green the tincture of violets.

SULPHIDES OF POTASSIUM.

Potassium will burn in vapor of sulphur. It unites with the latter body in five different proportions, forming the sulphides K^2S, K^2S^2, K^2S^3, K^2S^4, and K^2S^5.

Potassium monosulphide is formed when potassium sulphate is heated to redness in a current of hydrogen, or in a brasqued[1] and covered crucible with charcoal.

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[1] A brasqued crucible is a clay crucible into which powdered charcoal moistened with gum-water has been strongly pressed, and afterwards calcined. The substance to be reduced is placed in a cavity hollowed out in the charcoal.

$$\underset{\text{Potassium sulphate.}}{K^2SO^4} + 4C = 4CO + \underset{\text{Potassium monosulphide.}}{K^2S}$$

A reddish, deliquescent, and caustic mass is thus obtained. When a mixture of sulphur and potassium carbonate is fused, carbon dioxide is disengaged, and a brown mass is obtained on cooling, which is known as liver of sulphur. It is a mixture of *potassium polysulphide* with undecomposed carbonate and potassium sulphate or hyposulphite, according to the temperature and the proportions of sulphur which have been employed. With an excess of sulphur, potassium pentasulphide is obtained. Liver of sulphur dissolves in water with a brown-yellow color.

Potassium pentasulphide and hyposulphite are also formed when potassium hydrate is boiled with an excess of flowers of sulphur. The filtered solution is brown. When treated with hydrochloric acid, it evolves hydrogen sulphide, and finely-divided, yellowish, pulverulent sulphur is deposited.

$$K^2S^5 + 2HCl = 2KCl + H^2S + S^4$$

POTASSIUM CHLORIDE.

KCl

This salt is found crystallized in cubes in the neighborhood of certain fissures of Vesuvius, and in thin layers in the saline deposits at Stassfurt, Prussia, and in other localities. At Stassfurt there is found a double chloride of potassium and magnesium, *carnallite*, $KCl,MgCl^2 + 6H^2O$. When this is dissolved in hot water, the greater part of the potassium chloride is deposited on cooling while the magnesium chloride remains in solution.

Potassium chloride crystallizes in cubes, but it sometimes separates in octahedra from solutions containing free alkali. It is unaltered by the air. Its taste is more bitter than that of sodium chloride; it is more soluble in water than the latter, and produces a greater depression of temperature in dissolving. 1 part of chloride of potassium dissolves in 3 parts of water at 17.5°. 100 parts of water at 0° dissolve 29.23 parts of potassium chloride and 0.2738 additional for each degree of temperature.

POTASSIUM IODIDE AND POTASSIUM BROMIDE.

KI and KBr

These compounds are important on account of their use in medicine and photography. Potassium iodide is obtained by adding powdered iodine to a solution of potassium hydroxide until the latter is completely neutralized. Potassium iodide and iodate are formed, the latter being precipitated. The whole is evaporated to dryness, and the residue heated to redness, by which the iodate is converted into iodide. The mass is dissolved in hot water; on cooling the solution deposits the iodide in fine colorless and transparent crystals. These crystals are opaque if the solution contains any free alkali. They are cubic and anhydrous. They melt at a red heat without decomposition; their taste is salty and somewhat bitter. 100 parts of water at 18° dissolve 143 parts of potassium iodide.

A solution of potassium iodide dissolves iodine abundantly, assuming a dark-brown color.

If nitric acid be added to a solution of potassium iodide, iodine is at once deposited and red vapors are disengaged if the solution be concentrated (page 141).

This decomposition of potassium iodide takes place even in very dilute solutions. It may serve for the detection of the smallest trace of this salt if a solution of starch be previously added to the liquid; in this case a blue color will be produced.

Potassium bromide is prepared by a process similar to that which yields potassium iodide. It crystallizes in cubes which are soluble in about 1.5 parts of cold water.

POTASSIUM NITRATE.

KNO^3

This important salt, long known as nitre and saltpetre, impregnates the soil and sometimes effloresces upon its surface in certain regions of India, Egypt, Persia, Hungary, and Spain. In the United States, it is found in many localities, generally in caverns in limestone rock, called saltpetre caves. It is obtained by lixiviating the earthy matters containing it and evaporating the solution.

It is less abundant in northern climates. It is formed wherever nitrogenized organic substances decompose in presence of potash. Thus, it exists in small quantities in the soil of cellars, in moist walls, and in old crumbling mortar. In these cases it is mixed with a certain quantity of sodium nitrate and a large excess of calcium and magnesium nitrates. Formerly such materials were lixiviated to obtain the nitrates, all of which were then converted into potassium nitrate. Nitre is also manufactured artificially by exposing to the air mixtures of animal matters with wood-ashes and lime which are frequently moistened with stale urine or stable-drainings. By far the greater part of the saltpetre of commerce is now obtained from sodium nitrate, of which vast deposits occur in Chili and Peru.

The conversion of this *Chili saltpeter*, as it is called, into potassium nitrate is effected as follows. The recrystallized sodium nitrate is dissolved in water, and an equivalent molecular quantity of potassium chloride (obtained from Stassfurt salt) is added. The solution is boiled down until it attains a density of 1.5, when the *hot* liquid deposits sodium chloride, which is separated, and potassium nitrate crystallizes on cooling.

Properties.—This salt crystallizes from its aqueous solution in long, six-sided prisms, terminated by six-sided pyramids. Generally these crystals are grooved or striated. They belong to the orthorhombic system. Their taste is cooling and slightly bitter.

Potassium nitrate melts at about 350°; at a higher temperature it disengages oxygen and is converted into potassium nitrite, KNO^2, which is in its turn decomposed at a red heat, leaving a mixture of oxide and peroxide of potassium.

Potassium nitrate is very soluble in hot water: 100 parts of water at 0° dissolve only 13.32 parts of the salt, but at 18° they dissolve 29 parts; at 97°, 236 parts; and at 100°, 246 parts.

The facility with which potassium nitrate parts with its oxygen, of which it contains nearly half its weight, renders it an energetic oxidizer of many bodies.

If a small quantity of pulverized saltpetre be thrown upon glowing coals, the salt melts and decomposes, increasing the combustion at the point of contact with the fuel: it is said to deflagrate. The nitrate becomes converted into carbonate.

Ordinary black gunpowder is an intimate mixture of nitre, charcoal, and sulphur. Its average composition is 75 per cent. of nitre, 15 of charcoal, and 10 of sulphur. The combustion of this mixture is instantaneous, and gives rise to the sudden formation of gaseous products. The decomposition may be expressed generally by stating that the charcoal combines with the oxygen of the nitre to form carbon dioxide and carbon monoxide; the nitrogen is liberated, and the sulphur combines with the potassium, forming potassium sulphide. As the mixture contains all the oxygen necessary for its complete combustion, the latter can be effected in a limited and closed space. It can readily be understood that the explosive energy of the powder is due to a sudden evolution of gas occupying many times the volume of the powder, and of which the volume is still further augmented by the high temperature.

POTASSIUM SULPHATE.

K^2SO^4

This salt is obtained as a by-product in various industrial operations. It deposits from the mother-liquors of the soda from sea-weed when these are exposed to low temperatures. It may be made by saturating with potassium carbonate the potassium acid sulphate which is formed in the preparation of nitric acid by the decomposition of potassium nitrate with sulphuric acid, a process which is now but little employed.

It crystallizes in four-sided prisms or in double, six-sided pyramids belonging to the orthorhombic system. These crystals are hard, anhydrous, unaltered by the air, and melt at a red heat without decomposition. They are but slightly soluble in water and insoluble in absolute alcohol. 100 parts of water at 0° dissolve 8.36 parts, and 0.1741 part for each additional degree of heat.

POTASSIUM ACID SULPHATE.

$$\left.\begin{matrix}K\\H\end{matrix}\right\}SO^4$$

This salt may be obtained by fusing 13 parts of the neutral sulphate with 8 parts of concentrated sulphuric acid. The saline mass is dissolved in boiling water, and the solution when properly concentrated deposits rhombic octahedra or tabular crystals belonging to the orthorhombic system.

Potassium acid sulphate is much more soluble in water than the neutral salt; its solution is acid. When strongly heated, it first gives up water and then sulphuric oxide, leaving a residue of neutral sulphate.

POTASSIUM CHLORATE.

$KClO^3$

This salt is formed, together with potassium chloride, by the action of chlorine upon a concentrated solution of potassium hydrate or carbonate:

$$6Cl + 6KOH = KClO^3 + 5KCl + 3H^2O$$

It is less soluble than the chloride, and is consequently deposited in great part as the solution becomes saturated with chlorine. It is purified by several recrystallizations.

On a large scale it is obtained by the action of chlorine on milk of lime, and decomposing the resulting calcium chlorate with potassium chloride.

$$6Ca(OH)^2 + 6Cl^2 = Ca(ClO^3)^2 + 5CaCl^2 + 6H^2O$$

and

$$Ca(ClO^3)^2 + 2KCl = CaCl^2 + 2KClO^3.$$

Another process, recently introduced, depends upon the fact that an aqueous solution of potassium chloride is decomposed by the electric current into chlorine and potassium hydroxide which, under suitable conditions, will react and form the chlorate.

Potassium chlorate crystallizes in colorless, monoclinic tables. When very thin they present an iridescent reflection. It melts at 360°, and at a higher temperature is decomposed into oxygen and chloride and perchlorate of potassium, the latter of which is also decomposed when the temperature is raised still further.

$$2KClO^3 = KCl + KClO^4 + O^2$$
$$KClO^4 = KCl + O^4$$

Potassium chlorate deflagrates when thrown upon hot coals; when mixed with sulphur, it explodes by friction or percussion; the detonation becomes dangerous if the sulphur be replaced by phosphorus.

It is not very soluble in cold water. 100 parts of water at 0° dissolve 3.3 parts, and at 24°, 8.44 parts. It is much more soluble in boiling water.

POTASSIUM PERCHLORATE.

$KClO^4$

This salt is formed by the action of either heat or sulphuric acid upon potassium chlorate (page 134). It is but slightly soluble in water, requiring 65 parts at 15° for its solution. It crystallizes in anhydrous and transparent right rhombic prisms. Above 400° it decomposes into potassium chloride and oxygen.

POTASSIUM CARBONATES.

Potassium Neutral Carbonate, K^2CO^3.—This carbonate is found in commerce under the simple name potash, and is known according to its source as Russian or American potash.

It is obtained by lixiviating wood ashes; that is, exhausting them with water, evaporating the solution to dryness, and calcining the residue in the air. The potash thus obtained is impure carbonate mixed with other salts of potassium, principally the chloride and sulphate, and small quantities of silicate. It contains from 60 to 80 per cent. of carbonate.

Potassium carbonate is now manufactured from the native chloride, Stassfurt salt, by a process similar to that which will be described for the manufacture of sodium carbonate from common salt.

Pure potassium carbonate may be prepared by calcining potassium acid tartrate, or cream of tartar, at a red heat. A black mass is thus obtained from which water dissolves pure potassium carbonate, and the solution is evaporated to dryness.

Neutral potassium carbonate is very soluble in water, and absorbs moisture from the air. 1 part of the anhydrous salt dissolves in 1.05 parts of water at 3°, and in 0.49 parts at 70° (Osann). The solution has a decided alkaline reaction. A very concentrated hot solution deposits rhombic octahedra containing $K^2CO^3 + 2H^2O$ on cooling.

Potassium Acid Carbonate, $KHCO^3$.—When a current of carbonic acid gas is passed into a concentrated solution of potassium neutral carbonate, the gas is absorbed, and crystals of potassium acid carbonate, ordinarily known as bicarbonate of potash, are formed.

It represents carbonic acid in which a single atom of hydrogen is replaced by an atom of potassium.

$$\begin{aligned} CO^2 + H^2O &= H^2CO^3 \text{ carbonic acid (hypothetical).} \\ CO^2 + KHO &= \left.\begin{matrix} K \\ H \end{matrix}\right\} CO^3 \text{ potassium acid carbonate.} \\ CO^2 + K^2O &= K^2CO^3 \text{ potassium carbonate.} \end{aligned}$$

Potassium acid carbonate readily crystallizes in monoclinic prisms. It is much less soluble in water than the neutral carbonate, and its solution disengages carbonic acid gas on boiling. Its reaction is alkaline.

Characters of Potassium Salts.—The salts of potassium communicate a violet tint to flame. Their solutions are not precipitated either by hydrogen sulphide, ammonium sulphide, or sodium carbonate.

Perchloric acid occasions a white precipitate of potassium perchlorate.

Platinum tetrachloride produces a yellow, crystalline precipitate of platinum and potassium double chloride, $2KCl.PtCl^4$.

Hydrofluosilicic acid forms a white, gelatinous precipitate consisting of potassium fluosilicate.

SODIUM.

$Na = 22.88$

Sodium was discovered by Sir Humphry Davy in 1807. It was formerly obtained by a process analogous to that described for the preparation of potassium. An intimate mixture of sodium carbonate and charcoal was heated to whiteness in cast-iron cylinders, and the sodium vapor condensed in suitable vessels, carbon monoxide being disengaged.

$$Na^2CO^3 + 2C = 2Na + 3CO$$

For a number of years also the metal of commerce was manufactured by the more economical processes of Castner and Netto, in both of which it is extracted from sodium hydroxide. In Castner's process the reduction is effected by strongly heating a mixture of the hydroxide and carbide of iron, CFe^2.

$$6NaOH + 2C = 2Na^2CO^3 + 3H^2 + 2Na$$

That of Netto consists in allowing fused caustic soda to trickle over incandescent charcoal contained in an iron retort. The sodium carbonate, formed as in the preceding equation, is drawn off at the bottom of the retort, while the metal is distilled.

At the present time the bulk of the sodium of commerce is produced by electrolysis of fused sodium chloride.

$$2NaCl = 2Na + Cl^2$$

The salt used for this purpose is mixed with other chlorides—those of potassium and strontium are generally employed—in order to lower its melting point sufficiently to prevent the formation of a subchloride of sodium, and thus to increase the yield of metal.

Sodium is soft at the ordinary temperature. It has a silvery lustre, melts at 96°, and boils at 742°. Its affinity for oxygen is less powerful than that of potassium; it can be melted in the air without taking fire. When thrown upon water, it melts and runs around on the surface, producing a hissing noise. The water is decomposed with disengagement of hydrogen and the formation of sodium hydroxide. The reaction is analogous to that of potassium upon water, but is less energetic; frequently, however, it terminates by an explosion.

When sodium is heated in a current of hydrogen, and the temperature maintained at 300°, the gas is absorbed, *sodium hydride*, Na^2H, being formed. This compound has the appearance of silver, and a density of 0.96; at 240° it breaks up into its elements.

OXIDES AND HYDROXIDE OF SODIUM

Two oxides of sodium are known, a monoxide, Na^2O, and a dioxide, NaO or Na^2O^2. The former has not been obtained in the pure state, but is probably one of the products of the action of metallic sodium upon the hydroxide.

$$2Na + 2NaOH = 2Na^2O + H^2$$

Sodium hydroxide, $NaOH$, is frequently employed in the laboratory and in the arts under the name *caustic soda*. It is prepared by decomposing a rather dilute, boiling solution of sodium carbonate by milk of lime, in the manner described for the preparation of potassium hydroxide (page 298). It occurs as a white solid, which attracts moisture and carbonic acid from the air, and finally becomes transformed into a dry mass of carbonate. Sodium hydroxide is freely soluble in water, and is very caustic. It is known in commerce as *concentrated lye*.

Commercial caustic soda contains many impurities. The chemically pure hydroxide is best obtained by the action of metallic sodium upon water. For this purpose *very small* quantities of water and sodium are alternately introduced in a well-cooled and capacious silver dish. The resulting solution is evaporated by heating, and the fused residue cast into moulds.

Sodium dioxide, Na^2O^2 (sodium peroxide), is now produced on a commercial scale by heating the metal to 300° in a mixture of nitrogen and oxygen gases in which the proportion of the latter is gradually increased. It is a yellowish substance, and acts as a powerful oxidizing agent. Water decomposes it into hydrogen dioxide and sodium hydroxide. Its chief use is for bleaching silk and wool.

SODIUM SULPHIDE AND HYDROSULPHIDE.

Sodium sulphide, Na^2S, is prepared by the following process: A concentrated solution of sodium hydroxide is divided into two equal parts; one part is then saturated with hydrogen sulphide, sodium hydrosulphide being formed.

$$\underset{\text{Sodium hydroxide.}}{NaOH} + H^2S = \underset{\text{Sodium hydrosulphide.}}{NaSH} + H^2O$$

To this hydrosulphide the other portion of sodium hydroxide is added, and the solution is concentrated out of contact with the air. Hydrated crystals of sodium sulphide are deposited.

$$NaSH + NaOH = H^2O + Na^2S$$

These crystals are rectangular prisms terminated by four-faced points. When pure, they are colorless; they are very soluble in water.

SODIUM CHLORIDE.

$NaCl$

This body is common salt, or sea-salt. It is widely diffused in nature. It is found in the solid state, as rock-salt, in large deposits in many countries.

Sea-water contains a large proportion of sodium chloride, and this salt also exists in a number of mineral waters, of which it forms the most abundant constituent.

Much of the salt of commerce is obtained by the evaporation of sea-water along the Mediterranean. The water is led into basins, where it forms a shallow layer, which is continually swept by the summer winds. It thus becomes concentrated, and is kept in motion from one basin to another, until it arrives in the areas where the salt is deposited. In many localities salt is obtained by direct mining operations; more frequently, however, the crude salt is first dissolved in water, and after the insoluble residue has been separated the brine is evaporated. Thus, in Cheshire, England, bore-holes are sunk down to the salt bed, water is turned into these holes, and after it has become saturated with salt is pumped up and evaporated.

Sodium chloride is also obtained by the evaporation of the waters of brine springs. The operation is conducted in large sheet-iron boilers; the salt crystallizes from the hot liquid, and a double sulphate of calcium and sodium, which is but slightly soluble, incrusts the basins in the course of time.

Sodium chloride crystallizes from its aqueous solution in cubes. The crystals are generally small, and a great number of them frequently become agglomerated in symmetrical hopper-like masses (Fig. 99). These crystals are anhydrous, but contain a small quantity of interposed water; when heated they decrepitate, because this water is volatilized and suddenly separates the crystals. Sodium chloride fuses at a red heat and solidifies to a crystalline mass on cooling. It volatilizes at a white heat. It is very soluble in water, and its solubility increases only slightly with the temperature. According to Gay-Lussac,

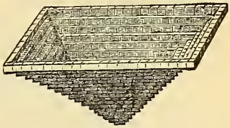


FIG. 99.

1 part of common salt dissolves in			2.78	parts of water at		14°
"	"	"	2.7	"	"	60°
"	"	"	2.48	"	"	109.7°

The saturated solution boils at 109.7°; its density at 8° is 1.205. Sodium chloride is insoluble in absolute alcohol.

SODIUM SULPHATE (Glauber's Salt).

Na^2SO^4

This salt is obtained in the arts by decomposing common salt with sulphuric acid (page 127).

This operation, which constitutes the first step in the manufacture of sodium carbonate, is conducted in a reverberatory furnace, connected with a suitable apparatus for the condensation of the hydrochloric acid which is disengaged. Sodium acid sulphate is first formed, and at a higher temperature this reacts upon another molecule of sodium chloride.

$$\underset{\text{Sodium acid sulphate.}}{\left.\begin{matrix}Na\\H\end{matrix}\right\}SO^4} + NaCl = \underset{\text{Sodium sulphate.}}{Na^2SO^4} + HCl$$

Sodium sulphate is now extensively produced by subjecting the mother-liquors from the manufacture of salt from sea-water to intense cold.

It crystallizes from water in four-sided, oblique rhombic prisms, containing 10 molecules of water of crystallization;

these crystals effloresce in the air. They possess a bitter, salty, and disagreeable taste. They are very soluble in water, and the temperature of their maximum solubility is 33°. According to Gay-Lussac,

100 parts	of water at	0°	dissolve	12	parts of	sodium sulphate.
"	"	18°	"	48	"	"
"	"	25°	"	100	"	"
"	"	33°	"	332.6	"	"
"	"	50°	"	263	"	"

When the solution saturated at 33° is heated, it deposits anhydrous sodium sulphate in orthorhombic octahedra, analogous to the anhydrous sodium sulphate found in nature (*thenardite*).

Sodium Acid Sulphate, $\left.\begin{matrix}Na\\H\end{matrix}\right\}SO^4$.—This salt may be obtained by dissolving in water the requisite proportions of sodium neutral sulphate and sulphuric acid. On cooling the saturated solution, oblique rhombic prisms are obtained, which, according to Mitscherlich, contain two molecules of water of crystallization. These crystals are very soluble in water, and have an acid taste. Alcohol decomposes them into sulphuric acid, which dissolves, and neutral sulphate, which precipitates.

SODIUM CARBONATE.

Na^2CO^3

This important salt, known also as *soda* and *soda ash*, is manufactured on an immense scale in the arts. It is used in the manufacture of soap and glass, for washing, and many other purposes. It was formerly obtained from the ashes of fuci, algæ, and other sea-plants which furnished Alicant soda. It is now most generally prepared from sodium chloride. One process, which is due to Le Blanc, consists of three distinct operations: 1st, the transformation of the sodium chloride into sulphate by sulphuric acid; 2d, the conversion of the sulphate into carbonate by calcination with a mixture of chalk and coal; 3d, lixiviation of the calcined mass and evaporation of the solution. Only the latter two operations need be described here: they are conducted in reverberatory furnaces, of which the doubly-arched roofs are licked by the flame of the combustible (Fig. 100).

A mixture of 1000 parts of sodium sulphate, 1040 parts of chalk, and 580 parts of coal is first introduced into compartment B of the furnace, where it is dried. It is then transferred to compartment A, where the temperature is very elevated, and where the sodium sulphate is reduced to sulphide by the coal. The sodium sulphide and chalk react upon each other, forming sodium carbonate and calcium sulphide (Kolb).

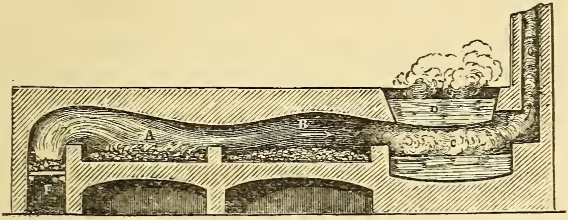


FIG. 100.

The results of the reaction may be expressed by the following equation:

$$Na^2SO^4 + CaCO^3 + C^4 = Na^2CO^3 + CaS + 4CO$$

There are, however, certain secondary reactions which take place at the same time; thus, a certain quantity of sodium oxide is formed by the action of the coal upon the carbonate.

$$Na^2CO^3 + C = 2CO + Na^2O$$

When the incandescent mass has become pasty, it is removed from the furnace, reduced to powder, and thoroughly lixiviated. The water dissolves the sodium carbonate, and leaves the insoluble calcium sulphide, which remains mixed with the lime produced by the decomposition of the excess of chalk employed (Gossage, Scheurer-Kestner). The solutions are concentrated in the boiler D, heated by the waste heat from the soda furnace. Finally, they are drawn off into the compartment C, where they are evaporated to dryness. The soda ash of commerce is thus obtained. When the properly-concentrated solution is allowed to cool, the crystallized soda (washing soda) of commerce is deposited.

Another process, known as the *ammonia-soda* process, has not only entered into successful competition with that of Leblanc, but appears to gradually supersede it. It is also known as Solvay's process.

It depends upon the double decomposition which takes place between ammonium acid carbonate and sodium chloride in concentrated aqueous solution.

$$NaCl + (NH^4)HCO^3 = NH^4Cl + NaHCO^3$$

The sodium acid carbonate, which is but slightly soluble, is precipitated; it is collected and converted into the neutral carbonate by the action of heat.

$$2NaHCO^3 = Na^2CO^3 + CO^2 + H^2O$$

It thus loses half of its carbonic acid, which is utilized for the preparation of a new quantity of ammonium acid carbonate. The other portion of the carbonic acid necessary for this operation is produced by the calcination of lime-stone (calcium carbonate), which at the same time yields the lime necessary for the liberation of the ammonia contained in the mother-liquor in the form of ammonium chloride.

A considerable quantity of sodium carbonate is also manufactured from *cryolite*, which is a double fluoride of sodium and aluminium, and of which large deposits exist in Greenland. The mineral is calcined with lime, calcium fluoride and aluminate of soda being formed.

$$\underset{\text{Cryolite.}}{2AlF^3.3NaF} + 6CaO = \underset{\text{Calcium fluoride.}}{6CaF^2} + \underset{\text{Aluminate of soda.}}{Al^2O^3,3Na^2O}$$

The latter compound is dissolved out by water and decomposed by carbonic acid gas, aluminium hydroxide being precipitated and sodium carbonate remaining in solution.

Sodium carbonate crystallizes in monoclinic prisms, containing 10 molecules of water of crystallization. When heated, they fuse in this water of crystallization, which they then abandon; they also lose it by efflorescence when exposed to the air.

Sodium carbonate is very soluble in water, and the solution has a strongly alkaline reaction. According to Poggiale,

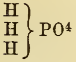
100 parts	of water at	0°	dissolve	7.08	parts of	sodium carbonate.
"	"	10°	"	16.06	"	"
"	"	20°	"	25.93	"	"
"	"	25°	"	30.83	"	"
"	"	30°	"	35.90	"	"
"	"	104.6°	"	48.5	"	"

The saturated solution boils at 104.6°. Sodium carbonate is insoluble in alcohol.

Sodium Acid Carbonate, $NaHCO^3$.—When carbonic acid gas is passed into a solution of sodium carbonate or over crystals of that salt, the gas is absorbed and sodium acid carbonate, commonly called bicarbonate of soda, is formed. This salt crystallizes in oblique, four-sided prisms, shortened into the form of tables. Its taste is salty and slightly alkaline. It is less soluble in water than the neutral carbonate. It restores the blue color to reddened litmus; its solution does not precipitate that of magnesium sulphate, and when boiled loses carbonic acid, neutral carbonate being formed.

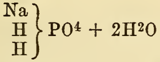
PHOSPHATES OF SODIUM.

There are three phosphates of sodium derived from ordinary or otho-phosphoric acid.



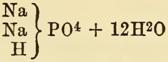
$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}PO^4$$

Phosphoric acid.



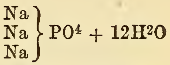
$$\left.\begin{matrix}Na\\H\\H\end{matrix}\right\}PO^4 + 2H^2O$$

Monosodium phosphate.



$$\left.\begin{matrix}Na\\Na\\H\end{matrix}\right\}PO^4 + 12H^2O$$

Disodium phosphate.



$$\left.\begin{matrix}Na\\Na\\Na\end{matrix}\right\}PO^4 + 12H^2O$$

Trisodium phosphate.

Monosodium phosphate reddens blue litmus; the disodium and trisodium salts have an alkaline reaction. The most important in the arts and in commerce is disodium phosphate, or common phosphate of soda. It is prepared by neutralizing the calcium acid phosphate, obtained by digesting bone-dust with dilute sulphuric acid and filtering, with sodium carbonate. Tricalcium phosphate is precipitated, and disodium phosphate remains in solution. By evaporation of the filtered liquid, the salt may be obtained in voluminous, transparent, monoclinic prisms, containing 12 molecules of water of crystallization. Monosodium phosphate exists in urine, and is the cause of the normal acidity of that excretion.

SODIUM BORATE, OR BORAX.

$Na^2B^4O^7$

This salt corresponds to tetraboric acid, containing $2B^2O^3 + H^2O = H^2B^4O^7$. It results from the action of one molecule of sodium oxide upon two molecules of boric oxide.

$$2(B^2O^3) + Na^2O = Na^2B^4O^7$$

It crystallizes with either 10 or 5 molecules of water.

Borax was formerly obtained from Asia, where it exists in solution in the waters of certain lakes. By the evaporation of these waters a product known as *tinkal* was obtained; this is natural borax. Part of the borax of commerce is obtained by saturating the boric acid of Tuscany with sodium carbonate, and evaporating the solution below 56°. Borax is found in abundance in certain lakes in California, and large quantities are now derived from the naturally occurring borates of calcium (*colemanite* and *borocalcite*) and magnesium (*boracite*). These yield borax by double decomposition with sodium carbonate. When a concentrated boiling solution of borax is allowed to cool, it deposits between 79° and 56° regular octahedral crystals containing 5 molecules of water of crystallization; below 56° the crystals deposited are rhombic prisms and contain 10 molecules of water. The latter form is that found in commerce. Borax solution is faintly alkaline.

When borax is heated, it melts in its own water, swells up and becomes dry, and then undergoes igneous fusion. Melted borax dissolves a large number of oxides, forming borates. On solidifying, the color and appearance of a number of these are highly characteristic. For this reason borax is a valuable agent in analysis. Anhydrous borax dissolves in 12 parts of cold and 2 parts of boiling water.

Borax possesses antiseptic properties and is used as a preservative.

Characters of Sodium Salts.—Sodium salts are not precipitated from their solutions by either hydrogen sulphide, ammonium sulphide, sodium carbonate, or platinic chloride. Hydrofluosilicic acid forms with them a white precipitate. A solution of potassium antimonate produces a white precipitate of sodium antimonate (Fremy).

Sodium salts impart a yellow color to non-luminous flames.

A small quantity of alcohol may be ignited in a saucer and will burn with an almost colorless flame, but the introduction of a small quantity of sodium hydrate, chloride, or any other sodium compound, at once colors the flame bright yellow.

This character is very sensitive, and the smallest trace of sodium may thus be recognized by introducing a platinum wire, dipped into the substance to be tested, into the colorless flame of the blow-pipe or of a Bunsen burner.

LITHIUM.

$Li = 6.97$

In 1817, Arfvedson, a Swedish chemist, discovered a new alkali, lithia, which is the hydroxide of lithium, LiOH, analogous to potassium hydroxide, KOH. To this hydroxide corresponds an oxide, Li^2O, and a chloride, LiCl. Bunsen was the first to obtain the metal lithium, which he prepared by electrolysis of the fused chloride. It is a silvery-white metal, but its surface rapidly tarnishes in the air. It is the lightest of the solid elements, its density being between 0.578 and 0.589. It melts at 180°. It is less oxidizable than either sodium or potassium. When heated above its point of fusion in the air or in oxygen, it burns with a brilliant white flame. It decomposes water at ordinary temperatures, but without melting like sodium.

The salts of lithium are soluble in water, but the carbonate and phosphate only slightly so. There exists also a double phosphate of sodium and lithium, which is but slightly soluble. The salts of lithium communicate a red color to the flame of alcohol or of the Bunsen burner.

The compounds of lithium are generally prepared from *lepidolite*, *triphyline*, *amblygonite*, or *spodumene*, minerals of complex composition containing small amounts of the element in the form of silicate or phosphate.

CÆSIUM AND RUBIDIUM.

SPECTRUM ANALYSIS.

Cæsium and rubidium are two alkaline metals discovered by Kirchhoff and Bunsen in 1860–61, by the aid of a new method of analysis. This method consists in the examination of spectra; hence the name spectrum analysis.

The solar spectrum formed upon a screen which intercepts a beam of solar light refracted by passage through a prism, consists of a series of colored bands. The different simple rays of which white light is composed are unequally refracted by the prism, and separate from each other on their emergence. The violet rays, which are farthest turned from their original direction, form the most deviated extremity of the spectrum.

The red rays, which are the least refracted, form the least deviated extremity. The visible spectrum of solar light presents not only a succession of variously-colored bands; when it is closely examined by the aid of magnifying instruments, it is found that the succession is not continuous, but that the luminous bands are traversed by dark lines. These lines, which were discovered by Wollaston and studied by Fraunhofer, are very numerous, and are irregularly distributed throughout the spectrum, from the red to the violet, but each one of them occupies a definite position, and for the principal lines that position has been determined by exact measurements. Fraunhofer designated them by the letters A, B, C, D, E, F, G, H. The D line is the most distinct of all: its place is in the yellow. Other lights, the stars, for example, give similar discontinuous spectra. On the contrary, an incandescent platinum wire, or any other luminous source which contains no volatile matter, gives a continuous spectrum.

Very interesting facts are observed when the sources of light are flames into which the vapors of volatile substances, particularly the metallic salts, are introduced. The spectra of such flames are formed exclusively of brilliant lines (see plate).

If a platinum wire which has been dipped into a solution of sodium chloride be introduced into the colorless flame of a Bunsen burner, the flame will assume a yellow color, and will give a visible spectrum, but one which is very incomplete, since it consists of a single yellow line. It has been found that this line exactly coincides with the dark line D, existing in the yellow of the solar spectrum. This line characterizes sodium in all of its compounds: it is the spectrum of sodium.

In the same manner, a flame into which a compound of potassium, lithium, barium, calcium, or other volatile metal is introduced, will give for each metal a particular spectrum formed of variously-colored lines. Each is perfectly characterized by the number, color, and position of the lines. Barium gives the most numerous and the widest lines; other metals give more complicated spectra. That of iron is composed of 70 brilliant lines.

Kirchhoff and Bunsen, who discovered these facts, made a happy application of them to analysis. To detect the presence of a metal in a compound or even in a mixture, a small portion of the substance is introduced into a colorless gas flame, and the spectrum then given by the flame is observed by the aid of an instrument called a spectroscope. The light to be examined is caused to pass through a narrow rectangular slit before falling on the prism. The image of the slit is then refracted to its own peculiar place in the spectrum.

The method is so sensitive that $\frac{1}{3,000,000}$ of a milligramme of sodium chloride will render the yellow sodium line distinctly visible. The discovery of two new metals, cæsium and rubidium, crowned the brilliant researches of Kirchhoff and Bunsen.

Since then, a number of new metals have been discovered by the aid of spectrum analysis: thallium, which gives a green line, indium, which gives an indigo-blue line, gallium, which gives two violet lines very close together, and several others which will be mentioned farther on. Spectrum analysis has been useful also in the discovery and characterization of the new gaseous elements, argon, helium, and krypton.

SILVER.

Ag (Argentum) = 107.11

Natural State.—Silver is found native and in combination in many minerals. Among these are the sulphide, the sulphantimonides and sulpharsenides, the antimonide, chloride, bromide, iodide, selenide, telluride, and lastly an amalgam of silver. It is found in small proportions in many galenas and copper pyrites.

Treatment of Silver Ores.—According to the nature of the ores the extraction of the silver is effected in the dry way or the wet way.

Argentiferous galena is reduced as described under lead, and the metal which contains all the silver is remelted and subjected to the process of cupellation (page 345), whereby the lead is removed as oxide, and the silver remains in the metallic state.

In case the lead contains but a very small proportion of silver, a process devised by Parkes is employed; it depends on the fact that when melted lead containing silver is agitated with a small proportion of zinc, the latter metal dissolves out all the silver, and the resulting alloy rises to the surface in the form of a scum. This is readily collected and the zinc and lead are removed, the first by distillation, the last by cupellation.

When the silver ore is free from lead, the extraction of the silver may be accomplished by means of mercury; an amalgam of silver is formed from which the mercury is separated by distillation.

Mexican Amalgamation or Patio Process.—American silver ore consists of sulpharsenide and sulphantimonide of silver, mixed with silver chloride and native silver, the whole being disseminated in silica, calcium carbonate, and ferric oxide. In Mexico, the following primitive process is still used. The finely-pulverized ore is mixed with two per cent. of common salt and thrown into circular areas paved with flag-stones, where it is rendered homogeneous by being trodden for several hours by mules. About one per cent. of copper pyrites which has been roasted in the air and contains cupric sulphate is then added. The latter salt reacts with the sodium chloride, forming sodium sulphate and cupric chloride, which latter decomposes the silver sulphide, forming silver chloride and cupric sulphide. Mercury is then added and reduces the silver chloride, with formation of chloride of mercury and metallic silver. During the whole time the mass is continually trodden by the mules, and the mercury comes in contact with the disseminated silver: the amalgam formed solidifies in about a fortnight. A second and finally a third addition of mercury is then made until 7 or 8 parts of that metal have been employed for one part of silver to be extracted. After a few months, the operation is terminated, and the mass is washed with large quantities of water to remove the earthy and salty matters. The amalgam remains, and is heated in order to extract the silver.

American or Washoe Process.—The above method of extraction is too slow to be employed for the vast quantities of silver ore that are mined on the Pacific Slope. The ore is there crushed and roasted with sodium chloride and a small proportion of cupric sulphate, in furnaces of a peculiar construction. By this means all of the silver is converted into chloride. The mass is made into a pulp with water and agitated with mercury in large tanks or "pans." The silver chloride is reduced as before, and the amalgam obtained is first squeezed out and afterwards heated to expel the mercury. To this end it is placed in horizontal iron retorts (Fig. 102), which are heated to cherry redness. The mercury distils and is collected under water, while an impure silver remains.

Silver may also be extracted in the wet way. The Patera process, which is applicable to sulphide ores, consists in transforming the silver into chloride by roasting the ore with salt, and lixiviating the product with sodium thiosulphate. Sulphide of silver is then precipitated by adding an alkaline sulphide to the solution.

Ziervogel's process depends on the conversion of sulphide of silver into sulphate by roasting the ore in the air. Upon treating the mass with hot water, the silver sulphate passes into solution, from which the metal may be precipitated by metallic copper.

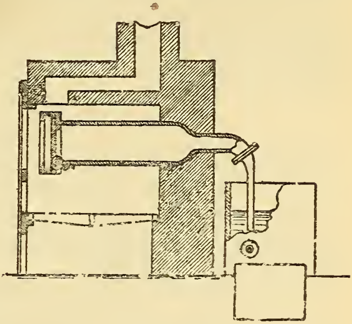


FIG. 102.

Properties.—Silver is the whitest and most brilliant of all the ordinary metals. Next to gold, it is the most malleable and the most ductile. Its density is 10.5. It is the best conductor of heat and electricity.

It melts towards 1000°, and when fused has the curious property of dissolving oxygen, of which it absorbs 22 times its volume. On solidifying, it again disengages the gas; this phenomenon, which occasionally causes the projection of portions of silver, is called *spitting*. Silver volatilizes at the high temperatures of the oxyhydrogen blow-pipe and the electric furnace. Its vapor is green.

It is unaltered by the air. In the presence of moisture, it is acted upon by ozone, being converted into the peroxide, AgO or Ag^2O^2.

It decomposes concentrated solution of hydriodic acid, disengaging hydrogen and forming silver iodide (Deville). Hydrochloric acid only attacks it superficially. Hydrogen sulphide blackens it, forming a pellicle of silver sulphide. Its best solvent is nitric acid which attacks it in the cold, yielding silver nitrate and disengaging red vapors.

The alkalies have no action upon silver; for this reason, silver vessels are used for fusing potassium hydroxide and concentrating its solution.

By precipitating silver solutions with various reducing agents, under peculiar circumstances, Carey Lea has obtained interesting allotropic forms of silver, red, blue, and gold in color, and having a high degree of lustre. They are readily reconverted into ordinary silver.

SILVER OXIDE.

Ag^2O

The only important oxide of silver is the monoxide, which is precipitated in the anhydrous state when potassium hydrate, free from chloride, is added to a solution of silver nitrate.

It forms an olive-brown, flocculent deposit which yields a brown powder on drying.

Silver oxide is readily decomposed by heat into silver and oxygen. It is reduced by hydrogen at a temperature below 100°. When recently precipitated, it is slightly soluble in water. It is an energetic base, perfectly neutralizing the acids, and displacing cupric oxide from the cupric salts.

When oxide of silver is digested with ammonia it is converted into a very explosive, black powder, known as fulminating silver. It appears to be the nitride Ag^3N.

SILVER SULPHIDE.

To the oxide of silver corresponds the sulphide Ag^2S, which occurs native, as *argentite*, crystallized in regular octahedra, ordinarily modified by facettes. It is soft and can be scratched by the finger-nail. Silver and sulphur combine readily by the aid of heat.

SILVER CHLORIDE.

$AgCl$

This body is found native and is known to mineralogists as *horn-silver*. It is sometimes found crystallized in cubes and octahedra. It is formed directly when silver is heated in chlorine gas, and is prepared by double decomposition by adding hydrochloric acid or a solution of sodium chloride to solution of nitrate of silver. A white, curdy precipitate is thus obtained, which assumes a violet tint when exposed to the action of light. The change of color is due to partial decomposition.

Silver chloride melts at about 260°, and solidifies on cooling to a gray, horn-like mass that can be cut with a knife.

If recently precipitated and moist silver chloride be placed upon a sheet of zinc, in a short time a dark color will appear on the borders of the chloride, and the whole of that body will soon be converted into a dark-gray powder of finely-divided silver. Zinc chloride is at the same time formed.

This reaction takes place much more rapidly if the silver chloride be moistened with hydrochloric acid. In this case the reduction is effected by nascent hydrogen produced by the action of the hydrochloric acid on the zinc.

When silver chloride is fused with the alkaline hydrates or carbonates, it is reduced to metallic silver: oxygen is disengaged, and an alkaline chloride is formed.

Recently-precipitated silver chloride dissolves readily in aqueous ammonia. When dry, it absorbs ammonia gas abundantly, and Faraday employed this compound for the preparation of liquid ammonia.

Silver chloride dissolves also in alkaline hyposulphites.

SILVER IODIDE.

AgI

Silver iodide is obtained as a yellow precipitate by adding potassium iodide to a solution of silver nitrate. It blackens on exposure to light. It is but very slightly soluble in ammonia, a property which distinguishes it from silver chloride.

SILVER NITRATE.

$AgNO^3$

This salt is prepared by dissolving silver in nitric acid. If the metal be pure, a colorless solution is obtained which after concentration and cooling deposits large, colorless tables of anhydrous silver nitrate. If silver coin be employed, the solution will be blue, containing, independently of silver nitrate, cupric nitrate. The latter may be removed by evaporating the residue to dryness and carefully heating it, so that the salt may remain fused for some time. The cupric nitrate is decomposed, while the silver nitrate remains mixed with cupric oxide, from which it may be freed by solution and filtration.

This salt dissolves in its own weight of cold, and in half its weight of boiling water. The solution is neutral to test-paper. When exposed to the air, it blackens, as do also the crystals and the fused salt, a partial reduction being produced by organic matters in the air. It blackens the skin from a similar cause.

Hydrogen slowly reduces the solution of silver nitrate with deposition of metallic silver (Beketoff).

Silver nitrate is extensively used in photography; it is also used in medicine, and when fused constitutes *lunar caustic.*

Characters of Silver Salts.—Solutions of silver are precipitated black by hydrogen sulphide and by ammonium sulphide.

Caustic alkalies give an olive-green precipitate of silver oxide, insoluble in excess. Ammonia does not precipitate them.

Hydrochloric acid and the soluble chlorides form a white precipitate of silver chloride, insoluble in either cold or boiling nitric acid, but soluble in ammonia.

Potassium iodide gives a yellow precipitate, almost insoluble in ammonia.

Silvering.—This operation consists in covering the common metals or glass with a coating of silver more or less thick.

The metals are silvered by either amalgamation or galvanic deposition. In the latter and preferable operation, a solution of the double cyanide of silver and potassium is generally used.

Mirrors and glass articles in general are silvered by the reduction of a silver salt by aldehyde, glucose, or tartaric acid. The following receipt is given by Liebig: a solution of 10 grammes of silver nitrate is supersaturated with ammonia and rendered strongly alkaline by caustic soda. The volume of the liquid should be 1450 c.c. Another solution is prepared by dissolving 1 part of milk sugar in 10 parts of water. The latter solution is mixed with its own volume of the first solution, and the glass to be silvered is washed with alcohol and immersed in the liquid. The reduction of the silver salt begins immediately, and does not require the aid of heat.

The experiment may easily be made in a glass flask, the interior of which will be uniformly silvered.

Assaying of Silver.—This name is applied to the methods which serve for the analysis of alloys of silver and copper, such as coin, medals, silverware, and jewelry. The assay may be conducted by the dry way or by the wet way.

The *dry assay* consists in the operation called *cupellation* (Fig. 103). A certain quantity of metallic lead is melted in a cupel of bone-ash in a reverberatory furnace, and a weighed quantity of the alloy of silver and copper, carefully wrapped in a small piece of paper, is placed upon the fused metal. The silver dissolves in the melted lead, and a ternary alloy is thus obtained which is exposed to the action of air at a red heat.

Under these conditions, the lead and copper become oxidized; the oxide of lead fuses, and the melted litharge, which should be in great excess in proportion to the oxide of copper, dissolves the latter, and with it is absorbed by the porous cupel. The phenomenon of brightening (page 346) indicates the termination of the process.

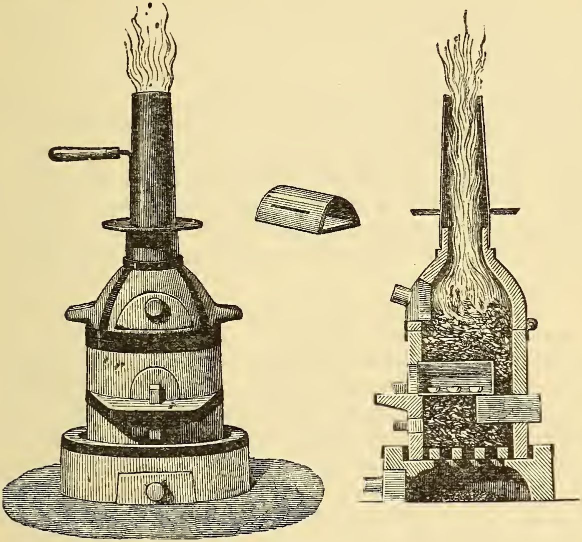


Fig. 103.

The *wet assay*, invented by Gay-Lussac, consists in adding to a solution in nitric acid of a known weight of the alloy of silver and copper, a titrated solution of sodium chloride, that is, a solution containing an exactly known weight of salt in one litre of water. This solution is cautiously added until it no longer precipitates silver chloride, and the quantity of silver present is calculated from the *volume* of the titrated solution that has been required to completely precipitate the silver in the form of chloride. As the latter readily deposits from a liquid that is carefully agitated, it is easy to ascertain the end of the operation, that is, the precise moment when all of the silver is precipitated and the addition of the titrated liquid must be arrested.

Process.—Two titrated solutions are used to precipitate the silver: 1st, a *normal* solution, containing 0.5417 gramme of sodium chloride per decilitre, a quantity sufficient to precipitate one gramme of silver; 2d, a *decinormal* solution, that is, one containing the same quantity of sodium chloride per litre, so that 1 c.c. of this liquid will precipitate one milligramme of silver. To analyze an alloy of silver, a coin, for example, such a quantity is weighed as would contain one gramme of silver, if the proportion of silver were a little less than the extreme limit allowed. If the alloy ought to contain 900 thousandths pure silver, with an allowance of 3 thousandths, it would be rejected should it contain less than 897 thousandths. We suppose, however, that the latter is its quality, and weigh a quantity of the alloy which would then contain one gramme of pure silver, that is, 1.1148 grammes. This alloy is dissolved in nitric acid, and one decilitre of the normal solution is added. All of the silver should not be precipitated, for the standard of the alloy should be above 897. This is determined by adding to the clarified liquid one or more cubic centimetres of the decinormal solution, until the liquid ceases to become cloudy on a fresh addition. As each cubic centimetre of this solution corresponds to one milligramme of silver, we must add to the gramme of silver at first precipitated as many milligrammes as we have added cubic centimetres of the decinormal solution, the last cubic centimetre added counting for only half a milligramme. Knowing the quantity of pure silver contained in 1.1148 grammes of the alloy analyzed, the standard of the latter is determined by a simple calculation.

CALCIUM.

$Ca = 39.8$

Lime, which is universally known, is the oxide of a metal called calcium. The latter was discovered by Davy in 1808, and isolated in 1854 by Matthiessen, who obtained it by decomposing fused calcium chloride by the voltaic current. According to Liès-Bodard and Jobin, calcium may be obtained by decomposing calcium iodide with sodium in an iron crucible.

Calcium has a yellow color when freshly filed, but it tarnishes rapidly in moist air and becomes covered with a grayish layer of hydroxide. When heated upon platinum-foil it takes fire and burns with a dazzling flame. It decomposes water at ordinary temperatures.

OXIDE AND HYDROXIDE OF CALCIUM.

Lime, or *calcium oxide*, CaO, is obtained by calcining the carbonate in special furnaces, which are called lime-kilns. As *quick-lime*, it forms large, compact, and hard grayish masses. It is infusible. When exposed to the air, it attracts moisture and carbonic acid, augments in volume, and is finally converted into a white powder, a mixture of calcium hydroxide and carbonate. When lime is sprinkled with water, it absorbs the liquid without giving rise to any particular phenomenon; but in a little while, the pieces saturated with water become hot, give off steam, and then they split and increase in volume. If enough water be used, the quick-lime will be converted into a white powder, which is called *slaked lime;* it is calcium hydroxide.

$$CaO + H^2O = CaO^2H^2 = Ca(OH)^2$$

When slaked lime is suspended in water, a white, creamy liquid is obtained that is called *milk of lime.* If this be filtered or allowed to settle, the clear, limpid liquid resulting will have an alkaline reaction, for it contains a small quantity of calcium hydroxide in solution: it is *lime-water.* Calcium hydroxide is more soluble in cold than in hot water.

Employment of Lime in Constructions.—Lime is largely employed for building purposes in both ordinary and submarine constructions. The limestone which is used for the preparation of lime is rarely pure, and consequently the product of its calcination presents different qualities, according to the proportions of foreign matters which remain in the lime, and which consist of a small quantity of magnesia, oxide of iron, and especially clay. *Fat limes* are those produced by the calcination of almost pure limestone; they develop much heat, and swell up very much on slaking. Such lime forms an unctuous and binding paste with water, and makes ordinary mortar when mixed with sand. Impure limestones yield *lean lime*, containing magnesia, oxide of iron, and clay. It is gray, and develops but little heat and increases but slightly in volume on slaking. The calcination of limestone containing from 10 to 30 per cent. of clay produces *hydraulic lime.* Such lime sets under water, that is, the mortar solidifies after a few days, and becomes very hard, even when immersed in water. On account of this curious property it is used in submarine constructions. Such lime is yellow; slaking it produces but little heat, and scarcely any increase in volume. The hydraulic mortar formed by its mixture with sand will harden under water. Mortars possessing this property may also be prepared by mixing lime with baked argillaceous materials, such as powdered tiles, pottery, bricks, etc. Certain argillaceous rocks of volcanic origin, the pozzolana so abundant near Vesuvius, for example, yield an excellent hydraulic lime when mixed with fat lime.

Cement is a variety of lime resulting from the calcination of limestones containing from 40 to 50 per cent. of slate. When mixed with water, such cement sets in a few minutes in a solid mass like plaster. Vicat has shown that the different varieties of hydraulic lime and cement can be prepared by properly calcining carbonate of lime, or chalk, with various proportions of clay. According to him, ordinary mortar sets because the lime gradually absorbs carbonic acid gas from the air, forming a carbonate which hardens and binds together the grains of sand. The hardening of hydraulic lime and mortar is due to another cause: on contact with water, the clay which they contain in the anhydrous state becomes hydrated and forms a double silicate of calcium and aluminium, or a silicate and aluminate of calcium, which are insoluble and very coherent.

CALCIUM CHLORIDE.

$CaCl^2$

This salt is prepared by dissolving white marble or chalk in hydrochloric acid. On evaporation, the solution deposits large, six-sided prisms, containing 6 molecules of water of crystallization. They are very deliquescent and lower the temperature when they are dissolved in water. If they be mixed with their own weight of snow, a cold of —45° may be produced. When they are heated, they melt in their water of crystallization, of which they lose 4 molecules at 200°, and the remainder at a red heat. At the latter point the mass enters into igneous fusion, and on cooling solidifies to a white, crystalline mass, in which form it is ordinarily employed for the desiccation of gases. Calcium chloride dissolves readily in alcohol.

CALCIUM CARBIDE.

CaC^2

At the high temperature of the electrical furnace lime is promptly reduced by carbon, but metallic calcium is not obtained. The reduced metal combines with part of the carbon, forming a black, homogeneous, crystalline mass, which is the carbide CaC^2 (H. Moissan). It has a density of 2.2, and is fusible at the high temperature at which it is formed. When heated in air, it burns into calcium carbonate. Water instantly reacts with it, forming calcium hydroxide and acetylene, C^2H^2.

CALCIUM NITRATE.

$Ca(NO^3)^2 + 4H^2O$

This salt is formed naturally in the neighborhood of dwellings, in the soils of cellars, and in damp walls. It is contained in what are known as saltpetre materials, and exists in certain spring and well waters. It may be made by saturating nitric acid with calcium carbonate. It is very soluble in water and in alcohol. It crystallizes with difficulty in six-sided, oblique rhombic prisms, which contain 4 molecules of water of crystallization: they are deliquescent.

CALCIUM CARBONATE.

$CaCO^3$

Calcium carbonate, commonly known as carbonate of lime, is found in great abundance in nature and under different forms. It is dimorphous, being found as *calcite* crystallized in rhombohedra and as *arragonite* in right rhombic prisms. *Iceland spar* is calcite which is colorless and perfectly transparent; the crystals are doubly refracting.

The various limestones and marbles constitute natural calcium carbonate in which crystalline structure is more or less apparent, and many varieties are colored by foreign matters. All the varieties of marble are susceptible of a high polish. *Statuary marble* is the whitest, and is made up of brilliant crystalline grains; *lithographic-stone* is exceedingly fine-grained, very compact, and has a yellowish-white color.

Chalk is a soft and amorphous calcium carbonate, made up of the mineral remains of marine animalcules.

Pure water dissolves but feeble traces of this salt; water charged with carbonic acid dissolves a larger quantity, converting it into dicarbonate. It is in this state that it is contained in hard waters. When the carbonic acid slowly evaporates, the calcium carbonate is deposited from such waters in compact form having crystalline structure, and when the water drips from the dome of a cave, large and fantastically shaped *stalactites* and *stalagmites* are frequently formed, consisting of almost pure calcium carbonate.

Calcium carbonate may be prepared by double decomposition between solutions of sodium carbonate and calcium chloride. When heated to bright redness, it is completely decomposed into lime and carbonic anhydride.

CALCIUM SULPHATE.

$CaSO^4$

This salt exists in two states in nature: anhydrous, it constitutes the *anhydrite* of mineralogists; combined with two molecules of water of crystallization, it forms *gypsum* or plaster stone. Gypsum sometimes occurs in lance-head-shaped crystals, grouped together; they are divisible into thin, transparent layers, easily scratched by the finger-nail. *Alabaster* and *satin-spar* are varieties of gypsum. All the forms of hydrated calcium sulphate contain 21 per cent. of water.

When heated to 80° in the air, or to 115° in closed vessels, the sulphate, $CaSO^4 + 2H^2O$, abandons its water of crystallization and is converted into the anhydrous sulphate. Between 120 and 130°, this dehydration is rapid and complete. It is operated on the large scale in plaster furnaces. In this state calcium sulphate will readily recombine with its water of crystallization. If the plaster be calcined at too high a temperature it will not again become hydrated.

If powdered plaster of Paris be mixed with enough water to form a creamy liquid, it may be poured into a mould, and in a few minutes will harden to a compact mass, completely filling every cavity of the mould. In becoming hydrated, the particles of calcium sulphate assume the crystalline form and increase in volume. These properties render plaster of Paris valuable in building operations, for ornamental work, and for making casts.

It is also employed to a large extent in agriculture.

Calcium sulphate is but slightly soluble in water. 1000 parts of boiling water dissolve a little more than 2 parts of the salt; at 35° they dissolve 2.64 parts; at 20°, 2.05 parts.

CHLORINATED LIME.

(BLEACHING-POWDER.)

This substance is largely employed in the arts under the name *chloride of lime*, and is obtained by exposing well-slaked lime to the action of chlorine. Its constitution is not perfectly understood; it was long regarded as a mixture of calcium chloride and calcium hypochlorite, $CaCl^2 + Ca(ClO)^2$, but recent researches have shown that it does not contain calcium hypochlorite already formed.

The formation of the alkaline hypochlorites by the action of chlorine on a solution of an alkaline hydrate is explained on page 133. With the hydrates of diatomic metals like calcium the action is more complicated, and is probably expressed by the equation

$$Ca(OH)^2 + Cl^2 = Ca(OCl)Cl + H^2O$$

Its manufacture is conducted by passing a current of chlorine over slaked lime placed in layers upon shelves arranged in the walls of masonry chambers (Fig. 104). The product always contains a certain proportion of lime which cannot possibly be chlorinated.

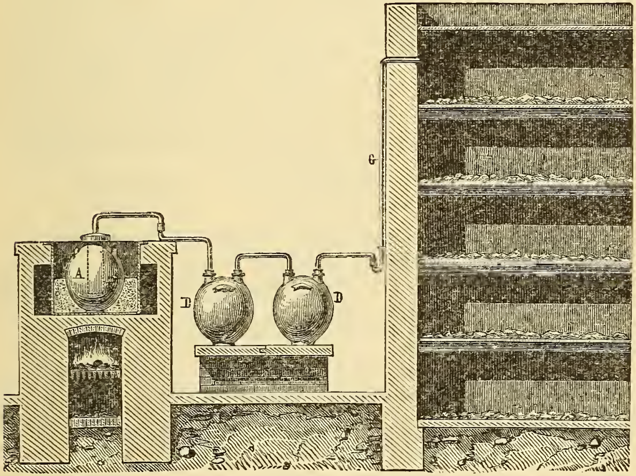
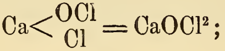


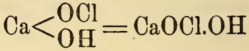
FIG. 104.

Chlorinated lime is an energetic bleaching agent; under the influence of acids it is decomposed, chlorine being set free. A solution of the compound is decomposed by the more feeble acids, even by carbonic acid gas, and decomposes spontaneously in a short time into calcium chloride and calcium hypochlorite.

Inasmuch as the substance is a mixture, and not a definite compound, its reactions may be interpreted in several different manners. It always contains water, calcium hydroxide, and a proportion of calcium chloride, and its active principle is probably expressed by one, or perhaps both, of the following formulæ:



$$Ca{<}\begin{matrix}OCl\\Cl\end{matrix} = CaOCl^2;$$



$$Ca{<}\begin{matrix}OCl\\OH\end{matrix} = CaOCl.OH$$

The reactions might then be written as follows:
The spontaneous decomposition of the solution,

$$2CaOCl^2 = \underset{\text{Calcium hypochlorite.}}{Ca(ClO)^2} + \underset{\text{Calcium chloride.}}{CaCl^2}$$

$$2CaOCl.OH = Ca(ClO)^2 + Ca(OH)^2;$$

its decomposition by hydrochloric acid,

$$CaOCl^2 + 2HCl = CaCl^2 + H^2O + Cl^2$$

$$CaOCl.OH + 3HCl = CaCl^2 + 2H^2O + Cl^2$$

When a solution of chlorinated lime is boiled, it is at once decomposed, yielding calcium chloride and calcium chlorate:

$$6CaOCl^2 = \underset{\text{Calcium chloride.}}{5CaCl^2} + \underset{\text{Calcium chlorate.}}{Ca(ClO^3)^2}$$

Characters of Calcium Salts.—Calcium salts are not precipitated either by hydrogen sulphide or ammonium sulphide. Sodium carbonate forms in them a white gelatinous precipitate. Sulphuric acid and the soluble sulphates produce a white precipitate, if the calcium solutions be concentrated or only moderately dilute. Oxalic acid, or better, ammonium oxalate, produces a white precipitate of calcium oxalate, even in the most dilute solutions of calcium salts. Calcium compounds impart an orange-red color to non-luminous flames.

STRONTIUM.

$Sr = 86.95$

Strontium was discovered by Davy in 1808, but the pure metal was first obtained by Bunsen and Matthiessen by a process similar to that which serves for the preparation of barium.

Matthiessen describes it as a yellow metal, having a density of 2.50–2.58, harder than lead, and decomposing cold water.

Strontium forms two oxides, a *monoxide*, SrO, and a *dioxide*, SrO^2.

Strontium chloride, $SrCl^2$, crystallizes in deliquescent needles which contain six molecules of water of crystallization. It is very soluble in water and fairly soluble in alcohol; the alcoholic solution burns with a red flame.

Strontium nitrate, $Sr(NO^3)^2$, which is prepared like barium nitrate, is deposited from its hot aqueous solution in anhydrous octahedra, and crystallizes at low temperatures in oblique rhombic tables containing 5 molecules of water of crystallization (Laurent).

The carbonate of strontium, $SrCO^3$ (*strontianite*), and the sulphate, $SrSO^4$ (*celestite*), are found native. These two salts are insoluble in water, and are deposited as white precipitates on adding a soluble carbonate or sulphate to the solution of a strontium salt. Strontium sulphate is less insoluble, however, than barium sulphate. Strontium salts color flames red, and the nitrate is used in red fire.

BARIUM.

Ba = 136.4

Bunsen obtained barium by the electrolysis of fused barium chloride; this metal is very avid of oxygen, and tarnishes rapidly. It decomposes cold water.

Barium Oxide, or Baryta, BaO.—Barium oxide is obtained by calcining barium nitrate. Its nature was first recognized in 1808, by Davy, who decomposed it by the voltaic current. It is a gray, porous substance, which unites energetically with water, producing a hissing noise and a great disengagement of steam, due to the elevation of temperature. The product of the reaction is a white hydrate, ordinarily known as caustic baryta.

$$\underset{\text{Barium oxide.}}{BaO} + H^2O = \underset{\text{Barium hydroxide.}}{Ba(OH)^2}$$

Barium hydroxide is soluble in two parts of boiling water, and on cooling is in great part deposited in large tabular crystals, containing 8 molecules of water. The solution of barium hydroxide in water is called baryta water.

Barium Dioxide, BaO^2.—When dry oxygen is passed over barium oxide heated to dull redness, the gas is absorbed and a dioxide, BaO^2, is formed. It is a gray, porous mass, sometimes greenish. It loses one atom of oxygen at a bright-red heat (see page 66). When brought in contact with water, it combines with the latter quietly and without disengagement of heat, forming a pulverulent hydrate.

This hydroxide is readily prepared pure by adding an excess of baryta water to a solution of hydrogen dioxide; it separates in beautiful scales. It reacts with cold dilute hydrochloric acid, forming barium chloride and hydrogen dioxide.

Barium Sulphide, BaS.—This is obtained by reducing barium sulphate with charcoal.

$$BaSO^4 + C^4 = BaS + 4CO$$

The sulphate is reduced to fine powder, and is mixed with a certain quantity of flour or rosin. The mixture is then made into a paste with linseed oil, and shaped into little balls. These are calcined at a bright-red heat in a covered crucible, and a porous, gray mass is thus obtained which, when treated with boiling water, yields a solution which deposits hexagonal tables after filtration and cooling. These crystals do not present a very constant composition, being a mixture of sulphide, hydrosulphide, and hydroxide of barium. Their solution has a light-yellow color.

BARIUM SALTS.

Barium Chloride, $BaCl^2 + 2H^2O$.—This salt is obtained by saturating the solution of barium sulphide with hydrochloric acid. Hydrogen sulphide is disengaged; the solution is boiled, filtered, and evaporated to crystallization. Barium chloride separates in quadrangular tables belonging to the type of the right rhombic prism. These crystals are inalterable in the air. 100 parts of water at 18° dissolve 43.5 parts of barium chloride, and 78 parts at 105.5°, the temperature of ebullition of the saturated solution (Gay-Lussac). Absolute alcohol dissolves $\frac{1}{400}$ of its weight of barium chloride.

Barium Nitrate, $Ba(NO^3)^2$.—Barium nitrate is prepared by decomposing barium sulphide or carbonate with dilute nitric acid, and filtering and evaporating the solution.

It crystallizes in regular octahedra, or in cubo-octahedra. The crystals are transparent and unaltered in the air. One part of this salt requires for its solution 20 parts of water at 0.12°; 5 parts of water at 15°; 2.8 parts at 106°, the temperature of ebullition (Gay-Lussac). When heated to redness, barium nitrate gives off oxygen, nitrogen, and red vapors, leaving a residue of oxide, BaO.

Barium Sulphate, $BaSO^4$.—This salt is found abundantly in nature as *heavy spar*, and sometimes occurs in right rhombic crystals. It is entirely insoluble in water and acids, with the exception of concentrated sulphuric acid. It is precipitated as a finely-divided, amorphous powder when sulphuric acid or a soluble sulphate is added to a solution, even very dilute, of a salt of barium.

Barium Carbonate, $BaCO^3$.—Barium carbonate constitutes an amorphous, white powder, which is obtained by double decomposition on adding solution of sodium carbonate to a solution of barium sulphide. Natural barium carbonate is an abundant mineral, and is found crystallized in right rhombic prisms; it is called *witherite.*

Characters of Barium Salts.—Barium salts are precipitated neither by hydrogen sulphide nor by ammonium sulphide. Sodium carbonate produces in them a white precipitate. Even when very dilute, the barium salts produce a white precipitate with sulphuric acid, which is insoluble in either cold or boiling nitric acid. The salts of barium communicate a green color to flames; the nitrate is used in green fire.

Glucinum, magnesium, zinc, and cadmium form a group in which the chemical analogies of the members are well marked. They are diatomic, forming oxides RO, and chlorides RCl^2.

GLUCINUM OR BERYLLIUM.

Gl, or Be = 9.01

The varieties of beryl, including the green precious stone *emerald* and *aqua-marine*, contain a double silicate of aluminium and glucinum. The latter metal was first isolated by Woehler in 1827.

Glucinum is prepared by the reduction of its chloride by potassium or sodium. It is white and brilliant, has a density of 1.6, and melts at a temperature below the fusing-point of silver. It does not decompose water, even by the aid of heat, but is readily attacked by hydrochloric and sulphuric acids, hydrogen being evolved and a chloride or sulphate formed.

Glucinum Oxide, GlO, is prepared from beryl, or by precipitating by ammonia a solution of glucinum chloride. In the latter case a hydrate $Gl(OH)^2$ is obtained, which is converted into oxide by heat.

The oxide is a light, white, infusible powder, soluble in acids and alkalies. When heated in the oxyhydrogen flame, it volatilizes like magnesium and zinc oxides.

Glucinum Chloride, $GlCl^2$.—This salt may be prepared by passing chlorine over an intimate mixture of the oxide and charcoal at a high temperature.

Glucinum chloride forms white, deliquescent crystals that fume in the air, condensing atmospheric moisture. It is fusible, and volatilizes at a low red heat. It is very soluble in water, and forms a hydrate which is decomposed by heat, yielding glucinum oxide and hydrochloric acid.

Glucinum forms a nitrate, and a sulphate which is isomorphous with magnesium sulphate.

The salts of glucinum possess a sweet taste, to which the metal owes its name.

MAGNESIUM.

$Mg = 24.18$

Magnesium was discovered by Bussy. Matthiessen obtained it by decomposing fused magnesium chloride by electricity.

Preparation.—Deville and Caron recommend the following process for the preparation of considerable quantities of magnesium. A mixture of 600 grammes of anhydrous magnesium chloride, 100 grammes of sodium chloride, 100 grammes of calcium fluoride, and 100 grammes of sodium cut into small pieces is heated to redness in a covered crucible. The magnesium chloride is reduced by the sodium, and the magnesium set free collects in little globules disseminated in the fused mass, which must be stirred with an iron rod. These little globules are removed from the scoriæ when cold, introduced into a charcoal boat, and heated to bright redness in a current of hydrogen. The magnesium volatilizes and condenses farther on in the tube; it may then be fused with a flux consisting of magnesium chloride, sodium chloride, and calcium fluoride. The metal collects at the bottom of the crucible.

Within recent years magnesium has acquired considerable commercial importance. It is manufactured by electrolyzing carnallite, the double chloride of magnesium and potassium. This salt is fused in an iron crucible (A, Fig. 105), which serves as a negative electrode. A carbon rod forms the anode, which is enclosed by a porcelain cylinder perforated at the bottom to permit free passage of the fused carnallite, and connected at the top with a pipe to carry off the evolved chlorine. In this manner the metal liberated at the cathode cannot come in contact with the chlorine, with which it would at once recombine, and it is protected from oxidation by the passage of an inert gas, such as nitrogen or hydrogen, through the space in the iron retort.

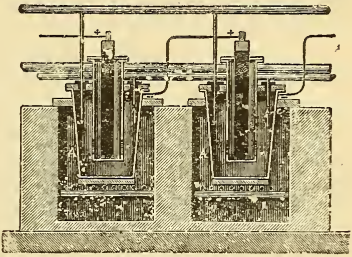


FIG. 105.

Properties.—Magnesium has a density of 1.74 or 1.75. It fuses at 500°. It decomposes water at ordinary temperatures but slowly. It may readily be rolled into ribbon or drawn into wire. The wire is grayish and not very brilliant. The end of a bundle of these wires may be heated in an alcohol lamp until they take fire, and the whole may then be plunged into a jar of oxygen. They burn with an incomparable splendor that the eye cannot support; at the same time the jar becomes filled with a white smoke, which condenses into a white powder, the product of the combustion; it is magnesia, the oxide of magnesium. Magnesium also combines directly with nitrogen.

In the form of powder, magnesium is employed in the flash-lights used in photography and in pyrotechnics.

MAGNESIUM OXIDE, OR MAGNESIA.

MgO

This body is obtained by calcining white magnesia, or magnesium hydrocarbonate. It is a white, voluminous powder, less fusible even than lime. It does not dissolve in water, but combines with that liquid forming a hydrate, $Mg(OH)^2 = MgO.H^2O$. This hydrate slowly restores the blue color to reddened litmus-paper.

Magnesium hydroxide is precipitated when a solution of caustic potash is added to the solution of a magnesium salt.

Calcined magnesia is frequently employed in medicine. On account of its great infusibility (it melts only at the temperature of the electric arc), crude magnesia is employed for lining furnaces and crucibles.

MAGNESIUM CHLORIDE.

$MgCl^2$

This salt is known in the anhydrous state and crystallized. Anhydrous magnesium chloride is prepared by dissolving the carbonate in hydrochloric acid, adding ammonium chloride to the solution and evaporating to dryness. A double chloride of magnesium and ammonium is thus obtained which may be perfectly dried; the dry mass is introduced into a clay crucible and heated; the ammonium chloride volatilizes, while the magnesium chloride remains, and solidifies on cooling to a colorless, pearly mass.

It is very soluble in water, and when properly concentrated, the solution deposits deliquescent, prismatic crystals containing six molecules of water of crystallization. These crystals cannot be dehydrated, nor can their solution be evaporated to dryness, without decomposing the chloride by the action of the water; under these circumstances the magnesium chloride is converted into hydrochloric acid and magnesia.

$$MgCl^2 + H^2O = 2HCl + MgO$$

MAGNESIUM CARBONATE.

$MgCO^3$

The anhydrous carbonate $MgCO^3$, known as *magnesite*, is found native, crystallized in rhombohedra, similar to those of calcium carbonate. Considerable deposits are also found of a double carbonate of magnesium and calcium, known as *dolomite*.

When a boiling solution of magnesium sulphate is precipitated by an excess of sodium carbonate, carbonic acid gas is disengaged, and a precipitate is formed containing at the same time magnesium carbonate and magnesium hydrate (magnesium hydrocarbonate).

When this is dried, it constitutes the *white magnesia* of the pharmacies.

MAGNESIUM SULPHATE.

$MgSO^4 + 7H^2O$

This salt exists in solution in sea-water and in certain purgative mineral waters, such as those of Epsom, in England. Its common name is Epsom salts.

At Stassfurt, it is found crystallized with one molecule of water (*kieserite*) and mixed with the anhydrous sulphate.

When it separates at ordinary temperatures from an aqueous solution that has been tolerably concentrated by heat, it crystallizes in transparent and colorless right rhombic prisms. At 0°, it crystallizes with 12 molecules of water; at 30°, with 6 molecules. Its taste is disagreeable, at the same time salty and bitter. When magnesium sulphate crystallized with 7 molecules of water is heated, it first melts in its water of crystallization, of which it loses 6 molecules. At 132°, it still retains one molecule, which it loses only at 210°. It is very soluble in water; 100 parts of water at 0° dissolve 25.76 parts of the anhydrous sulphate, and 0.47816 part for every additional degree (Gay-Lussac). It forms a double sulphate with potassium sulphate, $K^2SO^4.MgSO^4 + 6H^2O$.

Characters of Magnesium Salts.—They are precipitated by neither hydrogen sulphide nor ammonium sulphide. Sodium carbonate produces a white, flocculent precipitate. Caustic potash and ammonia form white precipitates, but ammonia will not precipitate magnesia from an acid solution or from one containing ammonium chloride. Sodium phosphate and ammonia together produce a crystalline precipitate of ammonio-magnesium phosphate. This is the most delicate test for magnesium.

ZINC.

$Zn = 64.91$

Treatment of Zinc Ores.—The most important ores of zinc are zinc spar (*smithsonite*), $ZnCO^3$; blende or *sphalerite*, ZnS; *calamine*, $Zn^2SiO^4 + H^2O$; *willemite*, Zn^2SiO^4; red zinc ore, ZnO, and *franklinite*, $(Zn,Fe)O.Fe^2O^3$.

Zinc ores are abundant in England, Silesia, Belgium, and throughout the United States. They are generally accompanied by other minerals; thus, blende is often mixed with pyrites and galena (lead sulphide). The ore is then first submitted to an ingenious system of washing, by which the various sulphides separate from each other by reason of their different densities.

In order to extract the zinc from blende separated by this method, or from zinc spar, the minerals are first roasted. By the action of heat zinc spar loses carbonic acid gas and water, and the blende disengages sulphur dioxide and is converted into zinc oxide. Thus converted into oxide, and rendered more friable by the heat, the zinc ores are pulverized and calcined with charcoal. Carbon monoxide is disengaged, and the zinc set at liberty volatilizes, and is condensed in suitable receivers.

The operation is conducted in cylinders of refractory clay, a number of which are arranged in a furnace, and their open extremities connected with conical recipients of galvanized iron (Fig. 106). In Silesia, these cylindrical retorts are replaced by muffles, which are heated in a furnace and communicate with recipients placed outside (Fig. 107).

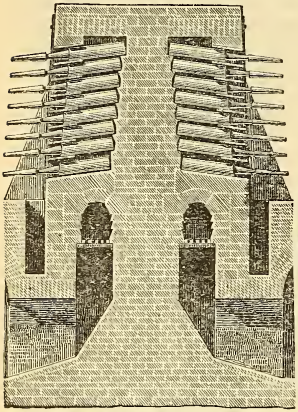


Fig. 106.

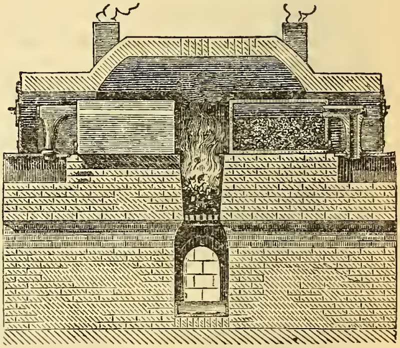


Fig. 107.

The zinc of commerce is impure. It contains small quantities of iron, copper, lead, cadmium, carbon, and arsenic. It may be purified by repeated meltings with small quantities of nitre. The last traces of impurities can be removed only by fractional distillation in vacuo (Morse).

Properties.—Zinc has a bluish-white color; its density varies from 6.86 to 7.2, according as it has been melted or rolled; its fracture is laminated and brilliant. Commercial zinc is brittle at ordinary temperatures; it becomes malleable at a few degrees above 100°, but when heated to 200° it again becomes brittle. It melts at 410°, and distils at about 1000°. Its vapor density compared to hydrogen indicates that the molecule contains but one atom. Its surface soon tarnishes in moist air, but the tarnish is only superficial. It is due to the formation of an impermeable layer of hydrocarbonate of zinc, which protects the metal from further oxidation.

When heated to redness in air, zinc volatilizes and burns with a greenish flame into a smoke of oxide, which falls in light, white flakes, formerly called flowers of zinc or philosopher's wool.

Zinc dissolves with evolution of hydrogen in hydrochloric and sulphuric acids, and in boiling solutions of potassium and sodium hydroxides. When perfectly pure, it is dissolved with difficulty by dilute sulphuric acid at ordinary temperatures, and the easy solubility of the metal of commerce must be attributed to the presence of small quantities of foreign metals. The latter being electro-negative in contact with zinc, form voltaic couples, in which the zinc is the more oxidizable metal.

Galvanized iron is iron covered with a thin layer of zinc; it is prepared by plunging carefully-cleaned iron objects into a bath of molten zinc.

Brass is an alloy of copper and zinc, obtained by melting the two metals together in crucibles.

ZINC OXIDE.

ZnO

This oxide is prepared in the arts by heating zinc in large muffles; the product is separated from traces of metallic zinc by suspending it in water and rapidly decanting the white liquid. The zinc sinks to the bottom of the vessel before the lighter white powder has time to deposit; the latter is therefore carried by the water into a second vessel, where it is allowed to settle. The process is called elutriation.

This oxide is now manufactured on an enormous scale by drawing an excess of air through a burning mixture of zinc ore and coal. The zinc is reduced and oxidized at one operation, and the oxide is drawn through the blower and collects in canvas bags through which the waste gases are forced.

Oxide of zinc is white; it turns yellow when heated, is infusible and is irreducible by heat and insoluble in water. The corresponding hydroxide is precipitated when caustic alkalies are added to the solution of a zinc salt.

$$\underset{\text{Zinc sulphate.}}{ZnSO^4} + 2KOH = K^2SO^4 + \underset{\text{Zinc hydroxide.}}{Zn(OH)^2}$$

An excess of alkali will redissolve the precipitate.

Zinc oxide is largely used in the arts as a substitute for white lead as a pigment.

ZINC SULPHIDE.

ZnS

The blende which occurs in nature is sulphide of zinc. It crystallizes in the isometric system, often in hemihedral forms. Sometimes it occurs as *wurtzite* in hexagonal prisms (Friedel).

On adding an alkaline sulphide to a neutral solution of a zinc salt a white precipitate is obtained, which is hydrated zinc sulphide. This precipitate is soluble in mineral acids.

When moderately heated in contact with the air, zinc sulphide absorbs four atoms of oxygen and is converted into sulphate. At a very high temperature it is converted into oxide, with formation of sulphurous oxide.

ZINC CHLORIDE.

$ZnCl^2$

Zinc reduced to thin sheets will burn in chlorine. Zinc chloride is prepared in the laboratory by dissolving zinc in hydrochloric acid. The aqueous solution, evaporated to a syrupy consistence, deposits a hydrated chloride, $ZnCl^2 + H^2O$, crystallizing in deliquescent octahedra. This salt loses its water when strongly heated, and melts at about 250°. On cooling, a solid white mass is obtained, which is the anhydrous chloride; in this state it is very avid of water and deliquesces when exposed to the air. It volatilizes without decomposition at a red heat. It is very soluble in water, and dissolves also in alcohol.

ZINC SULPHATE.

$ZnSO^4 + 7H^2O$

This salt was formerly known as *white vitriol.* It is obtained by moderately roasting blende. The latter being often mixed with pyrites, zinc sulphate and ferrous sulphate are formed, and when the product of the roasting is lixiviated a solution of the two salts is obtained. The solution is evaporated, and the dry residue moderately calcined. The ferrous sulphate decomposes, yielding sulphuric acid, which distils, and ferric oxide, which remains mixed with the zinc sulphate. The residue being exhausted with water, the zinc sulphate dissolves and is deposited in crystals on the cooling of the concentrated solution.

The salt may be prepared in the laboratory by dissolving zinc in dilute sulphuric acid: it is the residue in the preparation of hydrogen.

Sulphate of zinc crystallizes with 7 molecules of water. In this state it occurs as orthorhombic prisms, isomorphous with magnesium sulphate.

When heated, it melts in its water of crystallization, of which it loses 6 molecules; the seventh it abandons only at 238°.

At a high red heat it is decomposed into zinc oxide, sulphurous oxide, and oxygen.

Zinc sulphate is very soluble in water, of which 100 parts dissolve 48.36 parts of the anhydrous salt at 10°, and 95.6 parts at 100°. The solution has a styptic taste.

Zinc sulphate forms crystallizable double salts with the alkaline sulphates; thus, there is a double sulphate of zinc and potassium, containing

$$ZnSO^4.K^2SO^4 + 6H^2O$$

Characters of Zinc Salts.—The zinc salts are colorless unless the corresponding acid be colored. Their neutral solutions are partially decomposed by hydrogen sulphide, which precipitates white sulphide of zinc; the addition of a mineral acid prevents the precipitation; the zinc salts of organic acids, such as the acetate and lactate, are completely decomposed by hydrogen sulphide.

Ammonium sulphide produces a white precipitate of sulphide; this reaction is characteristic.

The alkaline hydroxides, and ammonia-water, form white precipitates, soluble in an excess of the reagent.

Potassium ferrocyanide gives a white precipitate.

CADMIUM.

$Cd = 111.08$

Natural State and Extraction.—Cadmium is generally found associated with zinc, either as oxide in calamine, or as sulphide in zinc blende. As it is more volatile than zinc, it becomes concentrated in the first products of distillation.

It is found especially, in the state of oxide, in the brown powder called *cadmies*, which condenses during the first hours of the distillation in the sheet-iron receivers adapted to the retorts (Fig. 106). When mixed with powdered charcoal and calcined, this powder yields an alloy of zinc and cadmium which distils.

The cadmium is extracted by dissolving the alloy in dilute sulphuric acid and passing a current of hydrogen sulphide through the acid liquid. The cadmium is precipitated as a yellow sulphide. This sulphide is dissolved in hydrochloric acid and the solution of cadmium chloride precipitated by ammonium carbonate. The cadmium carbonate thus obtained is calcined, and so converted into oxide, which is mixed with one-tenth its weight of powdered charcoal and heated in a clay retort. The cadmium distils.

Properties.—Pure cadmium has a white lustre, but soon tarnishes in the air. Its density is 8.60–8.69. It melts at 320°, and boils at 860°. Its vapor density is 56. It may be obtained crystallized in octahedra.

It dissolves in dilute sulphuric and hydrochloric acids with evolution of hydrogen.

Cadmium Oxide, CdO.—The oxide of cadmium may be obtained by calcining either the carbonate or nitrate. It has a yellowish-brown color, or a brown more or less deep. It is reduced at high temperatures by carbon and by hydrogen, its reduction taking place more readily than that of zinc oxide.

Cadmium Sulphide, CdS.—This sulphide occurs in nature as *greenockite* in the form of bright yellow, hexagonal prisms, terminated by six-sided pyramids.

It may be prepared in the laboratory by precipitating a solution of a cadmium salt by hydrogen sulphide or a soluble sulphide. An amorphous precipitate of a fine yellow color is thus obtained. In this form it is employed in oil painting.

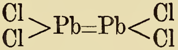
Cadmium Iodide, CdI^2.—This salt is prepared by digesting finely-divided cadmium with iodine in presence of water. It crystallizes from its aqueous solution in transparent and colorless, hexagonal prisms having a brilliant lustre. It is soluble in water and alcohol.

Cadmium Sulphate, $3CdSO^4 + 8H^2O$.—Cadmium Sulphate is obtained by dissolving the metal, or its oxide or carbonate, in dilute sulphuric acid. The neutral and concentrated solution deposits the salt in beautiful monoclinic prisms. These crystals are efflorescent.

LEAD.

Pb (Plumbum) = 205.4.

Lead is related to the diatomic metals by a series of normal salts, the chloride $PbCl^2$, sulphide PbS, oxide PbO, etc., but it is undoubtedly tetratomic in other compounds, among which are a tetrachloride $PbCl^4$, and a dioxide PbO^2. It is probable, however, that lead is tetratomic in all of its compounds, in which case the dichloride must be represented by the formula



$$\begin{matrix}Cl\\Cl\end{matrix}{>}Pb{=}Pb{<}\begin{matrix}Cl\\Cl\end{matrix}$$

the oxide by the formula OPb=PbO, and the other compounds in an analogous manner. It is convenient, in the absence of more positive data, to represent these molecules by the more simple formulæ, bearing in mind that they probably express only half the molecular weights.

Treatment of Lead Ores.—The minerals of lead which are worked are the carbonate, and especially the sulphide, known as *galena.*

The extraction of the metal from the carbonate is simple: it is heated with charcoal in a cupola-furnace, and the reduced lead collects on the hearth.

Two methods are employed for the reduction of galena. One consists in melting the ore with iron (granulated cast iron). Sulphide of iron is formed, and both it and the reduced lead enter into fusion and separate from each other by virtue of their different densities, the lead being much the heavier. This is the *precipitation method.* It is employed for impure ores having a silicious gangue.

By the other process, known as the *reaction method,* the galena is first roasted, by which the sulphide is partially transformed into oxide and sulphate; the openings of the furnace are now closed and the temperature is elevated. The excess of sulphide then reacts upon the oxide and upon the sulphate; sulphurous acid gas is disengaged, and metallic lead is formed. This is called *work-lead.*

$$PbS + 2PbO = 3Pb + SO^2$$
$$PbS + PbSO^4 = 2Pb + 2SO^2$$

The operation is conducted in a reverberatory furnace represented in Fig. 108. The ore is spread in thin layers on the hearth E, and heated to dull redness; the fire is at A, and the air enters by the openings D. These are closed when it is judged by the aspect of the mass that the roasting is sufficiently advanced. The heat is then increased.

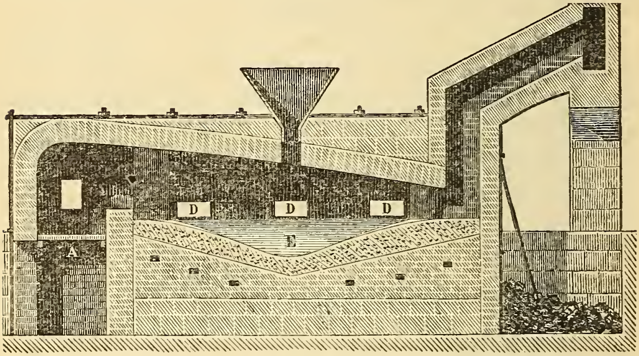


FIG. 108.

Independently of the portion of lead sulphide which reacts upon the oxide and sulphate, there is always an excess, which melts when the heat is increased, and separates in the form of *lead matte.* This is subjected to another operation by the same process of reaction, and furnishes a harder lead than that first obtained; it contains a small quantity of copper, and is known as *slag lead.*

In some works, charcoal-powder is added at a certain stage of the roasting, to remove the oxygen from the oxide and sulphate formed.

Treatment of Argentiferous Lead.—The lead produced by these methods, and especially the work-lead, often contains a small proportion of silver. In order to separate the latter metal, the lead is desilverized, as described on page 317, or is first refined by crystallization.

The object of *refining by crystallization* is the formation of an alloy of lead and silver, richer in silver than the work-lead. The argentiferous lead is melted and allowed to cool slowly; nearly pure lead separates in the form of crystals, which are deposited at the bottom of the molten metal. These are removed by a ladle as fast as they are formed; the richer alloy of lead and silver remains liquid. The crystals of lead still contain a little silver, and are submitted to another fusion; lead again crystallizes out on cooling, and a small quantity of an alloy still rich in silver is obtained. The same operation repeated a third time determines the separation of pure lead. The alloys of lead and silver thus obtained are themselves submitted to several successive fusions and crystallizations, and a still richer alloy results.

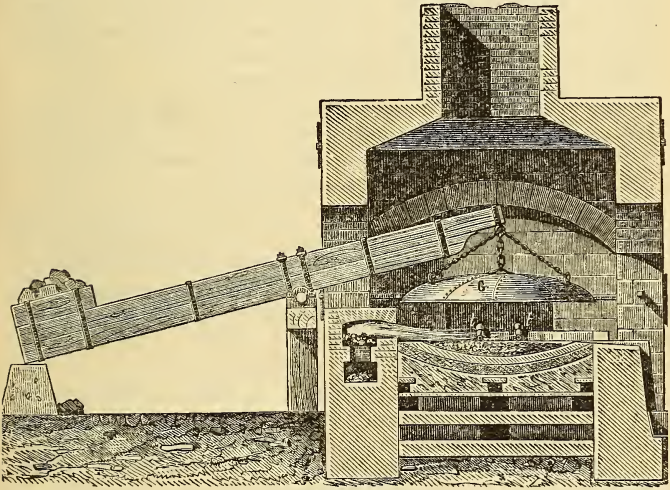


Fig. 109.

The alloy thus concentrated is cupelled. The operation consists in melting the lead in a reverberatory furnace (Fig. 109), of which the hearth has a hemispherical form, and is called the cupel. The vault of the furnace is formed by a sheet-iron cover, G, which can be raised and lowered at will. When the lead is melted, a strong blast of air is blown upon its surface through the tuyères *tt;* the lead is thus converted into oxide, which melts and, driven by the current of air, flows from the cupel through a notch cut in its edge down to the level of the molten metal, and which is gradually deepened as that level becomes lowered. The silver, which is not oxidizable, becomes concentrated in the cupel as the lead is eliminated; and when the last portions of the latter metal become oxidized, the surface of the silver is covered with only a thin layer of fused litharge, which breaks up suddenly and displays the brilliant surface of the metal. This phenomenon, called *brightening*, indicates the termination of the operation.

The oxide of lead formed first in the cupellation of work-lead is called *abstrich.* It is black, and still contains a little silver, as well as copper and antimony (Berthier). The oxide which flows out after the abstrich is *litharge.*

Properties of Lead.—Lead is a bluish-white metal, having a certain degree of lustre when its surface is freshly cut. It is the softest and least tenacious of all the common metals. It can easily be cut with a knife and scratched by the finger-nail. It may readily be reduced to thin sheets, but is not easily drawn into wire. Its density is 11.363 (H. Deville). It melts between 326 and 334°, and volatilizes at a white heat. It may sometimes be obtained crystallized in regular octahedra by allowing a large quantity of molten lead to cool slowly, and decanting the still liquid portion.

The brilliant surface of lead tarnishes in the air. When melted, it rapidly absorbs oxygen and becomes covered with a pellicle of oxide, which is transformed by the prolonged action of heat into a yellow powder, known as *massicot.*

On contact with aerated water, lead absorbs oxygen and carbon dioxide, and becomes covered with a thin layer of carbonate. This fact explains the presence of traces of lead in rain-water which has been collected from lead gutters, or kept in leaden reservoirs.

The presence of small quantities of sulphates and chlorides in water prevents this oxidation of lead, so that the metal can be used without danger for the distribution of most spring and river waters.

Lead is slowly attacked by concentrated and boiling hydrochloric acid. Dilute sulphuric acid does not attack it; the boiling concentrated acid converts it into sulphate with evolution of sulphurous acid gas. Nitric acid attacks and dissolves it at ordinary temperatures, disengaging red vapors and forming lead nitrate.

Lead and its compounds are poisonous. Its effects on the economy are especially manifested after the long-continued absorption of very small quantities of the metal, of which the accumulation in the system is made evident by various symptoms; the best known is *lead colic* or *painter's colic*. Plumbers, glaziers of pottery, painters, color-grinders, and the workmen employed in the manufacture of minium, or red lead, white lead, etc., are exposed to this chronic poisoning. The soluble sulphates are antidotes for acute cases of poisoning, and potassium iodide causes the elimination of lead from the system in chronic cases.

Uses of Lead.—This metal is used for the manufacture of shot, and pipes for the distribution of water and gas. When reduced to sheets it is made into gutters, the coverings of roofs, linings for troughs and reservoirs. Sheet-iron dipped into a bath of melted lead retains a coating of that metal, and is called leaded iron. Lead enters into the composition of type-metal, plumber's solder, pewter, etc.

LEAD MONOXIDE.

PbO

Massicot and *litharge*, of which the formation has been indicated, constitute the monoxide of lead.

Massicot is a yellow, amorphous powder. Litharge occurs in reddish-yellow, crystalline scales. It is rendered crystalline by the fusion and cooling through which it passes. It is sometimes met with in the form of rhombic octahedra (Mitscherlich).

Oxide of lead melts at a red heat; when fused it absorbs oxygen, which it again gives up on solidifying (F. Le Blanc). It cannot be melted in an earthen crucible without attacking and sometimes piercing the latter, owing to the formation of a very fusible silicate of lead.

Lead monoxide is easily reduced by hydrogen, charcoal, and carbon monoxide.

It is very slightly soluble in water, and possesses a sufficiently marked alkaline reaction to restore the blue color to feebly reddened litmus-paper.

When caustic alkalies or ammonia-water are added to solutions of lead salts, white precipitates of lead hydroxide, $Pb(OH)^2$, are produced. This hydroxide dissolves in an excess of potassium or sodium hydroxide, or in lime-water, and these solutions are precipitated black by hydrogen sulphide.

Litharge is used for the manufacture of lead acetate and white lead. It gives to linseed oil drying properties. It enters into the composition of various plasters, and different coloring matters (Cassel yellow).

LEAD DIOXIDE.

PbO^2

This body is made by treating minium, or intermediate oxide of lead, with dilute nitric acid. A brown powder remains and must be washed with boiling water. This is dioxide of lead; it is insoluble in water; it is readily decomposed by heat, losing half of its oxygen and being converted into monoxide. It is an energetic oxidizing agent. When it is briskly triturated with a small quantity of sulphur, the latter is inflamed.

If lead dioxide be introduced into a test-tube filled with sulphurous acid gas, the latter is immediately absorbed with formation of lead sulphate.

$$SO^2 + PbO^2 = PbSO^4$$

Hydrochloric acid poured upon lead dioxide determines the formation of lead chloride and the disengagement of chlorine.

$$PbO^2 + 4HCl = PbCl^2 + Cl^2 + 2H^2O$$

Lead dioxide unites with the alkalies forming veritable salts. Fremy has described a plumbate of potassium, $K^2PbO^3 + 3H^2O$, which crystallizes in cubes, and which is formed when dioxide of lead is gently heated with a very concentrated solution of potassium hydroxide in a silver crucible.

PLUMBOSO-PLUMBIC OXIDE (RED LEAD)

This oxide is prepared by heating massicot in furnaces to a temperature that should not exceed 300°. Under these conditions, the monoxide absorbs oxygen from the air, and is converted into a beautiful red powder known as *minium* or *red lead.* The product obtained by heating lead carbonate or white lead in contact with the air is called orange minium.

Minium is a combination of monoxide and dioxide of lead; its composition is variable, according to the length of time it is roasted. It ordinarily corresponds to the formula

$$Pb^3O^4 = 2PbO.PbO^2 \quad \text{(Jacquelain)}$$

Sometimes it contains less oxygen, having the composition

$$Pb^4O^5 = 3PbO.PbO^2 \quad \text{(Mulder)}$$

Red crystals of the latter composition have been found in the fissures of a minium furnace.

Minium has a scarlet-red color, which becomes much darker on heating. It gives up oxygen at a red heat, being reduced to monoxide. If red lead be sprinkled with nitric acid, the color disappears, giving place to a brown. The nitric acid removes the monoxide, forming nitrate, and leaves the brown dioxide.

Minium is used to color sealing-wax and wall-papers. It is employed in the manufacture of flint glass, which owes its fusibility, its perfect transparency and its refractive power, to silicate of lead. When mixed with stannic oxide, minium serves as an enamel for crockery-ware.

A mixture of red lead and white lead with a small quantity of oil is employed as a luting for steam-pipes, and as a cement.

LEAD SULPHIDE.

PbS

Galena or sulphide of lead occurs in nature in beautiful cubical crystals of a bluish-gray color and a metallic lustre; its density is 7.58. It melts at a red heat. When heated in contact with air, it is converted into oxide and sulphate, and by the reaction of an excess of sulphide upon these compounds metallic lead is produced. Hot fuming nitric acid converts lead sulphide into sulphate. Concentrated and boiling hydrochloric acid transforms it into chloride with evolution of hydrogen sulphide.

Galena is used for glazing common pottery. A broth of powdered galena and cow's dung mixed with water is applied to the surface of the previously well-dried vessels.

These are now baked, so that the sulphide melts and spreads over the surface, the organic matter preventing its oxidation. On exposing the articles to a higher temperature they become glazed by the formation of a fusible silicate of lead. The danger in using ware so glazed for culinary purposes is due to the fact that vinegar and other acids dissolve the poisonous lead compound.

LEAD CHLORIDE.

$PbCl^2$

This body may be obtained as a white, crystalline powder by heating litharge with hydrochloric acid. It is deposited as a dense, white precipitate when hydrochloric acid is added to a concentrated solution of acetate or nitrate of lead. It is not very soluble in water; 135 parts of water at 12.5°, or 33 parts of boiling water being required to dissolve one part of lead chloride. It may be obtained crystallized in long needles by allowing its saturated boiling solution to cool. Lead chloride melts below a red heat, and on cooling solidifies to a semi-transparent mass, which was formerly called horn-lead.

Mineral yellow, *Turner's yellow*, and *Cassel yellow*, employed in painting, are oxychlorides of lead, combinations of lead oxide and chloride in variable proportions.

LEAD TETRACHLORIDE, $PbCl^4$.—When lead dioxide is dissolved in hydrochloric acid at very low temperatures, this compound is produced. On addition of ammonium chloride it is precipitated as the double salt $PbCl^4.2NH^4Cl$, and this, treated with strong sulphuric acid at 0°, yields the pure tetrachloride (Friedrich).

It is a heavy yellow oil, which solidifies at —15°. Water decomposes it into lead chloride and chlorine.

LEAD IODIDE.

PbI^2

When a solution of potassium iodide is added to a solution of lead acetate, a beautiful yellow precipitate of lead iodide is formed.

This body melts to a red-brown liquid at a high temperature. It requires for solution 1235 parts of cold, or 194 parts of boiling water. On the cooling of its saturated, boiling solution, it is deposited in golden-yellow, hexagonal scales having a magnificent lustre.

LEAD NITRATE.

$Pb(NO^3)^2$

This body is prepared by dissolving litharge in dilute nitric acid. It crystallizes from its hot, saturated solution in anhydrous, white, regular octahedra. These crystals decrepitate when they are heated; they dissolve in $7\frac{1}{2}$ times their weight of cold water, and in a much less quantity of boiling water.

At a red heat this salt is decomposed into nitrogen peroxide, oxygen, and lead monoxide. It forms various basic compounds with lead monoxide.

When one molecule of the nitrate is boiled with one molecule of the monoxide, and the filtered solution is allowed to cool, a crystalline deposit is obtained, which is a dibasic nitrate, $Pb(NO^3)^2 + PbO + H^2O$ (Pelouze). This salt can be considered as derived from orthonitric acid, $H^3NO^4 = HNO^3 + H^2O$. Indeed

$$Pb(NO^3)^2 + PbO + H^2O = 2\left.\begin{matrix}Pb\\H\end{matrix}\right\}NO^4$$

This basic nitrate of lead corresponds to the basic nitrate of bismuth (page 379).

$Bi'''NO^4$	$\left.\begin{matrix}Pb''\\H\end{matrix}\right\}NO^4$
Bismuth subnitrate.	Lead subnitrate.

When a solution of nitrate of lead is boiled with thin sheet-lead, the latter is dissolved, and the liquid assumes a yellow color. Under these conditions soluble basic nitrites of lead are formed. On cooling the filtered liquid deposits yellow crystals having a variable composition. By a prolonged boiling a tetrabasic nitrite, $Pb(NO^2)^2 + 3PbO + H^2O$, is obtained. The solution of the latter, decomposed by carbon dioxide, gives the neutral nitrite $Pb(NO^2)^2 + H^2O$, crystallizing in long, yellow prisms (Peligot) or in yellow plates (Chevreul).

LEAD SULPHATE.

$PbSO^4$

This salt is found native, and beautifully crystallized, as *anglesite.* It can be prepared by double decomposition by precipitating the solution of any soluble lead salt, such as the nitrate or acetate, with sulphuric acid or solution of a sulphate. It is a white powder, insoluble in water.

At a high temperature, lead sulphate melts without decomposition. Charcoal reduces it, transforming it into sulphide, metal, or oxide, according to the proportions employed. Quickly heated with an excess of charcoal, it yields sulphide.

$$PbSO^4 + C^2 = 2CO^2 + PbS$$

By diminishing the proportion of charcoal, a residue of metal, or even of oxide, may be obtained.

$$PbSO^4 + C = CO^2 + SO^2 + Pb$$
$$2PbSO^4 + C = CO^2 + 2SO^2 + 2PbO$$

Iron and zinc, in contact with lead sulphate suspended in water, cause the separation of metallic lead.

LEAD CARBONATE.

$PbCO^3$

Crystallized lead carbonate is found in nature as the mineral *cerusite.* The salt may be obtained artificially, as an amorphous white powder, by precipitating a soluble lead salt by an excess of an alkaline carbonate.

A hydrated, and sometimes basic, carbonate of lead is known as *ceruse* or *white lead.* Its composition varies.

$$PbCO^3 + H^2O \text{ and } 2PbCO^3 + Pb(OH)^2$$

White lead is extensively used as a paint and paint body. It is prepared by several methods, the oldest of which is called the Dutch process. It consists in exposing sheets of lead to an atmosphere charged with acetic acid vapor and rich in carbonic acid gas. The leaden sheets are introduced into glazed earthen pots, A (Fig. 110), containing a small quantity of vinegar. The lead rests upon short projecting arms, B, below which is placed the crude vinegar. The pots are covered by a disk of lead, D, which incompletely closes them. They are then arranged in rows in large chambers; a row of pots is placed on a bed of spent tan or horse-manure; these are covered with planks, upon which more spent tan or horse-manure is placed, and then another layer of pots, and so on. The fer-

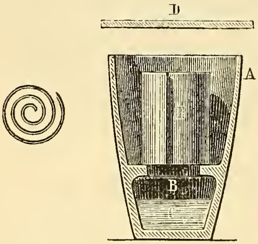


Fig. 110.

mentation of the tan or manure raises the temperature to 30 or 40°, and produces carbonic acid gas. On the other hand, the oxygen of the air intervenes, causing the lead to be attacked by the acetic acid, so that basic acetate of lead is formed upon the surface of the metal; but this salt is continually decomposed by the carbonic acid gas, so that the lead gradually becomes covered with a layer of carbonate.

Thenard suggested another process by which litharge is dissolved in a solution of lead acetate, and a current of carbon dioxide passed through the solution of subacetate so formed. Lead carbonate is precipitated and neutral acetate regenerated; the latter is then again transformed into basic acetate. The product so obtained is known as *Clichy white lead.*

LEAD CHROMATE.

$PbCrO^4$

This salt exists crystallized in nature, constituting the *crocoite* of Siberia. It is prepared by double decomposition between solutions of potassium chromate and lead acetate; a yellow precipitate is thus obtained, and is employed in painting under the name *chrome yellow.*

Lead chromate melts at a red heat; at a white heat it loses 4 per cent. of oxygen. It is easily reduced by charcoal and hydrogen. Insoluble in water, it dissolves readily in solutions of potassium hydroxide.

Characters of Lead Salts.—The soluble lead salts have a sweetish taste. Black precipitates are formed in their solutions by both hydrogen sulphide and ammonium sulphide.

The caustic alkalies give white precipitates, soluble in a large excess of the reagent. Ammonia gives a white precipitate, insoluble in excess.

Sulphuric acid forms a white precipitate even in the most dilute solutions of lead. Hydrochloric acid forms a white precipitate of lead chloride, but this precipitate is not produced in dilute solutions.

Potassium chromate throws down a yellow precipitate, soluble in potassium hydroxide.

When heated with sodium carbonate upon a piece of charcoal in the reducing flame of the blow-pipe, the lead salts yield a metallic globule which when cold can readily be flattened out by hammering.

THALLIUM.

$Tl = 202.6$

The spectroscopic green line given by this metal was first observed by William Crookes, who regarded it as characteristic of a new element. The honor of having isolated the latter and of establishing its true character belongs to Lamy.

Thallium is widely distributed in nature, but constitutes only a very small proportion of the minerals in which it occurs, excepting the very rare *crookesite*, which contains 16 to 18 per cent.

It is a heavy metal, rather whiter than lead; it is soft and sectile. Its density is 11.9, and it melts at 285°. It is soluble in dilute sulphuric and nitric acids.

Thallium forms two oxides, to which correspond two series of salts.

Thallous oxide, Tl^2O, is a black powder; the corresponding *hydroxide*, $TlOH$, is soluble and caustic like the alkalies, and crystallizes in yellowish prisms. *Thallous chloride*, $TlCl$, is sparingly soluble in water. The carbonate, Tl^2CO^3, is quite soluble in water.

Thallic oxide, Tl^2O^3, is obtained as a dark powder, when thallium burns in oxygen or when the hydroxide is heated. The compounds derived from this oxide are less stable than the thallous compounds: the chloride $TlCl^3$, sulphate $Tl^2(SO^4)^3$, and other thallic salts have been prepared.

COPPER.

Cu(Cuprum) $= 63.12$

Natural State.—Copper is found in the native state, sometimes crystallized in isometric forms, sometimes in masses. It is also found as cuprous oxide, Cu^2O, cupric oxide, CuO, and cupric carbonate, $CuCO^3$; but its most abundant minerals are cuprous sulphide, Cu^2S (*chalcocite*), and a double sulphide of copper and iron, $Cu^2S.Fe^2S^3$, designated as *copper pyrites*. Under the name *gray copper* are also worked various minerals containing cuprous sulphide combined with the sulphides of antimony and arsenic, and in which the copper is sometimes replaced by iron, zinc, silver, and mercury.

Treatment of Copper Ores.—Copper is easily extracted from cuprous oxide and cupric carbonate. These ores are melted with charcoal in suitable furnaces, and the metal is at once obtained. Copper pyrites, which is often mixed with cuprous sulphide, requires a more complicated treatment. The iron and sulphur must be eliminated, and for this reason the ore is subjected to an incomplete roasting. This operation is conducted in a reverberatory furnace (Fig. 111). The flame of the fire sweeps the arched vault of the furnace *vv*. The opening of the chimney is at C, and the ore is fed in from iron troughs placed above the furnace.

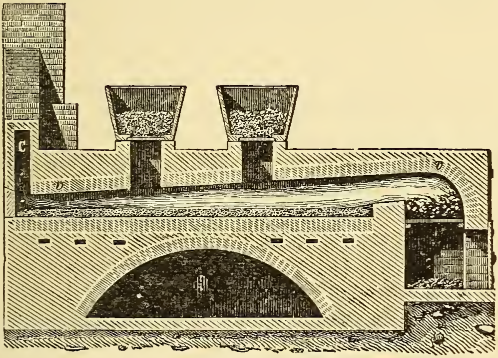


Fig. 111.

The first roasting drives out part of the sulphur, and the sulphides of iron and copper are partially converted into oxides and sulphates. An excess of sulphide remains, and the imperfectly-roasted ore is fused in presence of silicious materials. The scoriæ formed in roasting the *matte* (see farther on) are generally added, and sometimes fluor spar, to render the slag more fusible. This operation is conducted either in cupola-furnaces or in reverberatory furnaces of peculiar construction. In presence of the unattacked sulphide of iron, the cupric oxide formed during the roasting is converted into cuprous sulphide, and oxide of iron is formed. The latter unites with the silica, as does also the oxide produced by the roasting, both being reduced to ferrous oxide by the reducing gases of the fire. Ferrous silicate is thus formed, and constitutes a very fusible slag, below which accumulates the sulphide of copper containing much less sulphide of iron than the original pyrites. This product is the *matte*.

The sulphur, which was thus far necessary to expel the iron, must now be removed, and the matte is broken up and repeatedly roasted, by which the remainder of the iron is oxidized and nearly all of the sulphur expelled. The mineral is now again melted with silicious materials and the scoriæ produced in refining black copper, and rich in cupric oxide, are added. Ferrous silicate separates as a slag, and a metallic mass containing from 90 to 94 per cent. of copper, still alloyed with iron, lead, arsenic, sulphur, etc., is obtained. This is *black copper.*

Instead of reducing matte by successive roasting and melting as above, the sulphur is often removed by blowing air through the melted material in a vessel resembling a Bessemer converter (page 395) and lined with quartz: iron and copper are rapidly oxidized, while sulphur dioxide is given off. The resulting metal is much purer than that obtained by the older process.

Refining of Black Copper.—The impure metal is melted in a reverberatory furnace; the air-holes are then opened, and the impurities are partly volatilized, partly oxidized. The sulphur is driven off as sulphur dioxide, and iron and other metallic impurities, as well as copper, become oxidized and pass into the slag. This is skimmed off so that the metal may absorb more oxygen, which it transmits to the remaining sulphur. Finally the oxygen is eliminated by covering the surface of the metal with coal and plunging poles of green wood into it. The hydrocarbons and carbon monoxide so produced reduce the cuprous oxide to the metal.

Large quantities of copper are now refined by electrolysis. The crude metal is cast in plates which serve as anodes in an acid bath of copper sulphate solution, the cathodes being thin copper plates. Under the influence of the current the anodes are dissolved, and an equivalent quantity of pure copper is deposited on the cathodes. The precious metals remain undissolved, and accumulate in the *anode mud* at the bottom of the tanks, while other impurities, such as arsenic and antimony, are held in solution. The *electrolytic process* yields a product which is practically free from impurities, and it effects the extraction of the gold and silver from crude copper.

In the Lake Superior region, the native copper is separated mechanically from the rock and then subjected to refining operations analogous to those first described. The product is known as *Lake Copper*, and is of the highest grade.

Cement copper is copper precipitated from a solution of cupric sulphate by metallic iron. It is very pure.

Properties of Copper.—This metal has a characteristic red color that is universally known. When rubbed with the hand it exhales a peculiar, disagreeable odor. By fusion it crystallizes in cubes, but it may be deposited by electrolysis in regular octahedra. It melts towards 1100°, and may be volatilized by the heat of the oxyhydrogen blow-pipe or in the electric furnace.

Its density varies from 8.85 to 8.95. It is very malleable, ductile, and tenacious.

In dry air it is unaltered at ordinary temperatures, but it absorbs oxygen in presence of moisture and carbonic acid gas. Green spots are then formed upon the surface of the metal, constituting a hydrocarbonate of copper; this is the product ordinarily called verdigris.

At a high temperature copper absorbs oxygen with avidity, being converted into black, cupric oxide if the oxygen be in excess; but in the contrary case, red, cuprous oxide is formed. The oxidation is favored by division of the metal.

If some pulverulent copper, produced by the decomposition of copper acetate, be thrown upon a moderately hot tile and an incandescent coal be approached so as to heat one point, a black spot instantly forms there and rapidly extends throughout the mass, showing the progress of the oxidation.

In presence of acids or ammonia, copper rapidly absorbs oxygen at ordinary temperatures.

If some ammonia and copper-turnings be shaken up with air in a glass-stoppered bottle, the ammoniacal liquid becomes blue; if now the bottle be turned upside-down and opened under water, the latter will rise in the bottle, replacing the oxygen which was absorbed. The blue liquid contains in solution ammoniacal oxide of copper and nitrite of copper (Schönbein, Peligot).

This liquid is capable of dissolving cotton and lint, which are almost pure cellulose (Schweizer).

When heated with concentrated sulphuric acid, copper is converted into sulphate with disengagement of sulphurous acid gas. Nitric acid, even dilute, dissolves it readily, forming cupric nitrate and evolving nitric oxide. Boiling hydrochloric acid attacks it slowly, disengaging hydrogen and forming cuprous chloride.

Uses of Copper.—Copper is much employed for the construction of boilers, alembics, stills and worms, and for kitchen utensils. Owing to its high electric conductivity, enormous quantities are used in electric constructions for cables, dynamos, etc. Sheet-copper is used for coating the bottoms of ships and sometimes for roofing houses. This metal enters into the composition of many important alloys, such as brass, various bronzes, and German silver.

CUPROUS OXIDE.

Cu^2O

This oxide is found native as *cuprite*, sometimes in vitreous masses, sometimes in beautiful, red, regular octahedra.

It is ordinarily prepared in the wet way by boiling a solution of acetate of copper with glucose; a bright-red, crystalline powder is precipitated, which is anhydrous cuprous oxide. When heated in contact with air, it absorbs oxygen and is converted into cupric oxide.

When caustic potash is added to a solution of cuprous chloride, a yellow precipitate of cuprous hydroxide is thrown down. Cuprous oxide is used to communicate a red color to glass.

CUPRIC OXIDE.

CuO

Two processes are used for the preparation of this important body: calcination of copper in the air; calcination of cupric nitrate. The first method furnishes a granular, compact, black oxide; the second, a fine, deep-black powder.

Cupric oxide is easily reduced by both hydrogen and charcoal, with formation of either water or carbon dioxide.

Cupric hydroxide, $Cu(OH)^2$, is obtained as a voluminous, light-blue precipitate when caustic potash is added to the solution of a cupric salt. This hydroxide is converted into brown, anhydrous oxide by boiling with water. Cupric oxide is largely used in the laboratory in the analysis of organic substances. It is used in the arts to color glass, to which it imparts a green color.

SULPHIDES OF COPPER.

Copper forms two sulphides, corresponding to the oxides. *Cuprous sulphide*, Cu^2S, occurs in nature as *chalcocite* in fusible, steel-gray crystals, which may be scratched with a knife.

Cupric sulphide CuS, is formed in the wet way when a solution of a copper salt is precipitated by hydrogen sulphide. When strongly calcined, it loses sulphur and is reduced to cuprous sulphide.

If copper filings or turnings be thrown into a flask containing boiling sulphur, a brilliant incandescence takes place from the union of the two elements.

CHLORIDES OF COPPER.

Cuprous chloride, CuCl, is prepared by boiling copper-turnings in hydrochloric acid and adding small quantities of nitric acid from time to time. The nitro-muriatic acid formed converts the copper into cupric chloride, which is reduced by the excess of copper present. A brown liquid is thus obtained which, by continued boiling, becomes almost colorless. On adding water to this liquid, a white, crystalline precipitate of cuprous chloride is deposited. It is insoluble in water, but dissolves in aqueous ammonia, forming a liquid which remains colorless when kept in closed vessels in presence of an excess of copper, but becomes blue on exposure to the air, from which it absorbs oxygen.

Carbon monoxide is perfectly absorbed by a solution of cuprous chloride in hydrochloric acid or in ammonia.

Cupric chloride, $CuCl^2$, is obtained by dissolving cupric oxide in hydrochloric acid or copper in aqua regia. A green solution is formed, which, after concentration, deposits beautiful rhombic prisms of a bluish-green color, containing 2 molecules of water of crystallization.

CUPRIC SULPHATE.

$CuSO^4 + 5H^2O$

Preparation.—This salt is commonly called *blue vitriol*. It is a product of many industrial operations, such as roasting sulphurous copper ores, and the decomposition by copper of the silver sulphate resulting from the refining of gold,—that is, the treatment of silver coin containing gold with sulphuric acid.

Cupric sulphate produced by roasting copper ore contains more or less ferrous sulphate. The two salts crystallize together in monoclinic prisms, containing 7 molecules of water of crystallization. The mixture is called Salzburg vitriol.

Instead of copper pyrites, artificial cupric sulphide may be oxidized. Old copper plates are moistened and sprinkled with flowers of sulphur; they are then heated in a furnace, and the sulphide of copper first formed is converted into sulphate by the oxygen of the air drawn into the furnace. The still hot plates are plunged into water, which dissolves the layer of cupric sulphate, and the same operation is repeated until all of the metal is transformed into sulphate.

The simplest process consists in boiling copper turnings and clippings with sulphuric acid: sulphurous acid gas is disengaged, and cupric sulphate formed. In the arts, the operation is conducted in wooden tanks lined with lead and heated by steam.

Properties.—Cupric sulphate crystallizes in large tabular forms belonging to the triclinic system. These crystals have a fine blue color, and contain 5 molecules of water. When exposed to dry air they effloresce superficially: heated to 100°, they lose 4 molecules of water, disengaging the fifth only at 243°. The anhydrous salt is white. At a high heat, cupric sulphate is decomposed into cupric oxide, sulphurous oxide, and oxygen.

Cupric sulphate dissolves in 4 parts of cold, and in 2 parts of boiling water, and the concentrated solution has a pure blue color. It is insoluble in alcohol.

When an excess of ammonia is added to a solution of cupric sulphate, a beautiful, dark-blue liquid is obtained. It contains ammoniacal cupric sulphate, $CuSO^4 + 4NH^3 + H^2O$, which separates in dark-blue crystals when alcohol is added to the aqueous solution.

There are several basic sulphates of copper representing compounds of cupric sulphate and cupric hydroxide. One of them is obtained as a green powder when a solution of cupric sulphate is digested with cupric hydroxide. The bluish precipitates obtained by incompletely precipitating solutions of cupric sulphate with potassium hydroxide are basic sulphates.

Uses.—Cupric sulphate is employed as a caustic applicable to diseases of the eye. In the arts, it is used in the preparation of *blue ashes*, a mixture of calcium sulphate and cupric hydrate, made by decomposing cupric sulphate with milk of lime.

It is much used in dyeing, particularly in dyeing black on wool and cotton. It is also employed for preserving wood.

Large quantities of sulphate of copper are employed for electrotyping, and for electric batteries.

CARBONATES OF COPPER.

When cold solutions of sodium carbonate and cupric sulphate are mixed, a bluish-green precipitate is obtained, and at the same time carbonic acid gas is disengaged. The precipitate becomes green when washed with warm water. It is known as mineral green, and can be regarded as a combination of one molecule of cupric carbonate with one molecule of cupric hydroxide. It contains

$$CuCO^3 + Cu(OH)^2$$

A similar compound exists in nature, constituting *malachite.* This mineral occurs in green masses. When cut and polished, it presents veins of various tints, and is fashioned into ornamental objects, such as vases, cups, etc.

Azurite or *mountain blue*, which crystallizes in beautiful, blue, oblique rhombic prisms, can be regarded as a compound of two molecules of cupric carbonate with one of the hydrate.

$$2CuCO^3 + Cu(OH)^2$$

Debray has reproduced azurite artificially by leaving calcium carbonate for a long time in contact with cupric nitrate in sealed tubes.

ALLOYS OF COPPER.

Brass is an alloy of copper and zinc, ordinarily containing $\frac{1}{3}$ zinc and $\frac{2}{3}$ copper. It often contains a small proportion of tin and even of lead.

Bronze is an alloy of copper and tin (see table of alloys, page 249). While brass is malleable and ductile, bronze is brittle when it has been slowly cooled, but it becomes malleable after tempering,—that is, when it is heated to redness and then plunged into cold water.

German silver contains 25 per cent. of zinc, 25 of nickel, and 50 of copper.

Aluminium-bronze, phosphor-bronze, manganese-bronze, and silicon-bronze are very tenacious and valuable alloys of copper with the elements indicated by the names. Silicon-bronze is used for telegraph-wires, and manganese-bronze for the propellers of ships, as it resists the corroding action of salt water and is remarkably tenacious.

Characters of Copper Salts.—These salts are blue or green. Their solutions are precipitated brown by hydrogen sulphide and ammonium sulphide; an excess of the latter reagent will not dissolve the precipitate.

Potassium hydroxide forms a dense, light-blue precipitate, insoluble in excess. Ammonia-water first forms a pale-blue precipitate, which is then dissolved by an excess of the reagent with a rich sky-blue color.

Potassium ferrocyanide gives a reddish-brown precipitate even in very dilute cupric solutions.

An apple-green precipitate of cupric arsenite (Scheele's green) is formed when potassium arsenite is added to cupric sulphate.

A bright piece of iron plunged into a cupric solution instantly becomes covered with a deposit of metallic copper.

MERCURY.

Hg (Hydrargyrum) = 200

Natural State and Extraction.—Mercury occurs native, and especially combined with sulphur, mercuric sulphide or natural *cinnabar* being its principal ore. It is found in different localities in Europe and America, principally at Almaden, Spain; Idria, in Carniola; and in California.

The treatment of the ore is very simple. The sulphide is roasted in a current of air in furnaces of peculiar construction: the sulphur is oxidized, and passes off as sulphur dioxide, the mercury being set free. The metal volatilizes and is led, together with the gases from the combustion, either into condensation-chambers, or through long rows of little cylindrical vessels, where the mercury condenses.

Fig. 113 represents the furnaces employed at Almaden, with the fireplace, and the body, AB, charged with ore. The mercury-vapor passes by *o*, and condenses in a series of *aludels* entering one in the other, and arranged upon two inclined planes, *ab*, *bc*. The condensed metal runs into a channel, *b*, from which it is conducted into a reservoir. The sulphurous acid gas, still charged with vapor of mercury, passes into a chamber, C, descending to the floor, where it is cooled by contact with a trough filled with water, *d*. In this chamber the condensation of the mercury-vapor is completed.

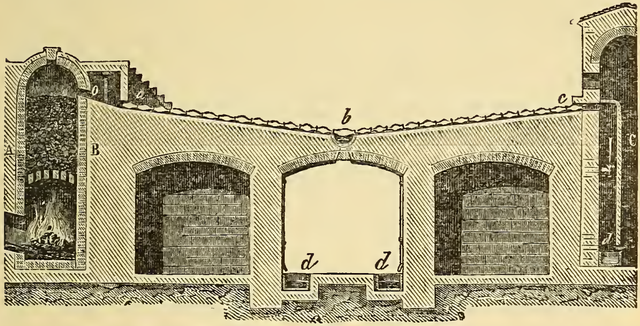


Fig. 113.

Fig. 114 represents the several-storied furnaces *aa*, *bb*, *cc*, and the condensation-chambers CC, used at Idria.

Cinnabar may also be reduced by iron or by lime.

The metal thus extracted is purified by filtration through ticking-cloth or chamois-skin. It is ordinarily transported in forged iron bottles.

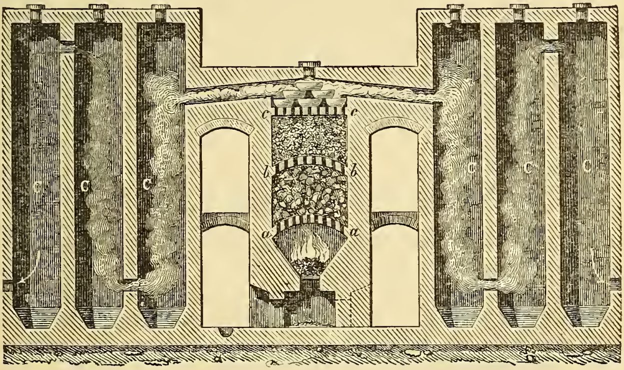


Fig. 114.

The mercury of commerce is nearly always alloyed with small quantities of other metals, such as lead, tin, copper, and bismuth. In this state its surface is not as brilliant as when pure, it does not run as readily, and the drops are drawn out to a point. They are said to form tails. It may be purified by distillation, an operation which requires certain precautions on account of the violent bumping of boiling mercury. This distillation is best effected under diminished pressure. Mercury may also be purified by digesting it for several days with one-thirtieth its weight of commercial nitric acid diluted with its own weight of water; the aqueous liquid is then decanted and the mercury washed, first with warm water acidulated with nitric acid, then with pure water, after which it can be dried. In this operation, the nitric acid removes the foreign metals, more oxidizable than the mercury, which displace the latter metal from its solution in the nitric acid.

Properties.—Mercury is liquid, but solidifies at —40°. The solid metal at this low temperature is malleable, and has a density of 14.4. The density of liquid mercury is 13.595. It boils at 350° of an air thermometer. Its vapor is colorless, and has a density of 6.976.

It is unaltered by contact with the air at ordinary temperatures, but at 300° it slowly absorbs oxygen, and its surface becomes covered with a red powder, which is mercuric oxide, called by the ancients *red precipitate.*

Mercury combines with chlorine, bromine, and iodine at ordinary temperatures, and with sulphur by the aid of a gentle heat.

Hydrochloric acid does not attack it. Dilute nitric acid dissolves it in the cold, forming mercurous nitrate. Hot nitric acid dissolves it, forming mercuric nitrate and evolving red vapors.

OXIDES OF MERCURY.

Two oxides of mercury are known, mercurous oxide, Hg^2O, and mercuric oxide, HgO.

The first is prepared by digesting mercurous chloride with potassium hydroxide; a black powder is obtained which is very unstable. By the action of light, or by a temperature above 100°, it decomposes into mercuric oxide and mercury.

Mercuric Oxide, HgO, can be obtained by either the dry or wet method. The first consists in decomposing mercuric nitrate by heat; the salt is gradually heated in a flask on a sand-bath until red vapors cease to be disengaged.

The oxide thus prepared is an orange-red, granular, and crystalline powder.

Mercuric oxide is prepared in the wet way by decomposing a solution of mercuric chloride by caustic potash. A yellow precipitate of anhydrous mercuric oxide is obtained.

When mercuric oxide is heated, it assumes a dark-red color and decomposes, if the temperature be above 400°, into oxygen and mercury. It yields its oxygen to many bodies, such as charcoal, sulphur, and phosphorus, which it oxidizes energetically. When heated with sulphur, it produces an explosion. In these reactions the finely-divided yellow oxide is more active than the red oxide.

MERCURIC SULPHIDE.

HgS

This is the cinnabar generally found in nature in compact masses, sometimes in transparent, red, hexagonal prisms or rhombohedra. It is manufactured by directly combining sulphur and mercury. The combination takes place when the bodies are triturated together in the cold, in the proportion of 100 parts of mercury and 18 parts of sulphur. A black mass is thus obtained which is sublimed in iron vessels.

Cinnabar prepared by sublimation occurs in dark-red masses, having a fibrous and crystalline structure. Its density is 8.124. At a high temperature, it volatilizes without melting. When heated in the air, it burns with a blue flame, yielding sulphurous acid gas and metallic mercury. It is decomposed by hydrogen, charcoal, and most of the metals. Boiling sulphuric acid decomposes it with formation of sulphurous acid gas and sulphate of mercury. Nitric acid scarcely attacks it, even when boiling.

Vermilion is a finely-divided mercuric sulphide having a rich scarlet color. It is prepared by triturating for several hours in a mortar, 300 parts of mercury and 114 parts of flowers of sulphur, and adding to the black sulphide thus obtained 75 parts of caustic potash and 400 parts of water. The mixture is maintained at a temperature of about 45°, being continually triturated with a pestle. As soon as the powder has acquired a fine scarlet color, it is rapidly washed with hot water and dried. It is employed in painting and also to color sealing-wax.

MERCUROUS CHLORIDE, OR CALOMEL.

$HgCl$

Mercurous chloride is largely used in medicine under the name *calomel* or *mild chloride of mercury.*

Preparation.—An intimate mixture of mercurous sulphate and sodium chloride is heated in a capacious glass matrass on a sand-bath. The mercurous chloride, formed by double decomposition, sublimes.

$$Hg^2SO^4 + 2NaCl = 2HgCl + Na^2SO^4$$

It is thus obtained in compact, crystalline masses. When it is strongly heated and its vapor passed into large stoneware vessels filled with steam, it condenses in an impalpable powder, in which form it is used by preference in medicine.

Calomel may also be prepared in the wet way by adding hydrochloric acid, or a solution of sodium chloride, to a solution of mercurous nitrate. A white, curdy precipitate is obtained which is washed and dried.

Properties.—Prepared in the dry way calomel occurs as dense, fibrous, crystalline and slightly transparent masses, one side of which is smooth, the other presenting the sharp points of the crystals. When exposed to light, it becomes yellow and even gray in time, being partially decomposed. Its density is 7.17. It melts and volatilizes at the same temperature: the density of the vapor is 8.12, and corresponds to the formula $HgCl$, which is analogous to that of silver chloride. When slowly sublimed, calomel crystallizes in tetragonal prisms. It is insoluble in water.

A solution of potassium iodide agitated with calomel converts it into a green powder of mercurous iodide. If an excess of potassium iodide be employed, the green powder disappears and is replaced by a gray precipitate of metallic mercury, the mercurous iodide at first formed being decomposed into mercury and mercuric iodide, which dissolves in the potassium iodide.

An analogous reaction takes place with the alkaline chlorides by the aid of heat, the mercurous chloride breaking up into mercuric chloride which dissolves, and metallic mercury which is deposited.

MERCURIC CHLORIDE, OR CORROSIVE SUBLIMATE.

$HgCl^2$

Preparation.—This body is obtained by double decomposition, by heating a mixture of mercuric sulphate and sodium chloride on a sand-bath. The mercuric chloride condenses in the upper part of the matrasses which are imbedded up to the neck in the sand.

$$HgSO^4 + 2NaCl = Na^2SO^4 + HgCl^2$$

Towards the close of the operation the heat is increased in order to agglomerate the sublimate by a partial fusion.

Another process consists in passing chlorine into heated mercury; the combination takes place with the production of luminous heat.

Properties.—Mercuric chloride prepared by the dry method occurs in compact, white, crystalline and friable masses, having a density of 6.5. It is an energetic poison. It melts at about 265°, and boils towards 295°. The density of its vapor is 9.42. By sublimation it may be obtained crystallized in rectangular octahedra.

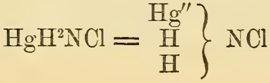
It is soluble in 19 parts of cold water, also in alcohol and ether. It is deposited from its hot, saturated, aqueous solution in long prisms, belonging to the type of the right rhombic prism. The crystals are anhydrous.

The aqueous solution of mercuric chloride produces a white precipitate in a solution of albumen of white of egg. This precipitate is a combination of mercuric chloride and albumen. Albumen is thus the antidote to corrosive sublimate. Corrosive sublimate is one of the most powerful antiseptics: it is used in surgery, medicine, taxidermy, preserving wood, etc.

When a slight excess of ammonia is added to a solution of corrosive sublimate, a white deposit is formed, known as *white precipitate*, of which the composition is HgH^2NCl.

$$HgCl^2 + 2NH^3 = NH^4Cl + HgH^2NCl$$

It may be regarded as the chloride of mercury-ammonium, that is, ammonium chloride in which 2 atoms of hydrogen are replaced by one atom of the diatomic metal mercury.



$$HgH^2NCl = \left.\begin{matrix} Hg'' \\ H \\ H \end{matrix}\right\} NCl$$

Corrosive sublimate forms crystallizable double combinations with the alkaline chlorides and with ammonium chloride.

MERCUROUS IODIDE.

HgI

This compound is ordinarily prepared by directly combining mercury and iodine. 100 parts of mercury and 63.5 parts of iodine are triturated with a small quantity of alcohol, until the whole is converted into a green powder, which is then washed with boiling alcohol and dried.

It may also be prepared by double decomposition by precipitating a solution of mercurous nitrate with potassium iodide, or by the reaction of the latter body upon calomel.

Mercurous iodide is not a stable compound. It is decomposed by light. Heat breaks it up into mercury and mercuric iodide, and the same decomposition is effected by potassium iodide and the alkaline chlorides.

MERCURIC IODIDE.

HgI^2

Mercuric iodide is prepared by pouring a solution of 100 parts of potassium iodide into a solution of 80 parts of corrosive sublimate. A beautiful scarlet-red precipitate of mercuric iodide is thrown down.

It is necessary that the bodies be employed in the proportions indicated; an excess of potassium iodide would dissolve the mercuric iodide first precipitated.

Mercuric iodide is almost insoluble in water; it is slightly soluble in boiling alcohol, which deposits it on cooling in small red octahedral crystals.

If mercuric iodide be heated in a small glass retort, it melts to a dark-yellow liquid which solidifies on cooling to a yellow mass. At a higher temperature the liquid boils and its vapor condenses in a dark-yellow liquid which solidifies to a yellow mass; at the same time, right rhombic prisms of a yellow color sublime. If these be rubbed with a glass rod or other hard body they instantly become red, first at the point of contact, then throughout the entire mass.

These two forms of mercuric iodide constitute one of the most curious examples of dimorphism.

Mercuric iodide forms a combination with potassium iodide which is soluble in water. A solution of this potassium-mercuric iodide is not precipitated by potassium hydroxide, but the liquid rendered alkaline by the latter reagent is a very sensitive test for ammonia (*Nessler's test*), with which it gives a precipitate or a brown cloud more or less intense, according to the quantity of ammonia present.

NITRATES OF MERCURY.

Neutral *mercurous nitrate*, $HgNO^3 + H^2O$, is obtained by the action of an excess of cold, dilute nitric acid upon metallic mercury. After some time, short colorless prisms are formed in the liquid, constituting the neutral salt. The latter is readily soluble in water charged with nitric acid.

When mercury is attacked by an excess of boiling nitric acid and the solution is evaporated, voluminous crystals of a basic mercuric nitrate separate, $Hg(NO^3)^2.HgO + 2H^2O$.

The syrupy liquid from which these crystals are deposited, contains neutral *mercuric nitrate*.

$$Hg(NO^3)^2 + 4H^2O$$

This salt is deposited in large, colorless, rhombic tables when the syrupy solution is cooled to —15°.

A large quantity of cold water decomposes this nitrate into nitric acid which dissolves, and a basic salt, $Hg(NO^3)^2.2HgO + H^2O$, forming a yellow powder.

SULPHATES OF MERCURY.

There is a *mercurous sulphate*, Hg^2SO^4, and a *mercuric sulphate*, $Hg''SO^4$.

The first is obtained by heating equal parts of mercury and sulphuric acid, arresting the operation when two-thirds of the mercury are converted into a white, crystalline powder. Mercurous sulphate is but slightly soluble in cold water.

To prepare mercuric sulphate, 1 part of mercury and 1½ parts of sulphuric acid are heated to dryness on a sand-bath.

$$Hg + 2H^2SO^4 = 2H^2O + HgSO^4 + SO^2$$

It is well to add a small quantity of nitric acid before drying.

Mercuric sulphate is an anhydrous, white powder. It decomposes at a red heat into metallic mercury, sulphurous acid gas, and oxygen. Charcoal reduces it readily, equal volumes of carbon dioxide and sulphur dioxide being disengaged.

Mercuric sulphate is slightly soluble in water: a large quantity of cold water converts it into a yellow, basic salt, $HgSO^4.2HgO$, known as *turpeth mineral.*

Characters of Mercurous Salts.—Their solutions are precipitated black by hydrogen sulphide, and also by potassium hydroxide and ammonia. Hydrochloric acid gives a white precipitate which is blackened by ammonia. Potassium iodide forms a green precipitate of mercurous iodide, converted by an excess of the reagent into mercuric iodide which dissolves, and gray metallic mercury.

Characters of Mercuric Salts.—Solutions of mercuric salts are precipitated black by an excess of hydrogen sulphide, and by ammonium sulphide.

Potassium hydroxide forms a yellow precipitate, insoluble in excess.

Ammonia yields a white precipitate in solutions of corrosive sublimate.

Hydrochloric acid does not precipitate the mercuric salts.

Iron, zinc, and copper precipitate metallic mercury from both mercurous and mercuric solutions. A strip of copper dipped into such solutions becomes covered with a gray coating which acquires brilliancy by rubbing.

Heated with lime in a glass tube, all of the mercury compounds yield metallic mercury which sublimes in small globules, easy to recognize under the microscope, and which can be characterized by the addition of iodine, the vapor of which converts the metallic globules into yellow or red mercuric iodide.

Atomicity of Copper and Mercury.—Copper and mercury form two series of compounds. In the cuprous and mercurous compounds they resemble silver, playing the part of monatomic elements. In other compounds, constituting the cupric and mercuric series, these metals are distinctly diatomic, like those of the magnesium group.

VANADIUM.

$V = 51$

Vanadium, niobium, tantalum, thallium, gold, and bismuth constitute a class of triatomic or pentatomic elements. The first three are more closely related to the non-metallic bodies than to the metals, and might properly be considered as members of the group of which nitrogen and phosphorus are types.

Vanadium is widely disseminated, occurring as vanadates of lead, copper, bismuth, zinc, calcium, etc., and in many argillaceous iron ores, but always in small quantity.

The compounds of the metal may be prepared most readily from the native vanadates *vanadinite* or *mottramite*. The powdered mineral is dissolved in hydrochloric acid, the solution concentrated, and ammonium chloride added; ammonium metavanadate separates. This is repeatedly recrystallized and converted into vanadic oxide, V^2O^5, by gentle ignition.

By heating vanadic oxide in hydrogen, it is converted into the trioxide V^2O^3, and with carbon it may be reduced to the dioxide V^2O^2. The metal has been obtained by the long-continued action of perfectly pure hydrogen upon the dichloride VCl^2 at a red heat (Roscoe), and also by heating the oxides with charcoal in the electric furnace (Moissan).

Its chemical relations place vanadium in the nitrogen group: the vanadates are isomorphous with the phosphates and arsenates. The oxides known are V^2O, V^2O^2, V^2O^3, V^2O^4, and V^2O^5, and the chlorides VCl^2, VCl^3, and VCl^4 have been obtained; there are also oxychlorides.

Although vanadium is not very abundant, vanadic acid is employed in certain dyeing operations, by reason of the facility with which it passes to a lower stage of oxidation and again becomes oxidized, thus transferring oxygen from the air to the dye-stuff. Metavanadic acid, HVO^3, is a brilliant yellow, metal-like substance, and has been proposed as a substitute for gold bronze.

NIOBIUM AND TANTALUM.

$Nb = 94$ $Ta = 182$

These elements are associated in several minerals, and were regarded as identical until 1846. Their principal sources are *columbite*, a niobate of iron and manganese, $(NbO^3)^2FeMn$, in which more or less of the niobium is usually replaced by tantalum; *tantalite*, a ferrous tantalite, $Fe(TaO^3)^3$, in which in like manner a portion of the tantalum is replaced by niobium; *pyrochlorite*, *fergusonite*, *yttrotantalite*, and *euxenite*, in which these elements are associated with yttrium, cerium, etc.

Niobium was obtained as steel-gray crusts by Roscoe, who passed through a red-hot tube the vapor of niobium chloride mixed with hydrogen. Its specific gravity is 7.06; it oxidizes with incandescence when heated in the air, and burns also in chlorine.

There are three oxides of niobium, Nb^2O^2, Nb^2O^4, and Nb^2O^5. A mixture of the latter with the corresponding tantalic oxide may be obtained by fusing niobiferous minerals with potassium acid sulphate, and boiling the fused mass with water. The residue is digested with ammonium sulphide, and the remaining powder boiled with hydrochloric acid. The two oxides, which are unaffected by this treatment, are then separated by converting them into fluotantalate and fluoniobate of potassium; the latter is much more soluble than the former. The potassium salts are then decomposed by boiling with sulphuric acid.

Niobic oxide, Nb^2O^5, is a white, insoluble, infusible powder, which is yellow while hot. When strongly heated in hydrogen it is reduced to the tetroxide, a bluish-black powder, which burns into the pentoxide when heated to redness in the air.

Niobium pentoxide is the anhydride of niobic acid, $HNbO^3$, which is obtained as a white powder by the reaction of niobium pentachloride, $NbCl^5$, with water. The normal niobates have the general composition $R'NbO^3$, and there is also a series of highly complicated niobates, derived from an unknown hydrate, $H^8Nb^6O^{19} + nH^2O$.

Niobium forms two chlorides, $NbCl^3$ and $NbCl^5$, and an oxychloride, $NbOCl^3$.

Tantalum has probably not been obtained in a pure state. Berzelius obtained it as a black powder by heating potassium fluotantalate with potassium.

There are two oxides, Ta^2O^4 and Ta^2O^5. *Tantalic oxide* is separated from the niobic acid, with which it is associated in its minerals, by the process already indicated. It is a white, infusible powder, and becomes crystalline when heated. By strong ignition with charcoal it is converted into the tetroxide.

Tantalic acid, $HTaO^3$, is analogous to niobic acid, and forms corresponding series of salts.

Tantalum chloride, $TaCl^5$, is formed by heating an intimate mixture of tantalic oxide and charcoal in a current of chlorine. Niobic chloride is formed in a similar manner. Both are fusible, volatile solids, crystallizing in yellow needles. There is no tantalum chloride corresponding to the niobous chloride $NbCl^3$.

GOLD.

Au (Aurum) = 195.74

Natural State.—Gold is one of the most anciently known metals. It is generally found in the native state, either in streaks or veins, or in sand. It ordinarily occurs in scales or rounded grains disseminated in alluvial sands, or in the rocks whose disintegration produces such sands. It is well known that gold-dust is suspended in the waters of certain rivers.

It is often found associated with ores of silver, lead, and copper; sometimes in combination with tellurium.

Extraction.—Gold is extracted from auriferous sand by washings, which remove the particles lighter than the gold. The sand, pebbles, and gold, and a strong stream of water are thrown into long wooden sluices arranged in zig-zag and provided with pockets; in the latter the gold sinks, while the lighter earthy material is carried on by the force of the stream. When the gold is in particles too minute to be separated mechanically from the sand, which still remains in small quantity, the whole is agitated with mercury; the gold dissolves. The amalgam thus obtained is compressed in a chamois-skin, which allows the passage of the excess of mercury. When the solid residue is distilled the gold remains.

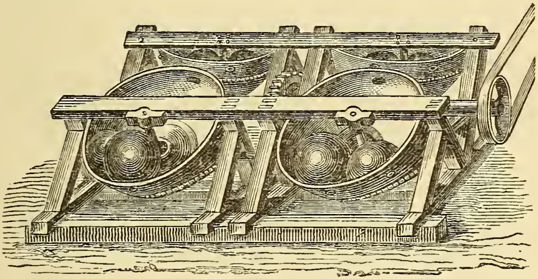


FIG. 115.

Auriferous quartz rocks are crushed to powder, which is then subjected to washings. Mercury is sometimes employed to extract the gold from the pulverized rock. The following process has been employed for some years in California and Australia. The crushed rock, with mercury, water, and two cast-iron balls, is introduced into basins, to which a rotating motion is given

(Fig. 115). By the friction of the balls it is soon reduced to an impalpable powder, which remains suspended in the water, and is carried out with the latter through openings in the upper part of the basins, while the gold amalgamates with the mercury.

Another process, known as the *cyanide process*, depends upon the solubility of finely divided gold in solution of potassium cyanide. A double cyanide of gold and potassium is formed, from which the gold is precipitated by metallic zinc.

$$4Au + 8KCN + 2H^2O + O^2 = 4KAu(CN)^2 + 4KOH$$
$$2KAu(CN)^2 + Zn = K^2Zn(CN)^4 + 2Au$$

From sulphide ores (pyrites) gold may be extracted by means of chlorine. The roasted ore is moistened and treated with chlorine gas. The mass is exhausted with water, when auric chloride goes into solution and the gold is precipitated by means of ferrous sulphate.

Native gold, as well as that extracted from different minerals, is nearly always alloyed with silver. The two metals are separated by the wet way, by attacking the alloy with either nitric or sulphuric acid. Nitrate or sulphate of silver is formed, the latter being soluble in hot water. The gold remains in a pulverulent state. It is to be remarked that the alloy of gold and silver must be rich in silver in order that this process, called refining, can be applied. Hence it is sometimes necessary to increase the proportion of silver by melting the alloy with that metal.

An alloy of gold and silver rich in gold may also be treated with aqua regia. Both metals are converted into chlorides; that of silver is insoluble, while that of gold dissolves. When ferrous sulphate is added to the yellow solution of chloride of gold, a precipitate of metallic gold is obtained, the chlorine acting upon the iron of the ferrous sulphate which is thus transformed into ferric salt.

Properties of Gold.—Pure gold has a beautiful yellow color. In thin leaves it is translucent, allowing the passage of a greenish light. Its density is 19.5. It is quite soft, and is the most malleable and most ductile of the metals.

It melts at 1075°, and volatilizes at a higher temperature. Its vapor is green.

It is unaltered by the air at all temperatures. Sulphuric, hydrochloric, nitric, and phosphoric acids have no action on it either in the cold or when aided by heat. It is dissolved by nitro-hydrochloric acid.

Some gold leaf may be boiled with hydrochloric acid in a test-tube; the gold will resist the action of the acid, and will retain its lustre. Some more gold leaf may be boiled with pure nitric acid in another tube, and again the metal will not be attacked. But on mixing the two liquids, the gold will be dissolved with disengagement of red vapors. Gold trichloride will be formed, and will color the liquid yellow.

OXIDES OF GOLD.

There are two compounds of gold and oxygen, a monoxide, Au^2O, and a trioxide, Au^2O^3. The latter forms compounds with the bases. When magnesia is added to solution of auric chloride, an insoluble yellow precipitate of magnesium aurate is formed; when this is decomposed by nitric acid it leaves auric hydroxide. This hydroxide is yellow; it easily parts with its water, and is converted into a brown-black powder of auric oxide. The latter is not stable, being decomposed by light and by a temperature of about 250°.

CHLORIDES OF GOLD.

Aurous chloride, $AuCl$, is obtained as an insoluble yellow powder by heating auric chloride to 230°.

Auric chloride or *trichloride of gold*, $AuCl^3$, is prepared by dissolving the metal in aqua regia. After concentration the liquid solidifies, on cooling, to a dark-red, crystalline and deliquescent mass.

The solution of auric chloride is yellowish-brown when concentrated, pure yellow when dilute. It is decomposed by light. It colors the skin violet, and is reduced by a great number of bodies. Phosphorus, and hypophosphorous, phosphorous and sulphurous acids precipitate from it metallic gold. It is the same with most of the metals, which combine with the chlorine, setting free the gold. A brown precipitate of metallic gold is immediately obtained on adding a solution of ferrous sulphate to a solution of auric chloride. Auric chloride dissolves in ether, which removes it from its aqueous solution when the two liquids are agitated together.

If a solution of auric chloride be added to a mixture of stannous and stannic chlorides in solution, a flocculent precipitate of a purple color, more or less pure according to the concentration of the solutions and the proportions of the mixture, will be formed. It is *purple of Cassius*, a compound employed in painting on glass and porcelain. It contains tin, gold, oxygen, and hydrogen, but its constitution is not well known.

Auric chloride forms crystalline compounds with the alkaline chlorides. When a mixture of chloride of gold and sodium chloride is evaporated until a pellicle forms on its surface, yellow crystals containing $NaCl.AuCl^3 + 2H^2O$, are formed on cooling.

Gilding.—Several processes are used for gilding metals, such as silver and copper. The objects may be gilded by amalgamation, or by galvanic deposition.

Gilding by Amalgamation.—Gold readily alloys with mercury, and the amalgam is used for gilding objects of silver and copper. The pieces are heated to destroy greasy matters, and are then cleaned by dipping them into dilute sulphuric acid, after which they are washed and dried with saw-dust. They are then rubbed with a brush of brass wires dipped into a solution of mercurous nitrate, and then with a brush impregnated with an amalgam of one part of gold and eight parts of mercury. They are afterwards heated to volatilize the mercury, an operation dangerous to the health of the workmen, and which should be conducted in a furnace having a good draught. The pieces thus gilded are dull; they become lustrous after suitable washings and polishings.

Electro-Gilding.—The copper objects, previously heated and cleaned by dilute sulphuric acid, are plunged for a few seconds into dilute nitric acid and then wiped dry. They are then connected with the negative pole of a battery and dipped into a bath composed of 1 part of cyanide of gold, 10 parts of potassium cyanide, and 100 parts of water. A plate of gold plunged into the same bath constitutes the positive pole. When the current passes, the objects become covered with a uniform and adherent coating of gold. As the metal is precipitated from the solution, it is replaced by an equivalent quantity from that which constitutes the positive pole, and which dissolves. The bath thus retains a constant composition. The same process is applicable to electro-silvering.

Assaying of Gold Alloys.—Gold is assayed by cupellation. The alloy is first melted with silver, so that the quantity of the latter metal present may be at least triple that of the gold. This alloy is submitted to cupellation, an operation which presents no difficulty, for silver rich in gold does not *spit.* The button is hammered out to a thin sheet, reheated and formed into a little cornet, which is introduced into a small flask and heated with nitric acid of 22° Baumé. After several minutes' boiling the greater part of the silver is dissolved; the liquid is then decanted and replaced by more concentrated nitric acid. All of the silver dissolves and the gold remains in the form of a but slightly coherent cornet. It is washed, heated to redness in a crucible to give it coherence, and finally weighed.

BISMUTH.

Bi = 206.54

Extraction.—This metal is found native in a quartzy gangue. It is extracted by simply heating the mineral in cast or sheet iron tubes, which are arranged in an inclined position in a furnace. The bismuth melts and runs out at an opening in the lower end of the tubes.

The bismuth of commerce is never pure ; it contains traces of other metals, nearly always of arsenic and sometimes of sulphur. It is purified by pulverizing it, mixing it with $\frac{1}{20}$ its weight of potassium nitrate, and heating the mixture to redness in a clay crucible. The foreign metals more oxidizable than the bismuth are thus converted into oxides, the arsenic into arsenate of potassium, and the sulphur into potassium sulphate. This treatment may be repeated a second time if necessary.

Properties.—Bismuth is a whitish-gray metal, having a reddish tinge. Its fracture is crystalline and laminated. Its density is 9.83, and it melts at 264°. On cooling, it crystallizes in rhombohedra, of which the surfaces become covered with a thin film of oxide, causing a beautiful iridescent play of colors like that on a soap-bubble.

Bismuth increases in volume on solidifying. It volatilizes at a white heat. It is unaltered by the air at ordinary temperatures, but at a red heat it absorbs oxygen and burns, forming bismuth oxide. Its best solvent is nitric acid, which converts it into nitrate.

The various compounds of bismuth present great analogy to those of antimony, next to which this metal might be placed in the group including nitrogen, phosphorus, arsenic, antimony, and bismuth.

This analogy is shown in the following synoptic table:

$BiCl^3$ Bismuth trichloride.	$SbCl^3$ Antimony trichloride.
Bi^2O^3 Bismuth trioxide.	Sb^2O^3 Antimony trioxide.
Bi^2O^5 Bismuthic anhydride.	Sb^2O^5 Antimonic anhydride.
Bi^2O^4 Bismuth bismuthate.	Sb^2O^4 Antimony antimonate.
Bi^2S^3 Bismuth trisulphide.	Sb^2S^3 Antimony trisulphide.

Otherwise, bismuth is related to the metals proper, not only by its properties, but by the facility with which it forms definite salts. It is triatomic in its more important combinations, the oxide, chloride, and nitrate.

BISMUTH TRIOXIDE.

Bi^2O^3

This body is obtained by decomposing the nitrate by heat. It is a straw-yellow powder, fusible at a red heat, and yielding on cooling a dark-yellow, vitreous mass. It attacks clay crucibles even more rapidly than litharge.

A hydroxide of bismuth is formed when the nitrate or subnitrate is treated with potassium hydroxide or ammonia. It is a white powder, insoluble in an excess of alkali, and when boiled with caustic potash it is converted into the crystalline anhydrous oxide.

BISMUTH TRICHLORIDE.

$BiCl^3$

Finely-divided bismuth will burn in chlorine, being converted into chloride. The latter is prepared by directing a current of chlorine upon melted bismuth contained in a retort. The chloride distils and solidifies in the receiver to a fusible, crystalline, and deliquescent mass, formerly known as butter of bismuth. A crystallized, hydrated chloride of bismuth may also be obtained by evaporating a solution of bismuth in nitrohydrochloric acid.

Bismuth chloride dissolves in water charged with hydrochloric acid, but is decomposed when treated with pure water;

in the latter case an oxychloride is formed and precipitated as a fine, white powder, hydrochloric acid being at the same time formed.

$$2BiCl^3 + 2H^2O = 2BiOCl + 4HCl$$

Bismuth oxychloride is known as *pearl-white.* It contains BiOCl.

BISMUTH NITRATE.

$Bi(NO^3)^3$

Bismuth dissolves readily in nitric acid, and the concentrated solution deposits large, four-sided prisms, which are colorless and deliquescent. They contain $Bi(NO^3)^3 + 3H^2O$. They are very soluble in water acidulated with nitric acid, but if this solution be poured into a large excess of water, a pulverulent, white precipitate is formed, and increases in volume if very dilute ammonia be gradually added to the liquid in order to partly neutralize the free acid.

This precipitate is much employed in medicine in cases of chronic diarrhœa under the name of subnitrate of bismuth. Its composition is generally expressed by the formula $BiNO^4 + H^2O = (BiO)'NO^3 + H^2O$.

It may be regarded as bismuthyl nitrate, that is, nitric acid, HNO^3, in which the monobasic atom of hydrogen is replaced by the monatomic group BiO. Or it may be considered as a derivative of orthonitric acid, H^3NO^4, corresponding to orthophosphoric acid, H^3PO^4 (page 191).

Boiling water removes still more nitric acid from this subnitrate, leaving a residue, which is used as a cosmetic, known as *blanc de fard.*

Characters of Solutions of Bismuth.—When mixed with a large quantity of water, bismuth solutions give white precipitates of sub-salts. Hydrogen sulphide, and the soluble sulphides form a brown precipitate of bismuth sulphide, insoluble in an excess of ammonium sulphide. The alkaline hydroxides and carbonates give white precipitates, insoluble in an excess of the reagent.

Bismuth solutions are not precipitated by either sulphuric or hydrochloric acid.

When heated with sodium carbonate in the reducing flame of the blow-pipe, compounds of bismuth yield a metallic globule, very brittle after cooling.

The following elements, from aluminium to manganese, form series of compounds in which they must be regarded as triatomic. In these compounds a single atom of the metal is united with three monatomic atoms or radicals, or two such atoms act as a hexatomic couple $(R^2)^{vi}$. The chlorides may consequently present either the general formula RCl^3 or R^2Cl^6, while the oxides are represented by R^2O^3. In addition, iron, nickel, cobalt, and manganese form compounds in which the metal appears to be diatomic; as, for example, iron in ferrous oxide, FeO, and ferrous sulphate, $FeSO^4$. The oxides of this latter class are strongly basic; the sesquioxides are also basic, but in the presence of more energetic bases may act as weak acids. Iron and manganese also form oxides of the composition FeO^3 and MnO^3, which act as the anhydrides of acids.

ALUMINIUM.

$Al = 26.91$

This metal long remained a chemical curiosity, and has only become common within a few years. It was discovered in 1827 by Wöhler, and in 1854, H. Saint-Claire Deville succeeded in producing it on a large scale by decomposing aluminium and sodium double chloride by sodium.

$$2AlCl^3,NaCl + 6Na = 8NaCl + 2Al$$

Aluminium is now produced most cheaply by the processes of Hall and Héroult. They consist in the electrolytic decomposition of alumina, Al^2O^3, dissolved in a bath of fused cryolite, $AlF^3.3NaF$. The latter is melted by the heat of the electric arc, and alumina constantly added while a powerful current is passing through the mass. The oxygen disengaged combines with the carbon forming the anode, and the aluminium collects upon the hearth, which serves as the cathode. The process is continuous: fresh alumina is constantly added to keep the bath saturated with it, and the furnace is tapped periodically.

Aluminium of a high degree of purity is obtained in this manner.

Aluminium is a white metal, with a somewhat bluish lustre when polished. It is ductile, malleable, very sonorous, and a good conductor of heat and electricity. It is as light as glass and porcelain, its density being only 2.56. It melts at 700°, and is not volatile.

Aluminium is unaltered by the air, even by moist air. When heated in thin sheets in a current of oxygen, it burns and is converted into alumina. Nitric and sulphuric acids scarcely attack it. Hydrochloric acid dissolves it rapidly, disengaging hydrogen. It is immediately attacked by boiling solutions of potassium or sodium hydroxide; hydrogen is disengaged and alkaline aluminates are formed.

ALUMINIUM OXIDE, OR ALUMINA.

Al^2O^3

Corundum, a very hard precious stone, consists of anhydrous alumina. It is named *oriental ruby* when it has a red color; *sapphire* when it is blue, and *oriental topaz* when it has a yellow tint. *Emery* is a sort of opaque corundum; it is granular and colored by a small quantity of oxide of iron.

When ammonium carbonate is added to a solution of alum, carbon dioxide is evolved, and a gelatinous precipitate of hydrated alumina is formed.

The precipitate dissolves readily in caustic potash. When heated, it loses water and is converted into anhydrous alumina; the latter is fusible only in the flame of the oxyhydrogen blow-pipe and in the electric furnace. It assumes crystalline structure upon solidifying.

Some of the precious stones above mentioned have been produced artificially by melting alumina with various fluxes and minute quantities of coloring matters (Gaudin, Fremy).

Alumina is reduced by carbon only at the high temperature of the electric furnace, but it readily yields to the joint action of carbon and chlorine, and is converted into aluminium chloride.

ALUMINIUM CHLORIDE.

$AlCl^3$ or Al^2Cl^6

When a current of chlorine is passed over an incandescent mixture of alumina and charcoal, aluminium chloride and carbon monoxide are formed (Oersted).

$$Al^2O^3 + 3C + 3Cl^2 = 3CO + 2AlCl^3$$

Aluminium chloride thus formed is a white, crystalline substance, sometimes having a light-yellow color. It is fusible, and volatilizes in the air at a temperature little above 100°. When exposed to the air it gives off white fumes and attracts moisture. It dissolves in water with production of heat.

A solution of aluminium chloride may be obtained by dissolving gelatinous alumina in hydrochloric acid. When this solution is evaporated, it decomposes as soon as it attains a certain degree of concentration, disengaging hydrochloric acid, and leaving alumina.

Aluminium chloride readily combines with sodium chloride, forming a double chloride, $AlCl^3.NaCl$, fusible towards 200°.

ALUMINIUM SULPHATE.

$$Al^2(SO^4)^3 + 18H^2O$$

This is obtained in the arts by decomposing non-ferruginous clays with sulphuric acid. It crystallizes with difficulty in needles and in thin, pearly scales. In this state it contains 18 molecules of water of crystallization. It dissolves in 2 parts of cold water. When heated, it first loses its water, and at a higher temperature it gives off sulphuric anhydride, leaving a residue of alumina.

$$Al^2(SO^4)^3 = 3SO^3 + Al^2O^3$$

It is seen that aluminium sulphate represents 3 molecules of sulphuric acid, in which the 6 atoms of hydrogen have been replaced by the hexatomic couple Al^2.

$$\left.\begin{matrix} H^2SO^4 \\ H^2SO^4 \\ H^2SO^4 \end{matrix}\right\} + Al^2O^3 = 3H^2O + (Al^2)^{vi}\left\{\begin{matrix} SO^4 \\ SO^4 \\ SO^4 \end{matrix}\right.$$

ALUMINIUM AND POTASSIUM DOUBLE SULPHATE, OR ALUM.

$$Al^2(SO^4)^3.K^2SO^4 + 24H^2O$$

If a concentrated solution of aluminium sulphate be added to a concentrated solution of potassium sulphate, and the mixture be stirred with a glass rod, a crystalline deposit soon forms from the union of the two salts to form a double sulphate which is alum.

This salt is not very soluble in cold water, but dissolves abundantly in boiling water, and is deposited on cooling in voluminous, transparent octahedra. When heated, these crystals melt in their water of crystallization (24 molecules), and in losing this water, the melted mass swells up considerably. Alum may be obtained crystallized in cubes, and it is prepared in this form in the neighborhood of Civita-Vecchia by working a mineral which contains the elements of alum with a large excess of alumina. The mineral is known as *aluminite*, and the cubical alum is called *Roman alum.*

This cubical variety may be prepared in the laboratory by adding a small quantity of potassium carbonate to a hot solution of ordinary alum, so that the precipitate first formed will be redissolved on agitating the liquid. On cooling, cubical crystals are deposited which are ordinarily opaque. These are formed under the influence of a small quantity of basic sulphate (aluminium sulphate combined with an excess of alumina) contained in the liquid, and which probably enters into the constitution of the crystals. With this slight difference, octahedral alum and cubical alum present the same composition, which is expressed by the formula $Al^2(SO^4)^3.K^2SO^4 + 24H^2O$.

Ammonia alum is obtained by adding ammonium sulphate to solution of aluminium sulphate. It possesses a constitution analogous to that of ordinary alum, with which it is isomorphous. It contains

$$Al^2(SO^4)^3.(NH^4)^2SO^4 + 24H^2O$$

It is often substituted in the arts for potassium alum, being cheaper than the latter.

When strongly calcined, it leaves a residue of pure alumina.

Other alums are known in which iron, manganese, and chromium play the part taken by aluminium in ordinary alum. These alums are all *isomorphous* (Mitscherlich). By the action of sulphuric acid on the sesquioxides of the above metals, sulphates are formed analogous to aluminium sulphate, and of which the composition is expressed by the general formula $(R^2)^{vi}(SO^4)^3$. With the sulphates M^2SO^4, they form alums, all of which crystallize in regular octahedra, and which can be mixed in one and the same crystal without the form of the latter being affected by the mixture.

The following are the most important of these compounds:

Manganese alum	$Mn^2(SO^4)^3.K^2SO^4 + 24H^2O$
Iron alum	$Fe^2(SO^4)^3.K^2SO^4 + 24H^2O$
Chromium alum	$Cr^2(SO^4)^3.K^2SO^4 + 24H^2O$

It is seen that each of these presents an atomic composition similar to that of ordinary alum.

The aluminium compounds are widely disseminated in nature. *Feldspar*, or *orthoclase*, is a double silicate of aluminium and potassium. The latter metal is replaced by sodium in *albite*, and by calcium in *anorthite* and *labradorite*.

Many other minerals contain aluminium silicate combined with alkaline or earthy silicates: such are *leucite*, *garnet*, *idocrase*, *mica*, etc. The *zeolites* are silicates of aluminium containing water of crystallization.

Clay is a hydrated silicate of aluminium; it results from the disintegration of feldspar by the action of water and air, the alkaline silicate being gradually dissolved and eliminated. The purest clay is *kaolin*, or porcelain clay; it contains alumina, silica, and water in the proportions indicated by the formula $2SiO^2,Al^2O^3,2H^2O$.

Plastic clays are those which form a binding paste when mixed with water, and acquire great hardness after being baked, without fusing. They are used for the manufacture of pottery, refractory fire-bricks, and crucibles. *Fuller's earth* is a clay which forms with water a paste that is but slightly adherent; it is employed in scouring and fulling cloth.

Marls are intimate mixtures of clay and chalk; they are employed in agriculture.

Pottery.—Clay is the basis of all pottery. Other matters, such as sand, powdered feldspar or quartz, etc., are generally added, for while they diminish the plasticity of the clay, they also diminish its shrinkage on baking. Pottery is classified as semivitrified pottery, such as porcelain and stoneware; porous pottery, such as faïence and bisque; and common pottery or terra-cotta.

Porcelains.—These are manufactured from kaolin, to which sand is added to prevent shrinkage, and feldspar, which causes the ware to undergo a partial fusion, and renders it translucent. These materials are finely pulverized, mixed with water, and the paste is kneaded for a long time in order to render it homogeneous. Pieces fashioned in this paste are submitted to a preliminary baking, which gives them a certain degree of coherence. The porous porcelain thus obtained must be coated with a varnish which will melt and spread upon its surface: this glaze is formed of a mixture of quartz and kaolin reduced to an impalpable powder; the latter is suspended in water, into which the pieces are dipped. They are then subjected to a second baking in ovens where the temperature is sufficiently elevated to fuse the glaze and partially vitrify the paste.

Ceramic Stonewares.—These are manufactured from the same materials as porcelain, but less pure; they are therefore slightly colored. They are baked at a high temperature, and are glazed by throwing common salt upon the incandescent objects in the furnace; hydrochloric acid is disengaged, and a double silicate of aluminium and sodium is formed, which fuses and spreads upon the surface of the ware.

Faïences are made from plastic clay mixed with quartz reduced to an impalpable powder. Articles formed of this paste are submitted to a preliminary baking, and are then coated with a fusible glaze, composed of quartz, potassium carbonate, and oxide of lead. A second baking causes the pieces to become covered with an impermeable, vitreous layer of silicate of lead and potassium. This glaze is transparent; for ordinary ware it is rendered opaque by the addition of oxide of tin. It is a true enamel.

Common pottery, which serves for culinary purposes, is made from ferruginous clay, mixed with sand and marl. The glazing is composed of a double silicate of aluminium and lead.

CERIUM, LANTHANUM, AND DIDYMIUM.

These rare metals are found associated as silicates in the mineral *cerite*, and as phosphates in *monazite*. Their separation is a matter of some difficulty. The mineral is treated with sulphuric acid, by the aid of heat, and the solution obtained after filtering from the separated silica is precipitated by ammonium oxalate. A mixture of the oxides is obtained when the oxalates are calcined: these oxides are converted into nitrates and these again into double nitrates with ammonium nitrate. By repeated and systematic fractional crystallization a clean separation of the elements is effected. The same process also serves to break up didymium, long supposed to be an element, into its components, *neodymium* and *praseodymium* (Auer v. Welsbach).

The metals have been isolated by decomposing their chlorides by electricity.

They possess about the hardness of lead, and a color and lustre resembling iron: didymium is rather more yellow. Their density is comprised between 6.05, that of lanthanum, and 6.7, of cerium. They are readily oxidized, and burn brilliantly when heated in the air.

The cerium metals are triatomic, cerium itself also tetratomic. It forms the oxides Ce^2O^3 and CeO^2. Lanthanum oxide has the composition La^2O^3; neodymium oxide is Nd^2O^3, while praseodymium forms two oxides, Pr^2O^3 and Pr^4O^7. The chlorides correspond to the formula RCl^3. The cerous compounds are mostly colorless; ceric compounds are yellow. Lanthanum salts are colorless, while the pink color of didymium salts is the resultant of a mixture of reddish-violet (neodymium) and apple-green (praseodymium).

The oxides of lanthanum and cerium, as well as several other oxides (zirconia, thoria), are employed in the Welsbach burner, in which a fine gauze cylinder of such oxides is rendered incandescent by the heat of a non-luminous gas-flame.

GALLIUM.

Ga = 69.9

In 1869, Mendelejeff predicted the existence of an unknown metal whose chemical relations should resemble those of aluminium, and whose atomic weight should be about 70. In 1876, Lecoq de Boisbaudran, while pursuing spectroscopic investigations, and in a line of research very different from that of Mendelejeff, discovered the missing element in a zinc blende. Since then it has been found in small quantity in many blendes: one of the richest, found in Westphalia, contains only one sixty-thousandth of its weight.

In order to extract the gallium, the ore is roasted, and the product dissolved in sulphuric acid. An acid liquor is thus obtained, containing principally sulphate of zinc, with sulphates of iron, aluminium, indium, etc., and a trace of gallium sulphate.

The following reactions are employed by Lecoq de Boisbaudran and Jungfleisch for the separation of the gallium:

1. When the liquid is neutralized, the ferric oxide, alumina, and gallium oxide, which is a sesquioxide, are precipitated. The precipitate is redissolved in sulphuric acid, and the same operation repeated after converting the ferric oxide into ferrous oxide, which remains dissolved in the neutral liquid. By this means the greater part of the iron is removed.

2. Gallium oxide dissolves, like alumina and zinc oxide, in an excess of potassium hydrate; when this solution is saturated with hydrogen sulphide, the zinc is precipitated as sulphide, while the gallium and aluminium remain in solution. The greater part of the zinc is thus separated.

3. When water is added to a boiling solution of gallium sulphate, the latter is precipitated as subsulphate, while aluminium sulphate remains in solution.

4. Gallium oxide dissolves in an excess of ammonia; alumina does not.

5. Gallium separates in the metallic state when a voltaic current is passed through an alkaline solution of gallium oxide.

Physical Properties.—Gallium has a metallic lustre recalling that of nickel. It readily crystallizes in forms derived from a right rhombic octahedron, generally in magnificent laminæ. Its density is 5.96. It melts at 29.5°, and has a tendency to remain in a state of superfusion. It is not volatile.

This collection of properties gives to gallium a special place among the metals.

Chemical Properties.—These are but little known at present. Gallium is oxidized but little, if at all, when heated in the air or in oxygen. It forms a sesquioxide, Ga^2O^3, which resembles alumina in that it forms alums. Gallium alum was obtained by Lecoq de Boisbaudran.

Gallium combines directly with chlorine, forming a solid, crystalline, and very volatile chloride.

INDIUM.

In = 113.4

This metal was discovered in 1863 by Reich and Richter in the zinc blendes of Freiberg (Saxony). It appears to exist in the majority of zinc blendes, and accompanies the zinc which is extracted from those minerals. It is ordinarily obtained from commercial zinc, which, however, contains only very small quantities of it.

Indium is a brilliant metal, possessing almost the lustre of silver. It is soft and ductile. It melts at 176°, and is volatile, but less so than zinc and cadmium. It approaches these metals in its general chemical properties, but is more electro-negative, both of the latter metals precipitating it from its solutions. Its position in the periodic system relates it to gallium and aluminium on the one hand, and to zinc and cadmium on the other.

Indium is characterized by several spectroscopic lines, among which are a very brilliant blue and a less marked violet line.

Two oxides of indium have been described, a *sesquioxide*, In^2O^3, and a *suboxide*, InO. The first is obtained by calcining the nitrate; it is yellow. When heated to 300° in a current of hydrogen, it is partially reduced, yielding a black suboxide.

Indium chloride, $InCl^3$, is formed when indium is heated in a current of chlorine. It is a snow-white, volatile solid.

Like aluminium and gallium, indium forms double sulphates, or alums; the ammonium double sulphate has the composition $In^2(SO^4)^3.(NH^4)^2SO^4 + 24H^2O$.

RARE EARTHS.

In 1794, Gadolin, a Finn, discovered in the mineral *gadolinite*, which bears his name, an oxide, which was named yttria. In 1843, Mosander concluded from researches on this earth that it contained at least three oxides, the metallic radicals of which were introduced into the list of elements under the names *erbium*, *terbium*, and *ytterbium* or yttrium.

Until recently little was known concerning these oxides, but the investigations of Crookes, Delafontaine, Lawrence Smith, Marignac, Cleve, and Nilson have shown that the earths formerly known as erbia and yttria are much more complex than was supposed. The oxides of at least six metals have been isolated, and it is possible that the series may be completed by the separation of others.

These elements exist in *gadolinite*, *euxenite*, *orthite*, *thorite*, and particularly in the *samarskite* of North Carolina, in which they occur as niobates and tantalates. Their quantity is so small, and the separation of their oxides is attended with such difficulties, that, excepting yttrium, the elements have not yet been isolated. Their oxides, and in some cases a number of salts, have been examined, and spectroscopic analysis has aided in setting aside all doubt as to the existence of the elements.

The following atomic weights of these elements are calculated to agree with the formula R^2O^3 for the oxides:

Scandium, discovered by Nilson and studied by Cleve, has an atomic weight of about 44; the oxide is white. The existence of scandium was predicted by Mendelejeff under the name ekaboron.

Samarium.—Atomic weight = 149. This element was named by Lecoq de Boisboudran, and appears to be identical with *decipium*, of which Delafontaine announced the existence in 1878; its oxide is white.

Holmium.—Atomic weight about 162 (Cleve).

Erbium.—Atomic weight = 166; forms a pink oxide and rose-colored salts (Cleve).

Thulium.—Atomic weight = 170.4; a white oxide.

Yttrium.—Atomic weight = 89.6. The metal has been prepared by electrolysis of the chloride, and also by reduction of the latter by sodium and magnesium. It is a gray powder. Yttria is a white oxide.

Ytterbium.—Atomic weight = 172.6.

IRON.

Fe (Ferrum) = 55.60

Natural State and Metallurgy.—Iron is the most important of the metals. Its preparation and working are difficult, therefore it was not the first metal used by civilized man. The bronze age preceded the iron age, and those who first employed the latter metal probably extracted it from the masses which fall from time to time upon the surface of the earth, and are known as meteorites. Their principal constituent is metallic iron, which is alloyed with nickel, cobalt, and chromium.

Iron is employed in three principal forms: soft or malleable iron, cast iron, and steel. Soft iron is almost pure iron; cast iron is a combination of iron with carbon and silicon; steel also contains carbon, but in smaller proportion than cast iron.

The principal ores of iron are the magnetic, or black oxide,

Fe^3O^4, *red hematite*, Fe^2O^3, and *spathic iron* or ferrous carbonate, $FeCO^3$. The various hydrates of the sesquioxide (*oölitic iron*, *brown hematite*, etc.) and ferrous carbonate mixed with clay (bog-iron ore), are more abundant than the preceding, but are not as rich and are less valuable.

All of these minerals are oxidized. If the ore contain sulphur, that element is first driven out by roasting. The metallurgy of iron then consists in reducing the oxide with carbon, and separating the reduced iron from the earthy matter, which is generally silicious. Two methods are employed for this purpose. The first consists in heating the rich ores with charcoal alone; part of the oxide of iron then combines with the gangue, forming a very fusible slag (double silicate of aluminium and iron). This is the *Catalan method.* The other consists in mixing the ore with coal and calcium carbonate; the gangue then combines with the lime, forming a double silicate of lime and aluminium, which fuses only at a very high temperature. Under these conditions the iron unites with a portion of the carbon, forming cast iron. This is the *blast-furnace* method.

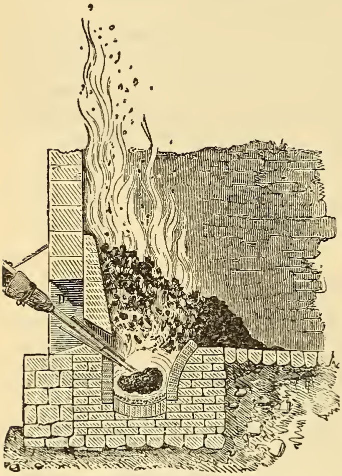


FIG. 116.

Catalan Method.—This is only applicable to very rich ores and in countries where combustibles are expensive, as in Spain, the Pyrenees, and in Corsica.

Fig. 116 represents a section of a Catalan furnace; it is a trough-shaped masonry furnace with a hearth. The materials are placed in two piles, side by side, upon a layer of well-ignited charcoal; one pile consists of charcoal and is next the tuyère; the other is the ore, equal to half the quantity of charcoal, and is placed opposite. The combustion is sustained by the blast from a tuyère, D, which reaches the border of the hearth. The carbon dioxide here formed is converted into carbon monoxide by the mass of incandescent charcoal, and the latter gas reduces the ore, again passing into the state of dioxide. Metallic iron is thus formed, and at the same time a portion of the ferric oxide is reduced to ferrous oxide, and combines with the gangue, forming a double, alumino-ferrous silicate, which is very fusible and constitutes the *slag*. The reduced iron collects in the bottom of the hearth in the form of a spongy mass, which is agglutinated and forged under the hammer.

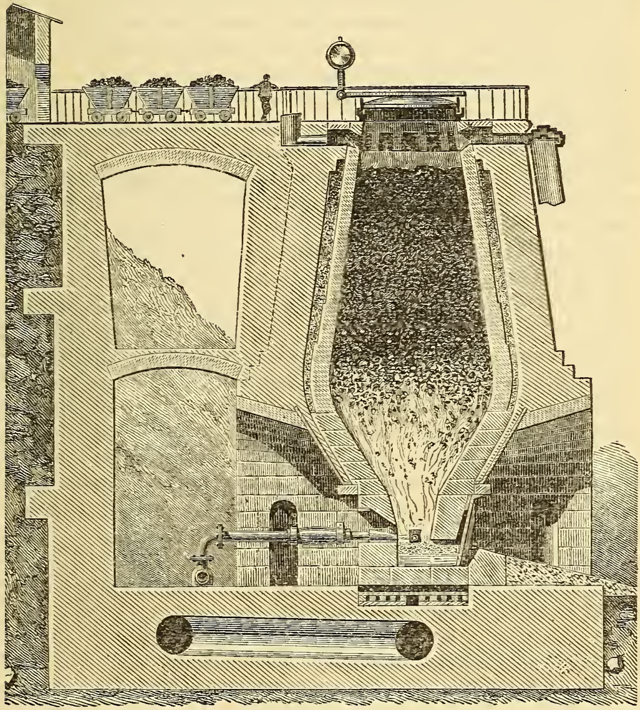


Fig. 117.

Blast-furnace Process.—All iron ores may be treated by this method. They are crushed and introduced with alternate layers of limestone and coal into the blast-furnace (Fig. 117). The latter has the form of two cones, the bases of which are joined together. It is closed at the bottom, and hot air is injected through tuyères to sustain the combustion. It is open at the top, where it is continually charged with fresh materials, as the incandescent mass sinks in the furnace and the molten materials are drawn off below. The latter first collect in a cavity placed below the vent of the tuyère, and separate on this hearth into metal, which sinks to the bottom, and slag, which floats and is drawn off periodically through an opening called the slag-hole. When the crucible is full of molten metal, the latter is run off into channels made in sand upon the floor of the casting-room. In these rough moulds it solidifies in bars having a semicircular section, which are called *pigs.*

The reactions which take place in the blast-furnace are of great interest. At the lower part, where the temperature is the highest, carbon dioxide is produced by the combustion of the coal; farther up, in the widest portion, this gas is reduced to carbon monoxide by the incandescent coal; still higher, where the furnace begins again to contract, and where the temperature is dull red, the carbon monoxide reduces the oxide of iron, and a spongy mass of metallic iron is there formed.

In descending, this iron unites with part of the carbon, and at the same time the silica of the gangue combines with the lime, forming a silicate which fuses and constitutes the slag.

A small quantity of silica is reduced in the hottest part of the furnace, and the silicon formed combines with the cast iron.

Cast iron is converted into soft iron by refining; this operation consists in removing from the cast iron the greater part of its carbon. For this purpose it is melted in contact with the air; the carbon, silicon, and a small proportion of iron are oxidized, forming a basic silicate, of which the excess of oxide is finally reduced by the carbon of the cast iron. The latter thus becomes less fusible, and is converted into a spongy mass of soft iron. Several of these masses are united and the scoriæ expressed from them by the blows of a steam-hammer. Or the metal is melted on the hearth of a reverberatory furnace under a layer of ferruginous scoriæ and scales of oxide of iron; the oxygen of these materials burns the carbon out of the cast iron, the whole mass being vigorously stirred. The latter operation is called puddling.

Preparation of Pure Iron.—Pure iron may be obtained by reducing ferric oxide by hydrogen at a temperature near redness, or by passing hydrogen over anhydrous ferrous chloride contained in an incandescent porcelain tube. Hydrochloric acid is formed and evolved, and the iron remains as a gray, spongy mass, having a metallic lustre where it has been in contact with the porcelain (Peligot).

Properties of Soft Iron.—Forged or bar iron is not pure. It contains a small quantity of carbon, and traces of silicon, sulphur, phosphorus, and even nitrogen. The purest soft iron is that used for the teeth of carding-machines and for piano-strings.

The density of forged iron varies from 7.4 to 7.9. It is very tenacious, ductile, and malleable. When rolled out, it is called sheet iron. Tin plate is sheet iron covered with a layer of tin. Galvanized iron is coated with a surface of zinc.

Iron melts only at the highest heats of a wind-furnace. When softened by a white heat, it may be soldered to itself, or welded, a very important property for the working of the metal.

0.05 per cent. of aluminium greatly lowers the melting point of iron, so that the presence of this quantity of aluminium permits iron castings to be made that otherwise would be impossible. They are called *mitis* castings.

Iron is attracted by the magnet; it is magnetic; but it is not, like steel, capable of retaining magnetism when removed from the magnetic influence.

It is not altered by dry air at ordinary temperatures, but at a red heat it absorbs oxygen and is converted into scales of black oxide of iron. Iron may be obtained as an impalpable powder by reducing finely-divided ferric oxide in a current of hydrogen at as low a temperature as possible. In this state it takes fire when exposed to air at ordinary temperatures: it is *pyrophoric.*

Iron rapidly becomes oxidized in moist air; it becomes covered with a layer of rust, which is ferric hydroxide. It is considered that the oxidation of iron moistened with water is first set up by the oxygen dissolved in the water; it continues with greater energy as soon as a light coat of ferric hydroxide has been formed on the metal. The hydroxide forms a voltaic couple with the iron itself, by which the water is decomposed; part of the hydrogen displaced by the iron combines with the nitrogen of the air, forming ammonia; indeed, rust always contains a small proportion of ammonia.

Iron decomposes water at a red heat, setting free the hydrogen. It dissolves readily in hydrochloric acid, liberating impure and fetid hydrogen. If dilute nitric acid be poured upon iron tacks, the metal is at once attacked, with an abundant disengagement of red vapors.

On the other hand, the metal is not attacked by concentrated nitric acid (sp. g. 1.45). After having been immersed in the strong acid, it may be put into dilute acid, and the latter will have no effect upon it. By the action of the concentrated acid (other oxidizing agents act in a similar manner) the iron has become *passive:* its surface is covered with a thin film of oxide which protects it. If now it be touched with a copper wire while in the dilute acid, the protecting film is ruptured and chemical action promptly re-established.

Cast Iron and Steel.—The properties and appearance of cast iron differ with the proportions of carbon and silicon which it contains. These elements appear to exist in the iron in a number of forms; they are partly in combination with the metal and partly only dissolved by it when it is liquid. When cast iron containing much carbon is quickly cooled, it becomes hard, brittle, whiter than soft iron, and seems homogeneous. This is *white iron.* When slowly cooled, a large proportion of the carbon is deposited as laminæ of graphite, and the less homogeneous iron then possesses a certain degree of malleability: it is *gray iron.*

Some cast irons contain sulphur and phosphorus, and remain white even after very slow cooling. Others are lamellar and glittering; they contain manganese and are rich in carbon (spiegeleisen and ferromanganese).

The proportion of carbon contained in cast iron varies from 2 to 5.5 per cent. *Steel* contains less carbon, from 0.7 to 2 per cent. The quantities of carbon contained in steel and even in cast iron render it difficult to suppose that these products are veritable carbides of iron.

Steel may be obtained by a partial decarbonization of cast iron. Manganiferous iron is especially applicable for this preparation. It is submitted to a partial refining, being maintained in the liquid state for some hours under a layer of scoriæ rich in oxide of iron. A part of the carbon is burned out by the oxygen of this oxide: *natural steel* is thus obtained.

Soft iron may be converted into steel. The operation is conducted in cases of refractory fire-clay, into which bars of iron, and charcoal-powder, mixed with a small quantity of ashes and common salt, are introduced in alternate layers. The bars being thus isolated in a bed of charcoal, the cases are closed and heated to redness in a furnace. The incandescent metal absorbs carbon, and at the termination of the operation is found converted into steel by *cementation.*

The most homogeneous and most valuable steel is *cast steel.* It is obtained by fusing crude steel in crucibles in a wind-furnace.

Bessemer has introduced an important improvement in the manufacture of steel. His process, which bears his name, consists in adding variable quantities of a properly-constituted cast iron to molten and perfectly refined soft iron.

In this process, the iron to be converted into steel is decarbonized by a current of air which is forced through the molten metal by strong pressure. The operation is conducted in an apparatus represented in Fig. 118, which is called the converter. It has an ovoid form, is constructed of strong plate iron, and is well-lined with refractory fire-bricks. It is arranged on trunnions, so that an oscillating movement may be given to it. The air arrives under pressure by the tuyères which open into the bottom of the converter. The latter is first filled with incandescent coke, which is brought into active combustion by the blast. When the interior of the converter is heated to whiteness, the coke is emptied out and replaced by the molten cast iron, the converter being inclined to prevent the entrance of the metal into the tuyères. The blast is then again turned on, and the compressed air bubbling through the molten metal burns out all of the carbon. A flame of great brilliancy rushes from the orifice of the apparatus, and the aspect of this flame indicates precisely the progress of the operation and its termination. At this moment the apparatus is inclined, the blast arrested, and a sufficient quantity of melted *spiegeleisen*, a crystalline cast iron rich in carbon, is added to the now refined iron to convert the whole into steel. The steel is then run out into suitable moulds.

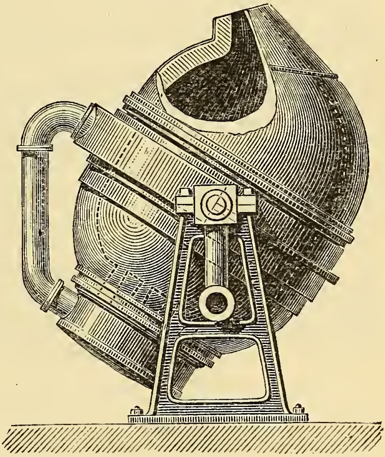


FIG. 118.

A lining of lime or magnesia is substituted for the fire-bricks when the iron to be converted into steel is rich in phosphorus. The latter is then carried into the slag as a phosphate.

Steel is susceptible of a high polish, and, like malleable iron, it can be forged. At the temperature at which malleable iron becomes soft, steel melts. It becomes hard and brittle when it is suddenly cooled after having been heated to redness. This operation, which is called tempering, develops new qualities in the steel,—elasticity and hardness. It assumes these properties in different degrees, according to the rapidity of the cooling, and the difference between the temperature to which it has been heated and that to which it is cooled. The greater this difference, and the more rapid the cooling, the harder will the steel become. Slow cooling makes it soft and malleable.

When tempered steel is heated, and allowed to cool slowly, it partly or entirely loses its hardness. It loses it entirely if it be heated to the temperature to which it was exposed before tempering. Its temper is *drawn* incompletely, that is, it retains a certain amount of hardness and elasticity, if it be reheated to inferior temperatures. The qualities which it will assume after cooling may be predicted from the various tints developed on its surface during the heating. Each of these tints corresponds to a determined temperature.

Straw-yellow	corresponds to	220°
Brown	"	255°
Light blue	"	285–290°
Indigo-blue	"	295°
Sea-green	"	331°

OXIDES OF IRON.

Three oxides of iron are known:

Ferrous oxide	FeO
Ferric oxide	Fe^2O^3
Ferroso-ferric oxide	Fe^3O^4

Fremy discovered the existence of a ferric acid, of which the composition is not certainly established.

Ferrous Oxide, FeO.—Debray obtained this oxide by heating ferric oxide in a current of gas formed of equal volumes of carbon monoxide and carbon dioxide. Ferrous oxide remains as a black powder.

$$Fe^2O^3 + CO = 2FeO + CO^2$$

Ferrous hydroxide, $Fe(OH)^2$, is formed as a white precipitate when an alkaline hydroxide is added to the solution of a ferrous salt. In presence of air it absorbs oxygen rapidly and becomes dark in color.

Ferric Oxide, Fe^2O^3.—This is found anhydrous in nature in red hematite and specular iron. It may be prepared by calcining ferrous sulphate, or green vitriol. This salt first loses its water, and then at a red heat decomposes into sulphuric anhydride, sulphurous oxide, and ferric oxide.

$$2FeSO^4 = SO^3 + SO^2 + Fe^2O^3$$

A red powder is thus obtained, which is known as *colcothar*, or jeweller's rouge.

This oxide is amorphous, while red hematite is crystallized in acute rhombohedra. H. Deville has succeeded in converting the amorphous oxide into the crystallized by heating the former to redness in a very slow current of hydrochloric acid.

Rust is ferric hydroxide, a combination of ferric oxide with water, and ordinarily presents the composition $2Fe^2O^3 + 3H^2O$. This hydroxide occurs native as *brown hematite*. Another mineral, known as *gœthite*, contains $Fe^2O^3 + H^2O$.

Ammonia or potassium hydroxide will at once produce a voluminous and flocculent, rust-colored precipitate in a solution of ferric chloride. This precipitate constitutes a ferric hydroxide.

But if an excess of tartaric acid be added to the solution of a ferric salt, the liquid may be saturated with potassium hydroxide and will still remain clear, no precipitate of ferric hydroxide being formed.

Advantage is taken of this property in analysis for the separation of ferric oxide from other oxides which tartaric acid does not retain in solution in an alkaline liquid.

If a solution of ferric acetate be poured into a dialyser (page 209), and the water in the exterior vessel be frequently changed, the salt will finally be entirely decomposed. Acetic acid will pass through the membrane, while ferric hydrate will remain dissolved in the water in the dialyser (Graham).

Ferroso-ferric Oxide, Fe^3O^4.—This compound, also called magnetic oxide of iron, occurs native as *magnetite*, and constitutes the black scales which form on the surface of iron when it is heated to redness in the air; it may be regarded as a compound of ferrous and ferric oxides.

$$FeO + Fe^2O^3 = Fe^3O^4$$

SULPHIDES OF IRON.

Several sulphides of iron are known.

The **disulphide**, or **pyrites**, FeS^2, a largely-diffused mineral, is the most important of these sulphides. It occurs in two distinct forms:

Pyrite, which crystallizes in brilliant cubes, or pentagonal dodecahedra, having a yellow color and a metallic lustre.

Marcasite, which forms rhombic prisms, variously modified, and presents a dull, greenish-yellow color. This variety is much more alterable than the other, and possesses a great tendency to attract oxygen from the air and become converted into sulphate. When heated in closed vessels, pyrites loses a part of its sulphur.

A combination of monosulphide and sesquisulphide of iron is encountered in nature; it crystallizes in regular hexagonal prisms and is called *magnetic pyrites*.

Monosulphide of Iron, FeS, is found in small quantity in many meteorites. It is ordinarily obtained by heating to redness in a covered crucible a mixture of three parts of iron-filings and two parts of sulphur. When the mixture has fused, it is poured out and solidifies to a brittle, blackish mass, having a metallic reflection. In this state, it is used for the preparation of hydrogen sulphide.

CHLORIDES OF IRON.

Ferrous Chloride, $FeCl^2$, is obtained anhydrous by the action of dry hydrochloric acid gas upon metallic iron. It forms white pearly scales. When iron is treated with aqueous hydrochloric acid, it dissolves, and hydrogen is disengaged. The green, filtered liquid deposits, when sufficiently concentrated, bluish-green, oblique rhombic prisms. This is hydrated ferrous chloride, $FeCl^2 + 4H^2O$.

Ferric Chloride, $FeCl^3$, is formed when a current of chlorine is passed over iron-turnings heated in a glass or porcelain tube. The two bodies combine with incandescence, and if the chlorine be in excess, ferric chloride will be obtained as a brilliant black, crystalline sublimate. The vapor density of ferric chloride above 700° corresponds to $FeCl^3$, but at lower temperatures its composition is probably Fe^2Cl^6.

This body is very soluble in water and forms a yellow-brown solution. The latter may be obtained by dissolving ferric oxide, such as powdered hematite, in hot hydrochloric acid, or by passing chlorine into a solution of ferrous chloride. Ferric chloride is also soluble in alcohol, ether, and benzene.

FERROUS SULPHATE.

$FeSO^4 + 7H^2O$

This salt has long been known under the names green vitriol and copperas. It is obtained by exposing iron pyrites to the air, or roasting that mineral at a moderate heat. It is generally prepared by dissolving iron in dilute sulphuric acid, and it is a residue from the preparation of hydrogen sulphide by means of iron sulphide and dilute sulphuric acid.

It crystallizes in oblique rhombic prisms, containing 7 molecules of water of crystallization. When exposed to the air, these crystals effloresce slightly, and at the same time their surface becomes yellow from absorption of oxygen and the formation of ferric subsulphate.

$$2FeSO^4 + O = Fe^2O(SO^4)^2 = Fe^2O^3.2SO^3$$

When heated, they lose their water, of which six molecules are disengaged at 114°, and the seventh only at 300°. At a higher temperature the salt decomposes into sulphurous oxide, and a ferric subsulphate different from the preceding.

$$2FeSO^4 = SO^2 + (Fe^2O^2)SO^4$$

The crystals of ferrous sulphate are freely soluble in water. 100 parts of the salt dissolve in 164 parts of water at 10°, and in 30 parts of boiling water. The green solution absorbs oxygen from the air, becomes troubled, and deposits yellow ferric subsulphate.

Other hydrates of ferrous sulphate are known. According to Mitscherlich, a saturated boiling solution of the salt deposits at 80° crystals containing four molecules of water. According to Marignac, when a solution of ferrous sulphate containing free sulphuric acid is evaporated in a vacuum, crystals are first deposited which contain 7 molecules of water, then a sulphate $FeSO^4 + 5H^2O$, and finally, $FeSO^4 + 4H^2O$.

The sulphate $FeSO^4 + 5H^2O$, is isomorphous with crystallized cupric sulphate (blue vitriol), and like it crystallizes in triclinic prisms.

FERRIC SULPHATE.

$Fe^2(SO^4)^3$

This salt is obtained by heating ferrous sulphate with nitric and sulphuric acids; the brown solution is evaporated, and the residue well dried.

$$2FeSO^4 + H^2SO^4 + O = H^2O + Fe^2(SO^4)^3$$

Ferric sulphate is a slightly-yellowish, white mass, which dissolves completely, but very slowly, in water. The solution is yellow-brown, and has an acid reaction.

When concentrated by evaporation, it deposits a deliquescent, yellowish, crystalline mass, which constitutes hydrated ferric sulphate.

There are several *ferric subsulphates;* those which have been mentioned above result from the action of one molecule of ferric oxide upon one or two molecules of sulphuric acid, the neutral sulphate resulting from the action of one molecule of ferric oxide upon three molecules of sulphuric acid.

$$H^2SO^4 + Fe^2O^3 = H^2O + (Fe^2O^2)''SO^4$$

Ferric monosulphate.

$$\begin{matrix}H^2SO^4\\H^2SO^4\end{matrix} + Fe^2O^3 = 2H^2O + (Fe^2O)^{iv}\left\{\begin{matrix}SO^4\\SO^4\end{matrix}\right.$$

Ferric disulphate.

$$\begin{matrix}H^2SO^4\\H^2SO^4\\H^2SO^4\end{matrix} + Fe^2O^3 = 3H^2O + (Fe^2)^{vi}\left\{\begin{matrix}SO^4\\SO^4\\SO^4\end{matrix}\right.$$

Ferric trisulphate (normal sulphate).

FERROUS CARBONATE.

$FeCO^3$

Spathic iron ore, which crystallizes in rhombohedra, is ferrous carbonate. When a solution of sodium carbonate is added to a solution of ferrous sulphate, a greenish-white precipitate is obtained, which rapidly becomes colored in the air, absorbing oxygen and losing carbonic acid. When recently precipitated, it dissolves in a large excess of carbonic acid.

Characters of Ferrous Salts.—The solutions of these salts are green; they are not precipitated by hydrogen sulphide, but ammonium sulphide forms a black precipitate of ferrous sulphide. Potassium hydroxide or ammonia produces a greenish-white precipitate of ferrous hydroxide, insoluble in an excess of the reagent, and rapidly becoming colored in the air. Potassium ferrocyanide (yellow prussiate of potash) forms with ferrous salts a light-blue precipitate. Potassium ferricyanide (red prussiate) forms a dark-blue precipitate. Solution of gall-nuts does not color ferrous salts.

Characters of Ferric Salts.—Hydrogen sulphide produces a precipitate of sulphur, reducing the salts to the ferrous state. Ammonium sulphide precipitates them black. Potassium hydroxide and ammonia form red-brown precipitates of ferric hydroxide, insoluble in an excess of the reagent. Potassium ferrocyanide forms a dark-blue precipitate which is *Prussian blue*.

Potassium ferricyanide produces a dark-brown color without precipitation. Potassium sulphocyanate gives a blood-red color.

Solution of gall-nuts forms a bluish-black precipitate which constitutes ink.

COBALT.

$Co = 58.55$

Cobalt was discovered by Brandt in 1735. It is found as *smaltite* in the arsenide, $CoAs^2$, and as *cobalt glance* in the sulph-arsenide, $CoAsS$. Its ores are worked principally for the production of a dark-blue, vitreous mass, a combination of cobalt silicate and potassium silicate, known as *smalt* or *azure blue*.

The metal is prepared in the laboratory by calcining its oxalate in a covered crucible.

$$\underset{\text{Cobalt oxalate.}}{CoC^2O^4} = Co + \underset{\text{Carbon dioxide.}}{2CO^2}$$

It may be obtained as a metallic button by heating the pulverulent metal in a lime crucible in a wind-furnace. The lime crucible is placed in another crucible of refractory clay, and the space between the two is filled up with fragments of quicklime (H. Sainte-Claire Deville).

Pure cobalt is silvery-white. It is very malleable; its density is 8.6, and it is magnetic. At ordinary temperatures it is unaffected by the air, but at a red heat it is converted into oxide.

Oxides of Cobalt.—The most important of these are the monoxide, CoO, the sesquioxide, Co^2O^3, and the intermediate cobaltoso-cobaltic oxide, Co^3O^4.

Cobalt monoxide is obtained as a greenish-gray powder by heating the carbonate or hydroxide out of contact with the air. It is reducible by hydrogen, carbon, and carbon monoxide.

Before the blow-pipe it dissolves in fused borax, imparting a deep-blue color to the latter. It is used for giving a blue color to glass and porcelain.

The *hydroxide*, $Co(OH)^2$, is obtained by adding an excess of potassium hydroxide to the solution of a cobalt salt, and boiling the mixture. Its color is pink.

Cobalt sesquioxide, Co^2O^3, results when anhydrous cobalt nitrate is very gently heated. Its hydroxide, $Co(OH)^3$, is obtained as a dark-brown precipitate when the pink-colored hydroxide is treated with bromine and caustic potash.

All these oxides and hydroxides are converted into the black *cobaltoso-cobaltic oxide*, Co^3O^4, when strongly ignited in the air.

Cobalt Chloride, $CoCl^2$.—When pulverulent cobalt is heated in a current of chlorine, it takes fire and is converted into a chloride, which sublimes in blue scales. A solution of this chloride may be obtained by dissolving either monoxide or carbonate of cobalt in hydrochloric acid. The neutral solution is currant-red, and on evaporation deposits hydrated crystals of the same color. But when it is concentrated, after having added hydrochloric or sulphuric acid, it becomes blue. This change of color, due to the formation of anhydrous chloride even in the midst of the hot liquid, has caused the employment of cobalt chloride as a sympathetic ink. Characters traced with the dilute solution, which is rose-colored, are invisible on white paper, and appear blue only when the paper is warmed, again becoming invisible on cooling, by the absorption of atmospheric moisture.

Cobalt Sulphate, $CoSO^4 + 7H^2O$.—This salt is found in nature, crystallized in oblique rhombic prisms. It may be obtained by dissolving the oxide or carbonate in dilute sulphuric acid and concentrating the red solution. At ordinary temperatures, the latter deposits red crystals, isomorphous with ferrous sulphate. Between 40° and 50°, it yields monoclinic crystals, containing 6 molecules of water, and isomorphous with magnesium sulphate of analogous composition.

Characters of Cobalt Salts.—The cobaltous salts are the more important. Their solutions are rose or currant-red, but when concentrated and hot they become blue, especially when an excess of acid is present. Hydrogen sulphide does not precipitate solutions of cobalt salts. Ammonium sulphide forms a black precipitate. Potassium hydroxide gives a blue precipitate of a basic salt, which, in presence of an excess of potash, is converted into hydroxide of cobalt, having a dirty rose color.

Ammonia forms a blue precipitate, soluble in excess.

When heated with borax in the blow-pipe flame, the salts of cobalt yield beads of a pure blue color.

NICKEL.

$Ni = 58.25$

This metal was discovered by Cronstedt in 1731.

Natural State and Extraction.—Nickel is a constituent of many minerals. It occurs as *kupfernickel* or *niccolite*, $NiAs$, as *nickel glance*, $NiAsS$, as *millerite*, NiS, and in silicates such as the *garnierite* of New Caledonia. It is also a common constituent of cobalt ores, and of magnetic pyrites. Nickeliferous pyrites are mined in enormous quantities at Sudbury, in Canada. The commercial extraction of nickel is effected by various processes, more or less complicated, according to the nature of the ore. The silicate yields a product which is free from cobalt. The oxides are readily reducible by carbon. Perfectly pure nickel is best obtained electrolytically.

Properties.—Pure nickel is grayish-white with a yellowish tinge. It is malleable, ductile, and very tenacious. Its density is 8.279, and may be increased to 8.666 by hammering. It is less fusible than iron and more fusible than manganese. It is magnetic at ordinary temperatures, but loses this property at about 250°. It is unaltered by the air at ordinary temperatures, but absorbs oxygen at a red heat. It dissolves slowly in dilute sulphuric and hydrochloric acids, rapidly in nitric acid. In contact with concentrated nitric acid it becomes passive like iron. Finely divided nickel combines with carbon monoxide at 100°, forming nickel carbonyl, $Ni(CO)^4$ (p. 219).

Nickel is used in various alloys. German silver contains 50 per cent. copper, 25 nickel, and 25 zinc. The five-cent coins of the United States contain 25 per cent. nickel and 75 copper. An alloy of nickel with steel is at present extensively used for armor plates.

Pure nickel is deposited as a brilliant metallic layer by the electrolysis of a solution of nickel and ammonium double sulphate, and this solution is used in nickel-plating.

Nickel Oxides.—A monoxide, NiO, and a sesquioxide, Ni^2O^3, are known. The *monoxide* is an ash-gray powder, obtained by strongly calcining the nitrate or carbonate. On adding potassium hydroxide to a nickel salt, an apple-green precipitate of *nickel hydroxide*, $Ni(OH)^2$, is formed.

Nickel sesquioxide may be obtained by moderately calcining the nitrate. It is black. When chlorine gas is passed into water holding nickel hydroxide in suspension, a dark-brown powder is obtained which is a hydrate of the sesquioxide. This hydroxide may also be made by precipitating a nickel salt with potassium hydroxide mixed with an alkaline hypochlorite.

When strongly calcined, nickel sesquioxide abandons part of its oxygen and is changed into monoxide. Treated with hydrochloric acid, it yields nickel chloride, and chlorine is disengaged.

$$Ni^2O^3 + 6HCl = 2NiCl^2 + 3H^2O + Cl^2$$

Nickel Chloride, $NiCl^2$.—This salt may be obtained anhydrous by the action of chlorine on nickel-filings ; it is volatile at a dull-red heat, and sublimes in golden-yellow scales. The hydrated chloride is formed by the action of boiling water on the anhydrous salt, or by the action of hydrochloric acid on the oxide or carbonate. Its solution is green, and after proper concentration deposits beautiful green crystals which contain $NiCl^2 + 6H^2O$.

Nickel Sulphate, $NiSO^4 + 7H^2O$.—The sulphate is deposited in fine, emerald-green, orthorhombic prisms, isomorphous with magnesium sulphate, when its solution is allowed to evaporate spontaneously below 15°. There is another hydrate containing $6H^2O$, which is dimorphous. When deposited between 20 and 30°, it crystallizes in square octahedra, but when its solution is made to crystallize between 60 and 70°, monoclinic crystals are obtained, isomorphous with the corresponding sulphates of magnesium, zinc, and cobalt.

Nickel sulphate dissolves in 3 times its weight of water at 10°.

Characters of Nickel Salts.—The nickel salts when hydrated or in solution have a fine emerald-green color. When anhydrous they are yellow.

Hydrogen sulphide does not precipitate them from acid solutions. Ammonium sulphide throws down a black precipitate. Potassium hydroxide and potassium carbonate form apple-green precipitates.

In neutral solutions, ammonia gives a green precipitate of nickel hydroxide, which dissolves in an excess of ammonia, forming a blue solution.

MANGANESE.

$Mn = 54.8$

This metal may be obtained from the chloride by electrolysis, or by reduction with sodium. It is more conveniently prepared by reducing its oxides with aluminium or carbon at high temperatures. The reduction with carbon is best effected in the electric furnace, and an excess of this element should be carefully avoided on account of the remarkable tendency of manganese to form a carbide.

The properties of manganese are greatly modified by the presence even of small amounts of impurities. The pure metal is described as rather soft and malleable, while the commercial product is very hard and brittle. The color of manganese is grayish white. Its density is about 7.4, and it melts only at a high white heat. It is unaffected by air or moisture at ordinary temperatures, but decomposes water and is superficially oxidized at 100°. It dissolves readily in dilute mineral acids.

Manganese enters into the important alloys ferromanganese and spiegeleisen, which are made directly in the blast furnace. Manganese bronze contains about 10 per cent. manganese and 90 per cent. copper.

MANGANESE OXIDES.

Manganese forms six compounds with oxygen:

Manganous oxide	MnO
Manganoso-manganic oxide	Mn^3O^4
Manganic oxide	Mn^2O^3
Manganese dioxide	MnO^2
Manganic anhydride	MnO^3
Permanganic anhydride	Mn^2O^7

Manganous oxide is formed when manganous carbonate is strongly heated in a current of hydrogen, or by reducing one of the higher oxides in a current of hydrogen or carbon monoxide. It is a grayish-green powder which slowly absorbs oxygen at ordinary temperatures, and takes fire at a temperature below redness, forming the *red oxide*, Mn^3O^4.

The latter body is also formed by the calcination of the dioxide. It is analogous to the magnetic oxide of iron, and constitutes the mineral known as *hausmannite*.

Manganic oxide, Mn^2O^3, occurs in nature in tetragonal pyramids as *braunite*.

MANGANESE DIOXIDE.

(BINOXIDE OR PEROXIDE OF MANGANESE.)

MnO^2

This important body is found abundantly in nature; it constitutes the mineral *pyrolusite.* It may be obtained pure and anhydrous by exposing a concentrated solution of manganous nitrate to heat and gradually raising the temperature to 155°. Nitrous vapors are evolved, and a brilliant brown-black mass is obtained, which is the dioxide.

$$Mn(NO^3)^2 = MnO^2 + 2NO^2$$

It loses one-third of its oxygen when heated to redness, and is converted into the red oxide. When heated with concentrated sulphuric acid, it loses half of its oxygen, manganous sulphate being formed.

$$MnO^2 + H^2SO^4 = MnSO^4 + H^2O + O$$

With hydrochloric acid it yields water, chlorine, and manganous chloride.

A hydrate of manganese dioxide is formed when an excess of chlorine is directed into water holding in suspension manganous hydrate or carbonate. This hydrate is a dark-brown powder.

Manganese dioxide is largely employed for the preparation of oxygen and chlorine. It is used to decolorize glass blackened by carbonaceous matters or rendered green by a trace of iron.

MANGANIC ACID.

When manganese dioxide is heated with potassium hydrate in a silver crucible, and the calcined mass is exhausted with water, the latter dissolves out potassium manganate. A dark-green liquor is thus obtained which, when evaporated in vacuo, deposits a crystalline mass. These crystals may be drained on a porous porcelain plate, and green needles of potassium manganate, K^2MnO^4, remain. The salt is isomorphous with the sulphate K^2SO^4.

When the green solution is boiled, it becomes red and deposits brown flakes of hydrated manganese dioxide: the red liquor is a solution of potassium permanganate, this salt being formed at the expense of the manganate, which breaks up into hydrated dioxide, potassium hydroxide, and permanganate.

$$\underset{\text{Potassium manganate.}}{3K^2MnO^4} + 3H^2O = \underset{\text{Potassium permanganate.}}{2KMnO^4} + \underset{\text{Hydrated manganese dioxide.}}{MnO^2.H^2O} + 4KOH$$

An analogous decomposition takes place when an acid is added to the green solution of manganate; a manganous salt and permanganic acid are formed, and the latter colors the liquid red.

PERMANGANIC ACID.

Potassium permanganate, $KMnO^4$, is an important salt. It is prepared by heating to dull redness a mixture of manganese dioxide, potassium hydroxide, and potassium chlorate. After cooling, the product is exhausted with boiling water, and when the liquid has assumed a purple color, it is decanted, and, after neutralization by nitric acid, is evaporated at a gentle heat. On cooling, it deposits crystals that may be dried on a porous tile.

Potassium permanganate crystallizes in almost black needles, having a metallic reflection. It dissolves in 15 or 16 parts of cold water, and its solution has a magnificent, intense purple color.

If solution of sulphurous acid be added to potassium permanganate solution, the latter is instantly decolorized, and the liquid contains only potassium sulphate and manganese sulphate.

If a drop of the solution of potassium permanganate be placed upon a sheet of paper, it loses its color and a brown stain of hydrated manganese dioxide is produced.

These experiments indicate the oxidizing properties of the permanganate. In the first, sulphurous acid was oxidized; in the second, it was paper, of which the carbon and hydrogen removed the oxygen from the permanganate, which was thus reduced to dioxide.

MANGANOUS SULPHATE.

$$MnSO^4 + 7H^2O$$

This salt may be prepared by dissolving manganous carbonate in sulphuric acid. The properly concentrated rose-colored solution deposits, between 0 and 6°, oblique rhombic prisms, isomorphous with green vitriol and containing 7 molecules of water.

Between 7 and 20°, manganous sulphate crystallizes with 5 molecules of water, like cupric sulphate, with which it is then isomorphous.

Between 20 and 30°, it is deposited in oblique rhombic prisms, according to Marignac, which contain only 4 molecules of water.

All of these crystals are pink-colored, and their color is deeper as they contain more water of crystallization. They are very soluble in water.

MANGANOUS CARBONATE.

$MnCO^3$

The residues from the preparation of chlorine may be used for making this salt. They are evaporated, without filtering, in a porcelain capsule, with frequent stirring, and the dry residue is calcined with an excess of manganese dioxide. The ferric chloride which was mixed with the manganous chloride is decomposed or volatilized during this operation. Ferric oxide remains, mixed with the excess of manganese dioxide and the manganous chloride, which resists the heat. The latter is extracted by exhausting the mass with boiling water. A rose-colored solution is thus obtained which often contains a small quantity of cobalt chloride. The latter is precipitated as sulphide by adding little by little a solution of sodium sulphide. As soon as the precipitate, which is at first blackish, begins to assume a flesh tint, the liquid is filtered and precipitated by sodium carbonate.

Manganese carbonate constitutes a white powder with a pale rose tint. When heated in contact with air, it gives up carbonic acid gas and is converted into red oxide of manganese.

Characters of Manganese Salts.—The salts of manganese are colorless or have a light pink color. Their solutions are not precipitated by hydrogen sulphide. Ammonium sulphide gives a flesh-colored precipitate; sodium carbonate, a dirty white. Potassium hydroxide produces a dirty white precipitate of manganous hydroxide, which rapidly becomes brown by absorbing oxygen from the air.

When heated in the blow-pipe flame with a small quantity of potassium hydroxide or nitrate, the salts of manganese give a bead which dissolves in water with a green color (manganate).

URANIUM.

$U = 237.8$

Uranium is related to manganese and iron by certain compounds, and there are others which relate it to chromium, molybdenum, and tungsten. The latter three elements combine with oxygen, forming the anhydrides of energetic acids, and their atoms may be regarded as hexatomic.

Uranium is not found in abundance, although it is widely distributed. It occurs in *pitchblende*, a uranoso-uranic oxide, *uranite*, a calcium uranyl-phosphate, and in other minerals, associated with copper, bismuth, arsenic, etc. *Euxenite* contains niobate and titanate of uranium.

The metal may be prepared by the action of sodium on a mixture of uranium chloride, UCl^4, and potassium chloride, the latter being employed as a flux. Moissan has recently prepared considerable quantities of uranium by reducing the oxides with carbon in the electric furnace.

So obtained, uranium is of an iron or nickel color, not quite as hard as steel, and has a density of 18.4. When heated in the air, it is oxidized with incandescence. It does not decompose water, but dissolves in dilute acids, disengaging hydrogen.

Uranium Oxides.—The principal oxides are UO^2 and UO^3, besides which there exist several intermediate oxides, and probably a uranic oxide, UO^4.

Uranium Dioxide, UO^2, was at first believed to be the free metal. It is a brown powder, and may be obtained by strongly heating uranic oxide with charcoal or in a current of hydrogen. Prepared in the latter manner, the monoxide is pyrophoric. A corresponding hydroxide is formed when solutions of uranous salts are precipitated by alkaline hydroxides.

Uranic Oxide, UO^3, is obtained as a light-brown powder by heating uranyl nitrate to 250°. When heated to redness, it is converted into green *uranoso-uranic oxide* U^3O^8. Uranic oxide combines with bases forming a series of salts of the general formula $R^2U^2O^7$, in which R is one atom of a monatomic metal. The uranates are yellow, insoluble in water, but soluble in acids. The alkaline uranates may be obtained by precipitating a uranyl salt (see farther on) with an excess of alkaline hydroxide.

Sodium Uranate, $Na^2U^2O^7$, is known in commerce as uranium yellow, and is used for painting on porcelain, and for coloring a yellow glass which is highly fluorescent. It is prepared in the arts by heating in a reverberatory furnace a mixture of lime and pitchblende. The calcium uranate so formed is decomposed by sulphuric acid, and the uranyl sulphate obtained is treated with sodium carbonate. On adding very dilute sulphuric acid, uranium yellow is precipitated.

Uranium Chlorides.—There are three chlorides, UCl^3, UCl^4, UCl^5, and an oxychloride, UO^2Cl^2. The tetrachloride is formed by the action of chlorine on a heated mixture of charcoal and any oxide of uranium. It is a very deliquescent body, crystallizing in lustrous black or dark-green regular octahedra.

Salts of Uranium.—These include the uranous salts, and those formed by the diatomic radical *uranyl*, UO^2. The former salts are green, and are converted by oxidizing agents into the corresponding uranyl salts which are yellow.

Uranyl nitrate, $UO^2(NO^3)^2$, which may serve as a starting-point for the preparation of uranium compounds, may be made from pitchblende. The latter is pulverized, roasted, and treated with nitric acid. The solution is evaporated to dryness, the residue exhausted with water, and the liquid filtered. The yellowish-green filtrate is concentrated, and the confused crystalline mass which separates on cooling is drained and recrystallized, first, from hot water, then from ether, which dissolves only the uranyl nitrate, leaving the impurities. Uranyl nitrate forms large, yellow, orthorhombic prisms.

Helium, He = 4.—When certain pitchblendes, notably *cleveite*, are treated with dilute acids, a colorless gas is given off (Hillebrand). Ramsay has shown that this gas, which was believed to be pure nitrogen, contains another element, to which he gave the name of helium, because he regards it to be identical with the hypothetical helium to which certain lines in the solar spectrum are ascribed. It appears probable that helium is a mixture of at least two new elements. Its density is 2, and its molecules consist of single atoms. Of all known gases, it has the smallest solubility in water and the lowest critical temperature. Dewar has succeeded in liquefying it. Like argon, helium is devoid of chemical affinity.

CHROMIUM.

Cr = 51.7

Chromium was discovered in 1797, by Vauquelin, in a mineral from Siberia known as *crocoite*, and which is chromate of lead. It forms one of the elements of chrome iron ore, a combination of chromium oxide with ferrous oxide, $Cr^2O^3.FeO$, which corresponds to magnetic oxide of iron, $Fe^2O^3.FeO$.

Chromium has only recently been obtained in the reguline state and in notable quantity by Moissan. He reduced the sesquioxide with carbon in the electrical furnace, thus obtaining a metal rich in carbon. The latter was eliminated as calcium carbide by fusing the mass successively with lime and with calcium chromium oxide. So prepared, chromium is a brilliant metal, its polished surface being whiter than iron. Its density is 6.92. It is infusible except in the electrical furnace. It is not very hard, though the carbides C^2Cr^3 and CCr^4, are exceedingly hard, and it is entirely non-magnetic. At high temperatures it combines energetically with oxygen and with sulphur. It also forms definite compounds with carbon, silicon, and boron. Hydrochloric and sulphuric acids dissolve it, especially by the aid of heat while it is unaffected by strong nitric acid.

Chromium has also been obtained by electrolysis of its chloride, as well as by reduction of its oxide by metals like aluminium and magnesium.

COMPOUNDS OF CHROMIUM AND OXYGEN.

There are two well-defined compounds of chromium and oxygen, the green oxide, Cr^2O^3, and chromic anhydride, CrO^3.

Chromium Oxide, Cr^2O^3, is a green powder; it may be obtained by calcining mercurous chromate.

$$2Hg^2CrO^4 = 4Hg + O^5 + Cr^2O^3$$

Another process consists in heating in a crucible a mixture of 2 parts of potassium dichromate with a little more than 1 part of flowers of sulphur. After cooling, the mass is treated with water, which dissolves out potassium sulphate and leaves chromium oxide.

Chromium oxide is undecomposable by heat, and melts only at the temperature of the forge. It forms several different hydrates. When ammonia is added to the green solution of chromic chloride, a green, flaky precipitate of chromic hydroxide is formed; it is soluble in acids and in potassium hydroxide.

Chromic Anhydride, CrO^3, is prepared by gradually adding to a cold saturated solution of potassium dichromate 1½ times its volume of sulphuric acid. The chromic anhydride, ordinarily called chromic acid, set free separates in needle-shaped crystals of a dark-red color, which should be drained and recrystalized in a small quantity of warm water.

It is deliquescent; its aqueous solution has a dark yellow-brown color. It is an energetic oxidizing agent. Hydrochloric acid converts it into chromic chloride, with evolution of chlorine.

$$2CrO^3 + 12HCl = 2CrCl^3 + 6H^2O + 3Cl^2$$

If a concentrated solution of sulphurous acid be added to a solution of chromic acid, the liquid immediately becomes green from the formation of chromic sulphate.

Chromates.—The most important chromates are those of potassium and lead.

Potassium neutral chromate, K^2CrO^4, crystallizes in lemon-yellow, right rhombic prisms, isomorphous with potassium sulphate. It is very soluble in water, to which it communicates an intense yellow color. So great is its coloring property, that one part of chromate will sensibly color 40,000 parts of water.

Potassium dichromate, $K^2Cr^2O^7$, is prepared from chrome iron ore. The finely-powdered mineral is intimately mixed with potash and nitre, and the mixture fused at a red heat. After cooling the mass is exhausted with water, which dissolves the neutral chromate. The requisite quantity of sulphuric or acetic acid is then added to convert this into the dichromate, and, after allowing it to settle (to remove silica, etc.), the red solution is evaporated to crystallization.

Potassium dichromate is a beautiful salt of an orange-red color. It crystallizes in quadrangular tables or prisms belonging to the triclinic system.

It dissolves in 8 or 10 parts of cold water and in a much less quantity of boiling water.

A strong heat decomposes it into neutral chromate, chromium oxide, and oxygen.

$$4K^2Cr^2O^7 = 4K^2CrO^4 + 2Cr^2O^3 + 3O^2$$

When heated with sulphuric acid, it loses oxygen and is converted into chromic sulphate and potassium sulphate.

$$2K^2Cr^2O^7 + 8H^2SO^4 = 2Cr^2(SO^4)^3 + 2K^2SO^4 + 8H^2O + 3O^2$$

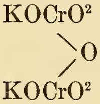
The residue when exhausted with water yields a green solution, which deposits on evaporation beautiful octahedral crystals of a violet-black color, constituting chrome alum.

$$\mathrm{Cr^2(SO^4)^3.K^2SO^4 + 24H^2O}$$

Sulphurous acid reduces potassium dichromate in the cold, also yielding chrome alum if sulphuric acid be added.

$$\mathrm{K^2Cr^2O^7 + 3SO^2 + H^2SO^4 = Cr^2(SO^4)^3.K^2SO^4 + H^2O}$$

The constitution of potassium dichromate is represented by the formula



$$\left.\begin{array}{l}\mathrm{KOCrO^2}\\ \mathrm{KOCrO^2}\end{array}\right\rangle \mathrm{O}$$

COMPOUNDS OF CHROMIUM AND CHLORINE.

Several combinations of chromium and chlorine are known. The most important is the violet chloride, $\mathrm{CrCl^3}$, corresponding to aluminium chloride and ferric chloride. It is prepared by passing chlorine gas over an intimate and perfectly dry mixture of chromium oxide and charcoal, heated to redness in a porcelain tube; carbon monoxide is disengaged, and chromic chloride sublimes into the cooler portion of the tube in brilliant peach-blossom-colored scales.

These crystals are almost insoluble in cold water, and dissolve but slowly in boiling water. Hydrogen reduces them at a red heat, with formation of hydrochloric acid, and a chloride, $\mathrm{CrCl^2}$, which crystallizes in white scales (Peligot).

$$\mathrm{2CrCl^3 + H^2 = 2HCl + 2CrCl^2}$$

If a small quantity of the chloride $\mathrm{CrCl^2}$, be added to hot water, holding in suspension the violet chloride $\mathrm{CrCl^3}$, the latter will be instantly dissolved, forming a green solution.

Chromyl chloride, $\mathrm{CrO^2Cl^2}$, is obtained by heating a previously fused mixture of common salt and potassium dichromate with sulphuric acid; abundant red vapors are disengaged, and condense to a blood-red liquid. This body boils at 116.8°. Its density at 25° is 1.920 (Thorpe). On contact with water it decomposes into hydrochloric acid and chromic anhydride.

$$\mathrm{CrO^2Cl^2 + H^2O = CrO^3 + 2HCl}$$

MOLYBDENUM.

$Mo = 96$

This metal is prepared by reducing molybdic oxide, MoO^3, by a current of hydrogen at a high temperature. It is a white, very hard, and almost infusible metal, having a density of 9.01. It forms five oxides, MoO, Mo^2O^3, MoO^2, Mo^2O^5, and MoO^3, and the chlorides $MoCl^2$, $MoCl^3$, $MoCl^4$, and $MoCl^5$.

Molybdic Oxide, MoO^3, is obtained by roasting the native sulphide, *molybdenite*, MoS^2, which occurs in black foliated masses closely resembling graphite, and capable of marking paper in the same manner. The roasting is conducted at a temperature not above redness, and the resulting oxide is dissolved in ammonia, and the solution filtered. On evaporation and cooling, crystals of ammonium molybdate are obtained which yield molybdic oxide when calcined in the air.

Molybdic oxide is a white, fusible, and volatile powder; it is but slightly soluble in water; the solution, however, being acid. It is the anhydride of an acid which forms a somewhat complicated series of salts, one of the most important being a molybdate of ammonium having the composition

$$Mo^7O^{24}(NH^4)^6 + 4H^2O = 3(NH^4)^2MoO^4 + 4H^2MoO^4.$$

This is the compound which is formed when a solution of molybdic oxide in ammonia is evaporated. It is employed in the laboratory as a test for phosphorus. When its solution in nitric acid is added to a warm solution containing phosphoric acid, a yellow precipitate containing molybdic acid, ammonia, and phosphoric acid, is thrown down. This precipitate is insoluble in nitric acid, but soluble in ammonia.

TUNGSTEN.

W (Wolframium) $= 184$

Tungsten occurs in a number of minerals, associated principally with tin ores. *Wolfram* is tungstate of iron and manganese. *Scheelite* is calcium tungstate; *stolzite* or *scheelitine* is tungstate of lead.

The metal may be obtained by reducing tungstic oxide, WO^3, by means of either carbon or hydrogen at very high temperatures. It is of a steel-gray color, very hard and brittle, and extremely refractory. Its density is 19.1. It is not tarnished by air under ordinary conditions, but when heated in the form of powder it takes fire, forming tungstic oxide. Another oxide, WO^2, and four different chlorides of tungsten —WCl^2, WCl^4, WCl^5, and WCl^6—are known to exist.

Tungstic Oxide, WO^3, occurs native in a yellow powder called *wolfram ochre.* It may be prepared from scheelite or from wolfram. The mineral is treated with nitro-muriatic acid, and the undissolved residue, consisting of tungstic oxide, is dissolved in ammonia. The filtered solution is evaporated to dryness, and on calcination the ammonium tungstate leaves tungstic oxide as pale yellow scales. It is fusible at a high temperature, insoluble in water and acids, soluble in alkaline solutions with formation of tungstates.

Tungstic oxide is the anhydride of several acids forming well-marked salts.

Normal tungstic acid, H^2WO^4, is precipitated as an insoluble yellow powder when the solution of a tungstate is decomposed by an excess of hot acid.

The alkaline normal tungstates have the general formula R^2WO^4. Besides these, there are highly complicated salts derived from the condensation of several molecules of the normal salts. One of these, known as sodium paratungstate, is prepared on a large scale by roasting wolfram with sodium hydrate and exhausting the mass with water. Its composition is $Na^{10}W^{12}O^{41}$: it is used as a mordant in dyeing, and has been recommended for rendering fabrics of vegetable origin non-inflammable. The goods are treated with a solution containing twenty per cent. of sodium tungstate and three per cent. of sodium phosphate.

The remaining elements are tetratomic, some of them at the same time forming unsaturated compounds in which the metallic atom may be diatomic, as in the oxides of tin, $Sn^{iv}O^2$ and $Sn''O$. Or two atoms of the metal may form a hexatomic couple, as in titanium sesquioxide, Ti^2O^3.

Tin, titanium, zirconium, and thorium form a group of which the chemical analogies become evident in a comparison of the composition and relations of similar compounds, while platinum is the most important member of another group of metals which are associated together in nature, and which are related by certain chemical and physical properties.

TIN.

Sn (Stannum) = 118.15

Natural State and Extraction.—The only mineral of tin which is worked is the dioxide (*cassiterite*). It is found in veins in the oldest formations, or disseminated in sand produced by their disaggregation. The principal tin mines are in India, in Malacca and the island of Banca, in Wales and in Saxony.

Tin ore generally occurs mixed with various other minerals, such as sulphide and sulph-arsenide of iron, sulphides of copper and tin, etc. It is crushed and washed in order to remove light, earthy matters, and then roasted. The sulphides and sulph-arsenides are thus oxidized and disintegrated, and the product is submitted to a second washing which removes the lighter oxides, leaving the cassiterite. The latter is then heated with charcoal in a cupola-furnace, represented in Fig. 119; it is a sort of prismatic furnace, having a hearth at the bottom where the melted metal collects. Air is blown in through the tuyère D. Carbon monoxide is formed, and this reduces the stannic oxide; the tin collects on the hearth, from which it is drawn into the basin I, where it is stirred with rods of green wood. The steam and gases produced by the carbonization of the wood, agitate the melted mass and bring to the surface the foreign matter or dross, which is removed. The tin is then run into moulds.

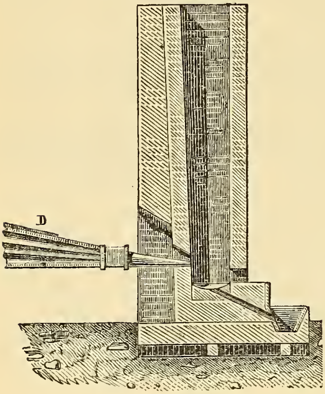


Fig. 119.

Thus obtained, tin generally contains small quantities of copper, iron, lead, antimony, and arsenic. It is purified by slowly heating it on the hearth of a reverberatory furnace; the pure tin melts first and runs out of the furnace, while the less fusible alloys remain upon the hearth. This method of purification is called *liquation*.

Properties.—Pure tin is a white metal, resembling silver in its color and lustre. It melts at 228°, and crystallizes when slowly cooled. Crystals of tin, belonging to the type of the right square prism, may also be obtained by galvanic precipitation of the metal. Their density is 7.178. That of the fused and slowly-cooled metal is 7.373 (H. Deville).

Tin is ductile and malleable. When a bar of tin is bent, it produces a peculiar noise called the *cry* of tin.

The metal is unaltered by the air, but when fused, rapidly becomes covered with a grayish pellicle of oxide. Tin dissolves in concentrated hydrochloric acid, disengaging hydrogen. The action is rapid when heat is applied.

If ordinary nitric acid be poured upon granulated tin, an energetic action takes place immediately. The tin is converted into a white powder of dioxide, and torrents of red vapors are evolved.

Very dilute nitric acid attacks tin almost without disengagement of gas. After some time the liquid will be found to contain a small quantity of tin nitrate and ammonium nitrate. The ammonia is formed by the simultaneous reduction of water and nitric acid by the tin.

$$HNO^3 + H^2O = 2O^2 + NH^3$$

When tin is heated with a concentrated solution of either potassium or sodium hydroxide, hydrogen is disengaged, and an alkaline stannate is formed.

Uses of Tin.—Tin enters into the composition of bronzes; it is made into dishes and covers, and the thin foil in which various substances, such as chocolate and tobacco, are enveloped.

Tinning of kitchen vessels consists in covering them with a thin coating of tin. This protects the copper or iron from the action of the acids which enter into the composition of various articles of food. The objects to be tinned are first well cleaned by rubbing them with sand, and are then dipped into melted tin. After separating the excess of metal, they are polished by rubbing with cloths dipped in sal ammoniac.

Tin-plate is sheet-iron covered with a thin layer of tin. The iron is first dipped into dilute sulphuric acid to remove the oxide; it is then rubbed with sand, and afterwards plunged successively into a bath of melted tallow and a bath of tin covered with tallow. On contact with the iron, the tin enters into combination, forming a true alloy, which becomes covered with a coating of pure tin.

When the surface of tin-plate is washed with a mixture of hydrochloric and nitric acids, the superficial coat of tin is dissolved, and the crystallized alloy of tin and iron is exposed. This is called crystallized tin-plate.

COMPOUNDS OF TIN AND OXYGEN.

Tin forms two compounds with oxygen, *stannous oxide*, SnO, and *stannic oxide*, SnO^2. The first is of but little importance. It is obtained by precipitating a solution of stannous chloride by potassium hydroxide, and boiling the precipitate, by which the white, stannous hydroxide first formed loses water and is converted into black stannous oxide. When the latter is moderately heated in contact with the air, it becomes incandescent and is converted into stannic oxide.

STANNIC OXIDE.

SnO^2

This body is found in nature as *cassiterite*, in the form of beautiful, hard, transparent crystals of a yellowish-brown color, belonging to the tetragonal system. From this mineral the tin of commerce is extracted.

The white powder obtained when the metal is treated with nitric acid is a stannic hydrate, which plays the part of an acid, and was named by Fremy metastannic acid. He attributes to it the composition $5(H^4SnO^4)$. It would be a polymer of normal stannic acid.

$$\left.\begin{matrix} Sn \\ H^4 \end{matrix}\right\} O^4 = (OH)^4Sn^{iv}$$

When heated to 100°, this hydrate loses half of its water; at a red heat, it loses the remainder and is converted into stannic oxide.

When ammonia is added to an aqueous solution of stannic chloride, a white, gelatinous precipitate is formed, constituting a hydrate.

$$H^2SnO^3 = \left.\begin{matrix} Sn^{iv} \\ H^2 \end{matrix}\right\} O^3$$

This is the stannic acid of Fremy. It dissolves readily in hydrochloric acid, and the solution behaves as would an aqueous solution of stannic chloride.

$$H^2SnO^3 + 4HCl = SnCl^4 + 3H^2O$$

It reacts with the bases, forming stannates of which the general composition is expressed by the formula:

$$R^2SnO^3 = \left.\begin{matrix}Sn \\ R^2\end{matrix}\right\} O^3$$

When heated to 140°, or even when dried for a long time in a vacuum, it becomes insoluble in acids.

SULPHIDES OF TIN.

Two sulphides of tin are known: a monosulphide, SnS, and a disulphide, SnS^2. The first is obtained by heating tin-filings with flowers of sulphur: the product still contains an excess of tin, and it is necessary to again heat it with a fresh quantity of sulphur. It is a crystalline, lead-colored mass.

Tin disulphide or stannic sulphide is prepared by first making an amalgam of 12 parts of tin and 6 parts of mercury; this is pulverized and the powder is mixed with 7 parts of flowers of sulphur and 6 parts of sal-ammoniac. The mixture is introduced into a matrass of hard glass and gradually heated to dull redness on a sand-bath. Sulphur, sal-ammoniac, sulphide of mercury, and stannous sulphide are condensed in the upper part of the matrass, of which the interior becomes covered with a yellow crystalline mass of stannic sulphide. The presence of sal-ammoniac and mercury, which volatilize in this operation, prevents an elevation of temperature, which would decompose the stannic sulphide. The latter is carried with their vapors, and condenses in brilliant, gold-like scales, which are greasy to the touch. This body is known as mosaic gold. It is decomposed by a red heat into stannous sulphide and sulphur. It is used for coating the cushions of electric machines, to imitate gilding, and very extensively as a pigment.

STANNOUS CHLORIDE.

$SnCl^2$

This compound may be prepared anhydrous by heating tin in hydrochloric acid gas. Hydrogen is evolved, and a white or grayish mass remains, which has a greasy appearance, and is almost transparent. It fuses at 250°, and boils at about 600°. This is stannous chloride.

When tin is dissolved in hot, concentrated hydrochloric acid and the limpid solution is evaporated and allowed to cool, beautiful transparent crystals are obtained, which contain

$SnCl^2 + 2H^2O$. This is known in commerce as tin salt or tin crystals.

The crystals of stannous chloride dissolve in a small quantity of water, forming a limpid liquid, but when treated with a large quantity of water, they yield a cloudy liquid, which holds in suspension a small quantity of white oxychloride. The atmospheric oxygen dissolved in the water takes part in this decomposition of stannous chloride, from which it removes part of the metal, a corresponding quantity of stannic chloride (tetrachloride) being formed.

Stannous chloride reduces many oxygenized and chlorinated compounds. It decomposes the salts of silver and mercury, setting free the metal. It instantly decolorizes the purple solution of potassium permanganate.

If a solution of stannous chloride be added to a solution of corrosive sublimate (mercuric chloride), a white precipitate of calomel (mercurous chloride) is instantly formed. By adding an excess of stannous chloride, all of the chlorine may be removed from the mercuric chloride, and a gray precipitate of metallic mercury will be formed.

Stannous chloride is employed as a mordant in dyeing.

STANNIC CHLORIDE (TETRACHLORIDE OF TIN).

$SnCl^4$

If thin tin-foil be thrown into a jar of chlorine gas, the metal will take fire, and in presence of an excess of chlorine will be converted into anhydrous stannic chloride. This is liquid, and gives off white fumes in the air. It was formerly known as *fuming liquor of Libavius.*

It is prepared by passing dry chlorine upon tin contained in a small retort. The anhydrous chloride condenses in the receiver in the form of a yellow liquid. It may be decolorized by rectification with a small quantity of mercury, which removes the excess of chlorine.

Tin tetrachloride boils at 120°. Its density is 2.28. A small quantity of water added to it is absorbed with a hissing noise, and the formation of a crystalline deposit of a hydrate, $SnCl^4 + 5H^2O$.

These crystals may also be obtained by dissolving tin in aqua regia and evaporating the solution, or, again, by passing chlorine into a solution of stannous chloride and concentrating the solution.

The crystals of hydrated stannic chloride dissolve in water, forming a clear solution.

Characters of Stannous Solutions.—Brown precipitates are formed by both hydrogen sulphide and ammonium sulphide; the precipitate dissolves in yellow ammonium sulphide.

Potassium hydroxide forms a white precipitate, soluble in an excess of reagent; ammonia yields a white precipitate, insoluble in excess.

An excess of stannous chloride produces a gray precipitate of metallic mercury in a solution of mercuric chloride.

Chloride of gold gives a purple precipitate (purple of Cassius) in dilute stannous solutions.

Characters of Stannic Solutions.—Hydrogen sulphide and ammonium sulphide form yellow precipitates, soluble in a large excess of the latter reagent. Potassium and sodium hydroxides, and ammonia water all form white precipitates, disappearing in an excess of the reagent.

Chloride of gold does not precipitate stannic solutions.

A sheet of iron or zinc will precipitate the tin from either stannous or stannic solutions in gray scales, which assume the metallic lustre when burnished.

TITANIUM.

$Ti = 47.79$

Titanium occurs as the dioxide, TiO^2, in *rutile*, *anatase*, and *brookite*, and with iron in *ilmenite* $(Fe,Ti)^2O^3$, and in many iron ores. Cubical copper-colored crystals of a nitrocyanide of titanium are frequently found in the cinders of blast-furnaces in which titaniferous ores are reduced. The metal has been obtained by reduction of the oxide by carbon in the electric furnace (Moissan). It manifests a remarkable affinity for nitrogen.

Titanium forms three chlorides, $TiCl^2$, Ti^2Cl^6, and $TiCl^4$; there are two well-defined oxides, Ti^2O^3 and TiO^2, and possibly a third, TiO. These compounds sufficiently characterize the element as a chemical analogue of tin.

Titanium Dioxide, TiO^2, as before mentioned, occurs in three different crystalline forms in nature; as square prisms in rutile, square octahedra in anatase, and orthorhombic prisms in brookite. When prepared in a pure form from either of these minerals, it is a white, infusible, insoluble powder. Like stannic oxide, it is the anhydride of an acid forming a well-marked series of titanates.

GERMANIUM.

$Ge = 72.3$

In 1886, Winkler discovered in a rare silver ore *argyrodite*, found near Freiberg, a new element corresponding in properties with one whose existence had been predicted by Mendelejeff under the name *ekasilicon*. This metal constitutes about 7 per cent. of argyrodite, and has also been found in euxenite. It may be isolated by the reduction of its oxide by hydrogen or carbon, or of potassium-germanium fluoride by hydrogen or sodium.

Germanium crystallizes in brilliant regular octahedra, having a density of 5.469, and melting at about 900°. It forms two oxides, GeO and GeO^2, a sulphide GeS, a chloride $GeCl^4$, and probably also a chloride $GeCl^2$. Its properties as well as most of those of its compounds agree remarkably with the predictions of Mendelejeff.

ZIRCONIUM.

$Zr = 89.9$

This metal also resembles tin in its chemical relations. Its principal mineral is a silicate known as *zircon*. It may be obtained crystallized, amorphous, and in a condition resembling graphite.

Crystallized zirconium may be made by fusing in a carbon crucible potassium zirconium double fluoride with aluminium. On cooling, the excess of aluminium is dissolved in dilute hydrochloric acid, and zirconium remains as crystalline plates containing small proportions of silicon and of aluminium. Its density is 4.15, and it is less fusible than silicon.

Zirconium forms but one chloride, $ZrCl^4$, which may be formed by the action of chlorine on a highly-heated mixture of zirconium oxide and charcoal. It is a white solid, which dissolves in water with the formation of a hydrated oxychloride.

Zirconium Oxide, ZrO^2, the only known oxide, may be obtained from the native silicate *zircon.* The pulverized mineral is fused with potassium hydroxide, then exhausted with hydrochloric acid, and the solution evaporated to dryness to separate the silica. The residue is dissolved in water, and the solution treated with ammonia, which precipitates hydrates of iron and zirconium. The precipitate is treated with oxalic acid, and ferric oxalate dissolves, while insoluble zirconium oxalate remains and yields zirconium oxide when calcined.

Zirconium oxide is a white powder, of a density between 4 and 5, according to the temperature of calcination. It is insoluble in acids, with the exception of hydrofluoric and sulphuric acids. It is infusible, and becomes highly incandescent when heated. It is an excellent substitute for lime in the oyxhydrogen light, and is extensively used for the Welsbach light.

Zirconium oxide acts both as a base and as the anhydride of an acid forming salts analogous to the silicates.

THORIUM.

$Th = 231.5$

Thorium was discovered by Berzelius, in 1828, in the mineral *thorite*, from Norway, in which it exists as an impure silicate. It occurs in the same form in *orangeite*, and associated with cerium and lanthanum as phosphate in *monazite.*

The metal has been obtained only as a gray powder by heating its chloride with potassium or sodium. It does not decompose water, but burns when heated in the air.

Thorium Oxide, ThO^2, may be prepared from thorite by boiling the powdered mineral with hydrochloric acid, evaporating to dryness, and exhausting the residue with boiling water. After passing hydrogen sulphide through the filtrate, the clear liquid is precipitated with ammonia. The precipitate is dissolved in hydrochloric acid and treated with potassium sulphate; a double sulphate crystallizes out, and this is redissolved in water and thorium hydroxide, $Th(OH)^4$, precipitated by the addition of ammonia.

The oxide obtained by igniting the hydroxide is hard, grayish, and translucent. It is infusible, and is not reduced by charcoal or attacked by fused alkalies. It is dissolved only by boiling sulphuric acid. When heated to incandescence it emits a more brilliant light than zirconia, and is the most valued earth for the Welsbach light.

Thorium Chloride, $ThCl^4$, is prepared by passing chlorine over a heated mixture of the oxide with charcoal. It then volatilizes in short, white prisms. It is deliquescent, and a solution of its hydrate may be obtained by dissolving thorium hydrate in hydrochloric acid. This hydrate contains $ThCl^4 + 8H^2O$, and, when heated, is decomposed with formation of hydrochloric acid.

Thorium forms oxysalts replacing four atoms of hydrogen in the acids.

PLATINUM.

$Pt = 193.41$

Natural State and Treatment of Platinum Ores.—The only compound of platinum found in nature is the arsenide $PtAs^2$ known as *sperrylite*, which is isomorphous with pyrite and is found in the nickel-mines of Sudbury, Ontario. Commercial platinum is derived from the native metal, which is generally found in alluvial sands. Its principal deposits are in the Ural Mountains, Brazil, and California. The platinum ore, extracted from the sand by washing, contains, independently of 73 to 86 per cent. of platinum, various other metals, such as iridium, palladium, rhodium, osmium, ruthenium, gold, iron, and copper; an alloy of osmium and iridium, and various minerals, such as titaniferous iron, chrome iron, pyrites, etc. The ore is well washed to remove the sand, and treated with dilute aqua regia which dissolves the gold, iron, and copper; it is then heated with concentrated hydrochloric acid and nitric acid is gradually added. The aqua regia dissolves the platinum and certain of its accompanying metals, leaving the osmium and iridium. A solution of ammonium chloride is added to the filtered liquid; it produces an abundant precipitate of ammonium and platinum double chloride, which generally contains a small quantity of ammonium and iridium double chloride. This precipitate is calcined at a dull-red heat, and leaves a dull-gray, spongy residue. It is *spongy platinum.*

To give coherence to this sponge and convert it into a malleable and ductile metal, it is reduced to powder in a wooden mortar and triturated with enough water to convert it into a perfectly homogeneous paste. This paste is introduced into a slightly-conical cylinder of brass or iron, and compressed first with a wooden piston, then by a steel rod. The compression is finished by the aid of a hydraulic press, and the slightly-conical cylinders so formed are heated to whiteness and forged under the hammer, as iron is forged.

To obtain perfectly pure platinum, the metal is dissolved in aqua regia, the excess of acid evaporated, and the residue heated to 150°; the iridium is thus converted into Ir^2Cl^6 which remains in solution when the platinum is precipitated with ammonium chloride.

H. Sainte-Claire Deville and Debray extracted the metal by simple fusion of the ore. The fusion is effected in a lenticular cavity cut in two large masses of quick-lime, placed one above the other. A current of illuminating gas is directed into this furnace, and the combustion is supported by a continual supply of oxygen.

Properties of Platinum.—Platinum has a grayish-white lustre. It melts only at the highest attainable temperatures. The density of the cast metal is 21.1; that of the forged metal 21.5. It softens at a white heat, and can then be forged and welded like iron.

The experiments of H. Deville and Troost have shown that a red-hot platinum tube allows hydrogen to pass through its pores.

Platinum has the curious property of condensing gases on its surface, and this property is the cause of certain chemical phenomena that were formerly attributed to mere contact of the metal.

If a morsel of platinum-sponge be introduced into a small jar filled with an explosive mixture of oxygen and hydrogen, the gases will combine instantly, with explosion.

This property is most highly developed in *platinum-black,* for in this form the metal exists in an extreme state of division. It may be prepared by reducing a solution of platinic chloride by zinc; or platinum dichloride may be boiled with potassium hydroxide, and alcohol or a solution of sugar gradually added to the liquid, which must be continually stirred. The platinum is precipitated as a black powder.

Platinum is unaltered by the air. It is not attacked by either nitric, hydrochloric, or sulphuric acid, even boiling. It dissolves in aqua regia. The alkaline hydroxides attack it at high temperatures on contact with the air. It is the same with the alkaline nitrates.

There are two oxides of platinum, a monoxide, PtO, and a dioxide, PtO^2.

CHLORIDES OF PLATINUM.

These are the more important compounds of platinum. There are two, a dichloride, $PtCl^2$, and a tetrachloride, $PtCl^4$.

Platinum dichloride is obtained by cautiously heating the tetrachloride to 200°. Chlorine is disengaged, and after cooling, the residue is exhausted with boiling water, which leaves an olive-green powder, constituting the dichloride. When ammonia is added to a solution of platinum dichloride in hydrochloric acid, a green, crystalline powder separates after some time. It is called *green salt of Magnus*, and contains

$$PtCl^2 + 2NH^3$$

It may be regarded as the dichloride of platinoso-diammonium.

$$\left.\begin{matrix} Pt'' \\ H^2 \\ H^2 \\ H^2 \end{matrix}\right\} N^2.Cl^2$$

It is derived from two molecules of ammonium chloride by the substitution of an atom of diatomic platinum for two atoms of hydrogen.

Platinum tetrachloride, or **platinic chloride,** $PtCl^4$, is formed when platinum is dissolved in aqua-regia. A red-brown solution is obtained, which, after concentration and cooling, deposits red-brown needles of hydrated platinic chloride. The crystals lose their water when heated, and are converted into a dark, red-brown mass, which constitutes the anhydrous chloride $PtCl^4$. This body absorbs moisture when exposed to the air. It is very soluble in water, alcohol, and ether.

If a solution of ammonium chloride be added to a solution of platinic chloride, a yellow, crystalline precipitate of platinum and ammonium double chloride is immediately formed.

This body is but little soluble in cold water, but more soluble in boiling water, from which it is deposited in microscopic, regular octahedra. It is almost insoluble in alcohol. It contains

$$PtCl^4.2NH^4Cl$$

A yellow, crystalline precipitate of double chloride of platinum and potassium is obtained, in the same manner, on adding a solution of platinic chloride to a solution of a potassium salt, if the liquids be not too dilute.

$$PtCl^4.2KCl$$

OTHER METALS OF THE PLATINUM GROUP.

Rhodium, ruthenium, palladium, iridium, and osmium are associated with native platinum, and are usually extracted from platinum residues. They are fusible with great difficulty, and not readily attacked by acids. Their separation from each other is accomplished by tedious and complicated reactions, but, with the exception of ruthenium and rhodium, they possess certain valuable properties which have found for them applications in the arts. They combine with oxygen, forming a series of feeble bases, and a series of acid oxides. With the exception of the volatile oxides of ruthenium and osmium, these compounds are decomposed by heat into metal and oxygen.

Rhodium is less fusible than platinum, and almost insoluble in aqua-regia, which, however, dissolves it if it be alloyed with the baser metals. Its specific gravity is 12.1. It forms oxides RhO, Rh^2O^3, and RhO^2, and a chloride Rh^2Cl^6.

Ruthenium is a hard metal, having a density of 12.26 at 0°, and is more infusible than iridium. It is hardly attacked by boiling aqua-regia. One of its most interesting compounds is a volatile oxide RuO^4. Its chloride has the composition Ru^2Cl^6.

Palladium has the lowest melting-point of the group of platinum metals, fusing at about the same temperature as wrought iron. Its specific gravity at ordinary temperatures is 11.4. When a bright piece of the metal is heated in the air, its surface becomes tarnished from the formation of a film of oxide, but at a higher temperature this oxide is again reduced to metal. The remarkable facility with which palladium absorbs hydrogen has already been mentioned (page 61). Palladium forms three oxides, Pd^2O, PdO, and PdO^2, and two chlorides, $PdCl^2$ and $PdCl^4$.

Iridium occurs with the platinum ores in grains of platiniridium and osmiridium. Its fusing-point is the highest after osmium and ruthenium. It is very hard, and next to osmium it has the highest specific gravity of any substance known, its density being 22.38. An alloy of platinum and iridium containing ten per cent. of the latter metal is as hard and elastic as steel, unalterable in the air, and less fusible than platinum. It is used for the points of gold pens.

Iridium forms two oxides, Ir^2O^3 and IrO^2, and two chlorides, Ir^2Cl^6 and $IrCl^4$.

Osmium has been obtained in cubical or rhombohedral crystals having a density of 22.48. Its melting-point is about 2500°. When strongly heated in the air it burns into a volatile oxide, OsO^4, which is dangerously poisonous. The native alloy, osmiridium, is used for the points of gold pens. Two chlorides are known, $OsCl^2$ and $OsCl^4$.

ORGANIC CHEMISTRY.

GENERAL IDEAS UPON THE CONSTITUTION OF ORGANIC COMPOUNDS.

ORGANIC CHEMISTRY studies the history of the compounds of carbon. The most simple of these are the gases carbon monoxide and carbon dioxide; each contains but a single atom of carbon. In this respect they resemble the inflammable gas which is disengaged from the mud of marshes; it contains one atom of carbon combined with four atoms of hydrogen.

The gas hydrogen dicarbide or ethylene, which has already been mentioned, contains two atoms of carbon united with four atoms of hydrogen. A great number of compounds are known which contain only carbon and hydrogen, and they are called hydrocarbons or carburetted hydrogens. The atoms of carbon are aggregated in them, together with the atoms of hydrogen. Other elements are often added to the preceding, forming molecules more or less complex. The carbon atoms form as it were the framework, and the carbon compounds possess peculiar properties precisely on account of the great facility with which the atoms of carbon accumulate in one and the same molecule, and link themselves in some manner one to another. The following developments will give some idea of the *mode of formation* and the *structure* of organic molecules.

The most Simple Organic Compounds.—Their Composition proves Carbon to be a Tetratomic Element.—The most simple of the hydrocarbons is marsh gas.

When this gas is submitted to the action of chlorine, one or more atoms of hydrogen may be removed from it; they combine with the chlorine and are disengaged in the form of hydrochloric acid gas. The curious fact, first noticed by Dumas, is then observed, that each atom of hydrogen which is removed is replaced by an atom of chlorine. This *substitution* gives rise to a series of chlorinated compounds, which present the most simple relations with marsh gas. The latter contains only carbon and hydrogen. The chlorine compounds derived from it by substitution, form with it the following series:

CH^4	marsh gas, or methane.
CH^3Cl	monochloromethane (methyl chloride).
CH^2Cl^2	dichloromethane (methylene chloride).
$CHCl^3$	trichloromethane (chloroform).
CCl^4	tetrachloromethane (carbon tetrachloride).

In each of these compounds a single atom of carbon is united with four monatomic atoms. We have seen that the atoms of chlorine and hydrogen are equivalent as regards their power of combination. In the preceding compounds, the sum of the atoms of hydrogen and chlorine which are combined with one atom of carbon is invariably four, and this number cannot be exceeded. But two atoms of a monatomic element may be replaced by one atom of a diatomic element. One atom of carbon, which unites with four atoms of hydrogen or chlorine, may unite with two atoms of oxygen to form carbon dioxide

$$CO''^2$$

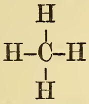
and this compound is *saturated* like those preceding, for one atom of oxygen is equivalent to two atoms of hydrogen or chlorine. In carbon monoxide, CO'', the affinity of carbon is not satisfied; hence this gas will unite directly with an atom of oxygen to form carbon dioxide, or with two atoms of chlorine to form carbonyl chloride.

$$CO''Cl^2$$

In ammonia, one atom of nitrogen is combined with three atoms of hydrogen; nitrogen is triatomic; hence it may replace three atoms of hydrogen. A body is known which represents marsh gas, in which three atoms of hydrogen are replaced by one atom of nitrogen. This is the dangerous poison known as prussic or hydrocyanic acid, and the composition of which is represented by the formula

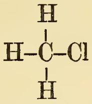
$$CN'''H$$

In all of the compounds which have just been mentioned a single atom of carbon is invariably united to a number of elements of which the sum of the atomicities is four, and never more nor less than that number. It is then reasonable to conclude that in them *carbon plays the part of a tetratomic* *element.* This important fact, first exposed by Kekulé, can be clearly understood if we represent the preceding atomic formulæ in a graphic manner, that is, by symbols so arranged as to show the reciprocal relations of the atoms and their mutual saturation. In these formulæ a saturated atomicity is indicated by a line of union, two atomicities by two lines, etc.



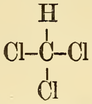
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H} \end{array}$$

Marsh gas.



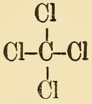
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}Cl} \\ | \\ \mathrm{H} \end{array}$$

Monochloromethane.



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

Trichloromethane. (Chloroform.)

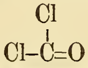


$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl{-}C{-}Cl} \\ | \\ \mathrm{Cl} \end{array}$$

Carbon tetrachloride.

$O{=}C{=}O$

Carbon dioxide.



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

Carbonyl chloride.

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

Hydrocyanic acid.

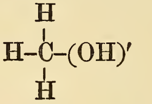
There exists a very volatile, ethereal liquid, which represents marsh gas, in which one atom of hydrogen is replaced by iodine. It is the body known as methyl iodide, CH^3I.

If this body be heated for a long time in a sealed tube with a solution of potassium hydroxide, potassium iodide will be gradually formed, and the solution will contain a volatile, spirituous liquid which can easily be separated by distillation, for it boils at 66°. It is the same body which constitutes the most volatile of the liquids which are formed in the destructive distillation of wood; it is called wood spirit, and its chemical name is methyl alcohol.

The reaction by which it is formed is very simple. The iodine of the methyl iodide combines with the potassium; but when this iodine is removed, the carbon remains united to but three atoms of hydrogen. It is no longer saturated, and it therefore combines with the oxygen and hydrogen which were united with the potassium in the potassium hydroxide.

$$CH^3I + KOH = CH^3.OH + KI$$

It will be seen that the atom of oxygen alone does not combine with the group CH^3, which is called methyl. It is accompanied by an atom of hydrogen, with which it remains united in the new compound, which is called methyl hydroxide or methyl alcohol. As has been said, this oxygen replaces the iodine in the iodide of methyl, but as it possesses two atomicities, and the carbon already united with H^3 has only one free atomicity, the atom of oxygen can only fix upon the carbon by one of its atomicities; the other remains saturated by the atom of hydrogen. The latter is then drawn into the combination, and is united, not to the carbon, but to the oxygen. The reaction takes place as if the atom of iodine were replaced by the group *hydroxyl* (OH) which is monatomic. Hence the relations between the atoms in methyl hydroxide are represented by the formula



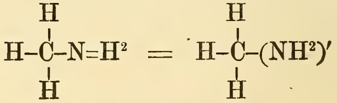
$$\begin{array}{c} H \\ | \\ H-C-(OH)' \\ | \\ H \end{array}$$

If we compare the constitution of the three bodies CH^3Cl, CH^3I, $CH^3(OH)$, we notice that they contain a common element, namely, the group CH^3, which is united to chlorine, to iodine, or to hydroxyl. Besides this, experiment has shown that methyl iodide can be transformed into the hydroxide. The group methyl hence presents a certain stability and can pass from one combination to another. This is expressed by saying that it is a *radical.*

If methyl iodide be heated with an aqueous solution of ammonia, among the products formed will be found the hydriodide of a base which represents ammonia in which one atom of hydrogen is replaced by the group methyl. Potassium hydroxide sets this base at liberty. At ordinary temperatures and pressures, it constitutes a gas, very soluble in water and possessing a strong ammoniacal odor. It is methylamine. The reaction by which it is formed is as follows: the iodine withdraws one atom of hydrogen from the ammonia, which atom of hydrogen is replaced by the group CH^3.

$$CH^3I + NH^3 = \underset{\text{Methylamine hydriodide.}}{CH^3(NH^2).HI.}$$

In methylamine then, the fourth atomicity of the carbon atom is saturated by nitrogen, but as this element is triatomic it brings into the combination two atoms of hydrogen which saturate its two other atomicities. It may then be said that in methylamine the fourth atomicity of carbon is saturated by the group NH^2. This is expressed in the following formulæ.



$$\begin{array}{c} H \\ | \\ H-C-N=H^2 \\ | \\ H \end{array} = \begin{array}{c} H \\ | \\ H-C-(NH^2)' \\ | \\ H \end{array}$$

Methylamine.

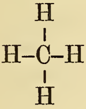
Formation of Hydrocarbons containing Several Atoms of Carbon.—The preceding compounds contain but a single atom of carbon, but starting with one of these compounds we may produce more complicated organic molecules containing several carbon atoms.

If methyl iodide be heated with sodium in sealed tubes, sodium iodide is formed, and a gas, a hydrocarbon, is confined under great pressure in the tubes. This gas escapes, and may be collected, when the drawn-out points of the tubes are opened in the blow-pipe flame. It is dimethyl, and has been formed according to the following reaction:

$$\underset{\text{Methyl iodide.}}{2CH^3I} + Na^2 = \underset{\text{Dimethyl, or ethane.}}{C^2H^6} + 2NaI$$

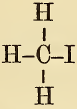
Two molecules of methyl iodide have entered into the reaction, and the whole of the carbon of these two molecules is found in one molecule of the hydrocarbon, $C^2H^6 = (CH^3)^2$, which results.

On losing their iodine the two methyl groups combine together. One of the carbon atoms attracts the other, exchanging with it the fourth atomicity set free by the loss of the iodine. Hence the iodine of one of the molecules of methyl iodide has been replaced by the carbon of the other, which fixes upon the group CH^3 by a single one of its atomicities, and at the same time brings into the combination the three atoms of hydrogen which saturate the other three atomicities. This is expressed in the following formulæ:



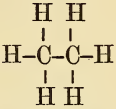
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Methane (methyl hydride).



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

Methyl iodide.



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

Dimethyl (ethyl hydride or ethane).

The mode of generation of this new hydrocarbon, which contains two atoms of carbon, is worthy of consideration. It results from the substitution of a methyl group for one atom of hydrogen in methyl hydride. One atom of carbon, accompanied by three atoms of hydrogen, fixes upon another atom of carbon of which it completes the saturation. By this exchange of atomicities each of the carbon atoms retains only three affinities which are satisfied by three atoms of hydrogen. The two methyl groups, $CH^3 + CH^3 = C^2H^6$, are then united by their carbon atoms, and are held together by the affinity of carbon for carbon. In methyl hydroxide the group hydroxyl is bound to the group CH^3 by the affinity of carbon for oxygen. In methylamine, the group NH^2 is united to the group CH^3 by the affinity of carbon for nitrogen. In dimethyl, it is carbon which is united to carbon. This has before been expressed by saying that the atoms of this element possess a faculty to accumulate in one and the same molecule.

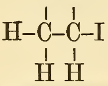
It is in this curious property that must be sought the reason for the existence of those innumerable compounds, more or less rich in atoms of carbon, which constitute the immense field of organic chemistry.

But it is important to study by new examples this mode of formation of organic compounds.

Dimethyl, which we have seen is produced by the action of sodium upon methyl iodide, is also known as ethyl hydride. If one of its atoms of hydrogen be replaced by an atom of chlorine, ethyl chloride, C^2H^5Cl, is obtained. Ethyl iodide, C^2H^5I, represents ethyl hydride, in which one atom of hydrogen has been replaced by iodine.

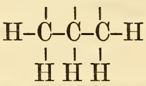
If a mixture of methyl iodide and ethyl iodide be heated with sodium, among the products of the reaction will be found a gas containing C^3H^8; this gas is methyl-ethyl, and it results from the combination of methyl, CH^3, with the group ethyl, C^2H^5. It represents ethyl iodide in which the atom of iodine has been replaced by a methyl group, the carbon of the latter group being fixed by one of its atomicities to one of the carbon atoms of the group C^2H^5.

In the same manner, by heating a mixture of propyl iodide, C^3H^7I, and methyl iodide with sodium, we may add to the propyl group, C^3H^7, a new atom of carbon escorted by its three atoms of hydrogen.



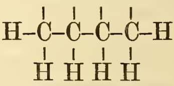
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -I \\ & | & & | & \\ & H & & H & \end{array}$$

Ethyl iodide.



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

Methyl-ethyl (propane).



$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & -H, \text{ etc.} \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

Methyl-propyl (butane).

Nothing prevents the continuation of these additions of carbon to incomplete hydrocarbons, that is, to the residues of the subtraction of iodine from the saturated iodides, of which the following are the names and formulæ:

CH^3I	C^2H^5I	C^3H^7I	C^4H^9I	$C^5H^{11}I$, etc.
Methyl iodide.	Ethyl iodide.	Propyl iodide.	Butyl iodide.	Amyl iodide.

The following hydrocarbons would then be formed successively:

$CH^3–CH^3$	$C^2H^5–CH^3$	$C^3H^7–CH^3$	$C^4H^9–CH^3$	$C^5H^{11}–CH^3$, etc.
Methyl-methyl	Methyl-ethyl	Methyl-propyl	Methyl-butyl	Methyl-amyl
(Ethane).	(Propane).	(Butane).	(Pentane).	(Hexane).

In all of these cases, the atoms of carbon united together form, as it were, a continued chain, and the atoms of hydrogen are grouped around them as satellites.

Homologous Bodies.—Very simple relations exist between the hydrocarbons of which we have just studied the mode of formation. They form a series of which each member differs from the preceding by the addition of CH^2. These relations will appear clearly if the formulæ already given be replaced by the crude formulæ:

$C\,H^4$	methane.
C^2H^6	ethane.
C^3H^8	propane.
C^4H^{10}	butane.
C^5H^{12}	pentane.

This group of hydrocarbons constitutes what is called the homologous series of marsh gas, or the series C^nH^{2n+2}.

Many other series are known, the terms of which are related to each other in the same manner, and the bodies which form part of them may present the greatest differences in composition. Sometimes they contain only carbon and hydrogen. Again, they may contain oxygen or nitrogen in addition to these elements; in this case the former elements are united to carbon by one or more of their atomicities, as has already been indicated.

In any organic body whatever, if an atom of hydrogen united with carbon be replaced by a methyl group, CH^3, the *superior homologue* of that body is obtained, that is, the compound which differs from the original body by the addition of CH^2. There is a great resemblance in physical and chemical properties between such homologues.

Some of these homologous series will be indicated farther on.

Composition and Classification of Organic Compounds.—The elements carbon, hydrogen, oxygen, and nitrogen are the most common constituents of organic compounds. Those which occur in the vegetable kingdom consist, for the most part, of the three first named, although there are also many nitrogenous bodies of vegetable origin. Animal matter, as a rule, contains all four of the elements mentioned and not infrequently sulphur and phosphorus in addition. But nearly all of the other elements can be introduced artificially into organic compounds; it is thus with chlorine, bromine, iodine, arsenic, boron, silicon, and a great number of the metals.

In uniting with carbon, in different manners and in various proportions, these elements form an innumerable multitude of compounds, each of which has a fixed composition and definite properties. These bodies constitute the *chemical species*, so to say. When submitted to the action of reagents, all may be modified in a thousand manners, and transformed into each other. Sometimes their composition is simplified, one or more carbon atoms being removed from the chain. Sometimes it is complicated by *synthesis;* that is, the addition of new atoms of carbon.

All these bodies contain carbon, and are distinguished:

1. By the number of carbon atoms contained in the molecule.
2. By the nature and arrangement of the other atoms combined with the carbon.
3. By the arrangement of all the atoms in the molecule.

The facts relative to the atomic composition of organic compounds are obtained by elementary analysis and by the determination of the molecular weight.

ELEMENTARY ANALYSIS.

The object of elementary analysis is the determination of the nature and proportion of the elements contained in any given organic body. We can give here but a summary description of the processes employed, considering only those which have for object the determination of carbon, hydrogen, and nitrogen. Oxygen is almost invariably estimated by difference.

The percentages of carbon and hydrogen are determined in one operation. In case nitrogen or other elements are present, the relative quantity of each of these must be ascertained by separate operations.

Determination of Carbon and Hydrogen.—To determine the proportion of carbon and hydrogen contained in 100 parts of any given organic substance, the carbon is converted into carbon dioxide, which is collected and weighed, and the hydrogen into water, which is condensed and weighed. These operations are conducted according to a method devised by Liebig.

For this end, the organic matter, previously dried with care, is burned with an excess of cupric oxide. The operation is executed in a combustion-tube of hard glass, which is wrapped with a spiral of metallic foil to prevent it from bending and swelling under the influence of the heat. Well-dried cupric oxide is introduced into the tube, then an intimate mixture of the substance to be analyzed with a large excess of the same oxide, and the remainder of the tube is filled with pure cupric oxide.

The tube is then placed in a combustion furnace, and its open extremity is put in communication with (1) an U tube, *jg* (Fig. 120), containing fragments of calcium chloride in the first branch, and pumice-stone impregnated with sulphuric acid in the second; (2) a tube with five bulbs, *h*, called Liebig's potash bulbs, containing a concentrated solution of potassium hydroxide, and followed by a small U tube, *i*, containing pumice-stone impregnated with potassium hydroxide in the first branch, and fragments of potassium hydroxide in the second. These different tubes have first been accurately weighed. When the apparatus is arranged, the combustion-tube is slowly heated, commencing at the extremity B, and gradually extending the heat so that each part of the tube is successively heated to redness. The water formed by the combustion is collected in the first U tube, the carbon dioxide is absorbed by the potassium hydroxide in the bulbs. When the operation is terminated, a rubber tube connected with an oxygen reservoir is slipped over the drawn-out end of the combustion tube which is then crushed within the rubber tube. An excess of oxygen is then passed through the combustion-tube, in order to drive out the traces of carbon dioxide and aqueous vapor which it contains at the end of the combustion. It is then only necessary to weigh the water tube and the carbon dioxide tubes. The increase in weight which is found indicates, on one hand, the quantity of water, and on the other the quantity of carbon dioxide, produced by the combustion of the organic matter. The composition of water and of carbon dioxide being known, it is easy to deduce from the weight of these two bodies the quantities of hydrogen and carbon contained in the analyzed substance, and consequently the proportion of these two elements contained in 100 parts of that substance.

Fig. 120 represents the operation towards its close: the combustion-tube is in the gas-furnace, B, and communicates, on the right with the tubes *g*, *h*, *i*, destined to receive the pro-

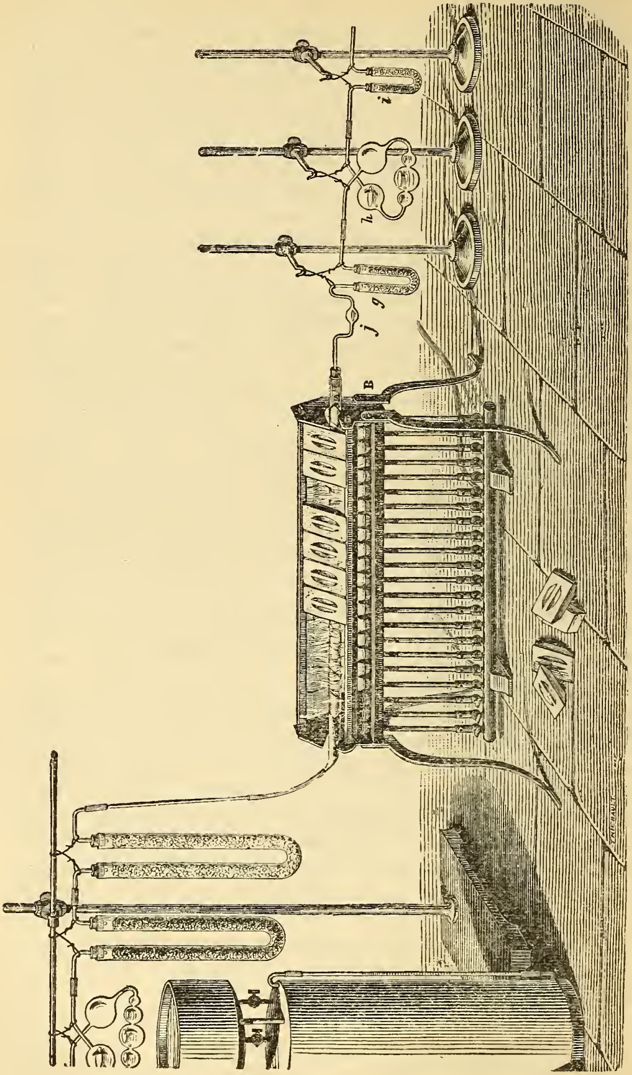


FIG. 120.

ducts of the combustion, on the left with two large U tubes, the first of which is filled with pumice-stone impregnated with potassium hydroxide to absorb traces of carbon dioxide, the second with pumice-stone saturated with sulphuric acid to absorb moisture. Through these tubes is passed the oxygen, at the close of the operation, to expel the last portions of carbon dioxide and vapor of water.

When the substance contains carbon, hydrogen, and oxygen, the proportion of oxygen is the difference between the total percentage of carbon and hydrogen found and 100.

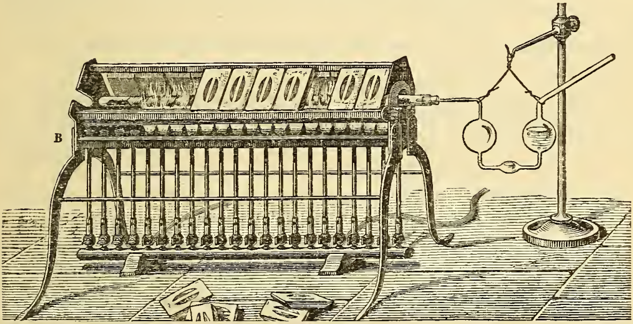


Fig. 121.

Determination of Nitrogen.—Nitrogen may be determined by several methods. One of these is to burn a given weight of the nitrogenous substance with an excess of cupric oxide. The carbon of the substance is converted into carbon dioxide; the hydrogen is converted into water; the nitrogen is disengaged. The gases, nitrogen and carbon dioxide, are received in a graduated jar standing on the mercury-trough and containing potassium hydroxide. The carbon dioxide is absorbed, the nitrogen remains. At the close of the operation, the last traces of nitrogen are expelled by a current of carbon dioxide. The volume of nitrogen is then measured, and its weight deduced from its volume (Dumas).

Another process (Fig. 121) consists in decomposing the nitrogenous organic matter with an alkali at a high temperature. By this means all of the nitrogen is converted into ammonia. The substance is intimately mixed with soda lime, that is, lime impregnated with caustic soda. The mixture is heated to redness in a tube of hard glass, and the ammonia is received in a tube with three bulbs containing dilute hydrochloric acid. Ammonium chloride is formed; when the operation is terminated, the liquid containing the salt is mixed with a solution of platinic chloride. It is then evaporated and exhausted with alcohol, which leaves the platinum and ammonium double chloride, $2(NH^4Cl) + PtCl^4$. The latter is collected upon a tared filter, then washed and dried. From its weight is calculated that of the nitrogen contained in the organic substance (Will and Varrentrapp).

The ammonia disengaged may also be received in 10 cubic centimetres of a normal solution of sulphuric acid, that is, an acid liquor containing a known quantity of sulphuric acid in a determined volume.

The strength of this acid is determined by neutralizing 10 c.c. of it with a dilute alkaline solution of known strength and noting the volume of the latter required. The same operation is repeated with the 10 c.c. of which the acid has been partially neutralized by the ammonia. The quantity of ammonia corresponds to the difference between the volumes of the alkaline liquid employed in these two operations, and can easily be calculated by simple proportion (Peligot).

Still another mode of estimating nitrogen, devised by Kjeldahl, depends upon the fact that the nitrogen of organic bodies is quantitatively converted into ammonia, when such bodies are heated with strong sulphuric acid. After an excess of caustic soda has been added to neutralize the acid, the ammonia liberated is distilled off and estimated as above described.

Determination of the Molecular Weight of Organic Substances.—Elementary analysis permits the determination of the centesimal composition of organic substances. This is indispensable, but it is insufficient for the establishment of their atomic composition, that is, the number of atoms of carbon, hydrogen, oxygen, and nitrogen which are contained in a single molecule of a given organic compound. But if the weight of the molecule be known (hydrogen being taken as unity), it is easy to deduce the atomic composition from the figures given by elementary analysis, as will be seen by the following example. By elementary analysis it is found that 100 parts of acetic acid contain

Carbon	40.
Hydrogen	6.67
Oxygen	53.33
	100.00

On the other hand, methods which will be described have shown that the molecular weight of acetic acid is 60; that is to say, the total weight of the atoms of carbon, hydrogen, and oxygen contained in a molecule of acetic acid, is 60.

Hence by the following proportions:

If 100 parts acetic acid contain 40 of carbon, 60 parts contain x.
" " " 6.67 of hydrogen, " " y.
" " " 53.33 of oxygen " " z.
From which, $x = 24$; $y = 4$; $z = 32$.

Hence 24 represents the weight of the atoms of C contained in a molecule of acetic acid.
4 represents the weight of the atoms of H contained in a molecule of acetic acid.
32 represents the weight of the atoms of O contained in a molecule of acetic acid.

By dividing these numbers by the weights of the respective atoms, the number of atoms of C, H, and O contained in a molecule of acetic acid is readily determined.

$24 \div 12 = 2$ atoms of carbon.
$4 \div 1 = 4$ " hydrogen.
$32 \div 16 = 2$ " oxygen.

Hence the formula of acetic acid is $C^2H^4O^2$.

After the analysis of an organic substance has been made, it is only necessary to determine the molecular weight in order to establish the atomic composition. Several processes are employed for this determination, of which the most convenient, when applicable, is the determination of the vapor density.

The vapor density is most conveniently determined by measuring the volume occupied by the vapor of a known weight of the substance and dividing this weight by that of an equal volume of hydrogen at the same temperature and pressure. An apparatus devised by Victor Meyer and shown in Fig. 122 is generally employed for this purpose. The inner vessel *b* is heated by the vapor of some liquid whose boiling-point is considerably higher than that of the given substance. When the temperature becomes constant, which is indicated by air ceasing to escape through *f*, a graduated tube filled with water is inverted over the mouth of *f*. A small stoppered tube filled with a weighed quantity of the substance has been supported by the glass rod *c h*, and is caused to fall by slightly withdrawing the rod. On reaching the bottom the substance instantly volatilizes, and the vapor displaces an equal volume of air of the same temperature and pressure; this escapes through f, and is collected and measured in the graduated tube, and its volume under normal conditions calculated by aid of the formula

$$v_{\circ} = \frac{v\,(P - h)}{(1 + .003665\,t)\,760},$$

in which v is the measured volume, P the pressure under which the air is measured, h the tension of aqueous vapor at the temperature, t, at which the air is measured. The weight of an equal volume of hydrogen is then divided into the weight of substance taken, and the quotient is the required density. The vapor density of acetic acid compared to hydrogen is thus found to be 30; the molecular weight corresponding would be 60.

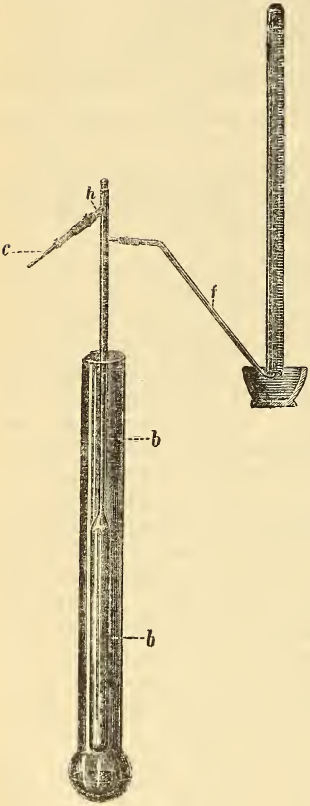


FIG. 122.

Other methods must be employed for determining the molecular weights of substances that cannot be vaporized without decomposition, and advantage has been taken of the fact that in dilute solutions substances behave in many respects like gases or vapors. The most accurate and most convenient of the methods based on this principle is the *cryoscopic* method, devised by Raoult. When a dilute solution of a compound is cooled to its freezing-point, the latter is found to be lower than the freezing-point of the pure solvent. Within certain limits of concentration this *depression* of the freezing-point is directly proportional to the weight of the substance dissolved, and has been shown by Raoult to be proportional to the number of molecules of the substance dissolved in a certain weight of the solvent, and independent of the nature of the substance. Hence, if several substances in equimolecular proportions be dissolved in like quantities of the same solvent, each will produce the same depression of the freezing-point. The depression produced by the number of grammes corresponding to the molecular weight of the substance in 100 grammes of the solvent is called the *molecular depression* of the solvent; different solvents have different molecular depressions. If this constant be known for any solvent, the molecular weight of a substance may be deduced by determining the depression produced by a known proportion of the substance. If c be the depression observed when p grammes of the substances are dissolved in l grammes of the solvent, then $\frac{100\,p}{l}$ grammes of the substance must be dissolved in 100 grammes of solvent to produce the same depression. If T represent the molecular depression of the solvent and M the required molecular weight, $\frac{100\,p}{l} : M = c : T$, and

$$M = \frac{100\,p\,T}{l\,c}.$$

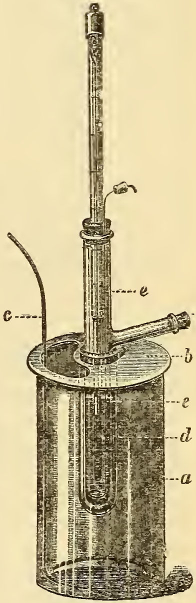


Fig. 123.

Fig. 123 represents an apparatus, described by Beckmann, for accurate measurements of the depression of the freezing-point. e is a wide tube having a capacity of about 25 c. c. up to the lateral tube, and closed by a cork carrying a stout platinum stirring-rod and a thermometer graduated to .01°. e is surrounded by a wider tube, d, which is fixed in the metal lid of the vessel a, which contains a liquid cooled to about 5° below the freezing-point of the solvent. The annular space between e and d contains air, which prevents too rapid cooling.

A weighed quantity, about 15 grammes, of the solvent is introduced into e, and constantly stirred with the rod until it begins to freeze; as soon as the temperature becomes constant the freezing-point is noted. The tube *e* is now withdrawn and the solvent allowed to melt, when the tube is replaced, and a weighed quantity of the substance is dropped in through the lateral tube. The freezing-point of the solution is noted, and the difference between the two readings is the depression.

When for any reason neither of the methods already described can be applied to determine the molecular weight, a chemical method may be employed. We will again consider acetic acid. Salts may be formed with this acid, and we know that these salts contain one atom of metal. We may then analyze silver acetate. 100 parts of that salt contain 64.67 parts of silver. This fact being known, it is easy to determine the molecular weight of silver acetate. Since the latter contains one atom of silver, we can conclude, if 64.67 parts of silver are contained in 100 parts of silver acetate, 108 parts of silver, that is, one atom, are contained in x parts of silver acetate; whence $x = 167$. This number represents the molecular weight of silver acetate. That of acetic acid may be deduced by substituting the atomic weight of hydrogen for that of silver, which gives for the molecular weight of acetic acid 60.

Analogous operations and reasoning permit the determination of the molecular weights of bodies playing the part of bases. They are combined with an acid, the molecular weight of which is known, and the composition of the combination furnishes the data for the calculation of the molecular weight of the base. This method can be applied in a large number of analogous cases, and presents a great generality.

Determination of Melting-Points and Boiling-Points.—A knowledge of the color, density, crystalline form, temperatures of freezing and boiling, and other physical constants of carbon compounds, is of importance not only as means of identification, but in the development of the theory which shall throw light on the influence of composition on properties. Many carbon compounds are fusible and volatile without decomposition, and the exact temperatures at which these changes of state occur are highly characteristic, and are determined with great care.

For the determination of the melting-point, a small quantity of the substance in fine powder is introduced into a capillary tube closed at one end, which is then attached by the side of a chemical thermometer so that the substance shall be on the same level as the bulb; a caoutchouc band or a fine platinum wire keeps the capillary tube in position. The thermometer is then supported over a beaker, *b* (Fig. 124), in which the thermometer bulb and substance are just immersed in a liquid of high boiling-point, such as sulphuric acid or paraffin oil. The whole is cautiously heated while agitating by the stirrer *s*, and the temperature of fusion is noted.

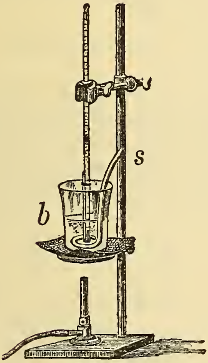


FIG. 124.

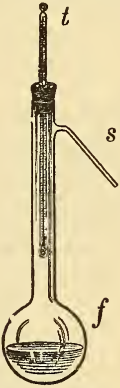


FIG. 125.

Boiling-points are determined by distilling a small quantity of the substance in a "Wurtz distilling tube" (Fig. 125), which is a small, long-necked flask, *f*, with a side tube, *s*, through the cork of which passes the thermometer *t*. It is advisable that the neck of the flask should be so long that the whole mercurial column at the given boiling-point is surrounded by the vapor.

ISOMERISM, METAMERISM, POLYMERISM.

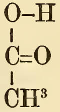
Elementary analysis demonstrates that many bodies which differ in their physical and chemical properties, possess exactly the same centesimal composition. Such bodies are said to be *isomeric*. Two kinds of isomerism exist. Sometimes the isomeric bodies contain the same number of similar atoms in molecules of the same size, and differ only by the arrangement of these atoms; sometimes they contain similar atoms united in the same proportion, but not in the same number, in molecules of unequal magnitude.

In both cases the centesimal composition is the same, for it depends only on the relative number of the atoms.

The first kind of isomerism constitutes *metamerism;* the second, *polymerism.* Acetic acid and methyl formate are an example of two metameric bodies. Each contains 2 atoms of carbon, 4 of hydrogen, and 2 of oxygen; their molecules are equal in size, but different in atomic structure. The latter fact may be expressed by the following formulæ:

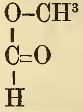
$C^2H^3O.OH$ acetic acid
$CH^3O.OCH$ methyl formate

The first expresses that acetic acid contains a group of atoms, C^2H^3O, acetyl, which is united with hydroxyl, OH; the second, that methyl formate contains a group, CHO, formyl, which is united with oxymethyl, CH^3O. The difference in the atomic arrangement becomes evident, if the preceding formulæ be developed in the graphic manner.



$$\begin{array}{c} O-H \\ | \\ C=O \\ | \\ CH^3 \end{array}$$

Acetic acid.



$$\begin{array}{c} O-CH^3 \\ | \\ C=O \\ | \\ H \end{array}$$

Methyl formate.

The theory of atomicity has thus enabled to discover the atomic structure of a great number of combinations, and to explain numerous isomerisms.

Acetic acid and glucose or grape-sugar present an example of *polymerism.* Both contain the atoms of carbon, hydrogen, and oxygen, united together in the same proportions, but the molecule of the second contains three times as many of each as that of the first.

$$\begin{array}{r l} & C^2H^4O^2 \text{ acetic acid.} \\ 3 \times C^2H^4O^2 = & C^6H^{12}O^6 \text{ glucose.} \end{array}$$

Among the more important and better known cases of polymerism, may be mentioned the numerous hydrocarbons which present the centesimal composition of ethylene or olefiant gas, and which differ from it by the regularly increasing number of their atoms of carbon and hydrogen. These bodies form the following homologous series:

C^2H^4 ethylene. C^3H^6 propylene. C^4H^8 butylene. C^5H^{10} amylene.

Within recent years chemists have been called upon to explain still another kind of isomerism; the atoms constituting the molecules of different substances may be not only the same in kind and number, they may be even similarly grouped. Thus there are three acids known to have the formula COOH.CH(OH).CH(OH).COOH, but they differ markedly in certain physical properties. In such cases it is now generally held that the differences are caused by different arrangement of the atoms in space. (See page 614.)

FUNCTIONS OF ORGANIC COMPOUNDS.

In the study of mineral chemistry it has been seen that bodies present great differences in properties, according to their composition. Some are simple and apt to enter into combination; others are compound and indifferent; the first are more or less energetic in their affinities, the others saturated and satisfied. In one case, we have examined either more or less powerful acids or bases, some of which are hydroxides, as potassa and soda, others are oxides, as those of lead and silver. In the other case we have studied the salts resulting from the union of the former bodies.

In organic chemistry we again encounter various kinds of bodies which have different functions, according to their composition.

It may be said, in a general manner, that the properties of compound bodies depend upon the nature of the atoms and their arrangement in the molecule. In treating of isomerism, the influence of the latter condition has been indicated; that of the former is still more powerful.

Water and potassium hydroxide are both constituted, and in an analogous manner, of three elementary atoms. Each contains one atom of oxygen united to two monatomic atoms.

HOH	KOH
Water.	Potassium hydroxide

But what a difference in their properties! But may not this be expected when it is considered that one contains the energetic metal potassium, in the place occupied in the other by the light gas hydrogen? Is the difference between potash and water greater than that between potassium and hydrogen?

And if for the two atoms of hydrogen we substitute two atoms of chlorine, is it not to be expected that hypochlorous oxide

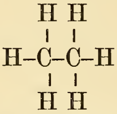
$$Cl-O-Cl$$

the molecule of which is similar in structure to that of water, shall differ from the latter in its properties as much as chlorine differs from hydrogen? It is thus that the nature of the elements contained in compound bodies is the dominant condition in the manifestation of their properties.

The following considerations are of a nature to demonstrate the truth of this proposition inasmuch as concerns organic compounds:

MONATOMIC RADICALS.

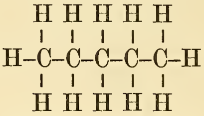
Saturated Hydrocarbons.—The hydrocarbons belonging to the series of marsh gas are all saturated. Consider, for example, C^2H^6; all of the atomicities of two atoms of carbon are satisfied by the union of the latter together and with six atoms of hydrogen.



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

Ethane, or ethyl hydride.

It is the same with all of its homologues; the hydrides of propyl, butyl, amyl, etc., are all *saturated hydrocarbons*, as will be seen by developing the formula of any one of them, pentane, for example:



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

Pentane, or amyl hydride.

All of these bodies are incapable of fixing other elements by *direct addition*, but they may be modified by *substitution*, that is, one or several of their atoms of hydrogen may be replaced by other elements.

Monatomic Chlorides, Bromides, and Iodides.—By the reaction of bromine upon any of the hydrocarbons, we may obtain compounds containing an atom of bromine in the place of an atom of hydrogen.

$$\underset{\text{Ethane.}}{C^2H^6} + Br^2 = \underset{\text{Ethyl bromide.}}{C^2H^5Br} + HBr$$

A saturated and indifferent hydrocarbon is thus converted into a bromide.

The corresponding chloride and iodide exist, possessing the same constitution as the primitive hydrocarbon, and forming with it the following series:

C^2H^6	ethane.
C^2H^5Cl	ethyl chloride.
C^2H^5Br	ethyl bromide.
C^2H^5I	ethyl iodide.

To the other hydrocarbons correspond chlorides, bromides, and iodides analogous to the preceding. Thus, the following groups are known:

CH^4	methane.	C^5H^{12}	pentane.
CH^3Cl	methyl chloride.	$C^5H^{11}Cl$	amyl chloride.
CH^3Br	methyl bromide.	$C^5H^{11}Br$	amyl bromide.
CH^3I	methyl iodide.	$C^5H^{11}I$	amyl iodide.

All of these bodies may be made to undergo the most varied transformations. They may be attacked by a number of reagents, to which they present a hold, as it were, since the chlorine, bromine, and iodine which they contain are gifted with powerful affinities.

The residues resulting from the subtraction of the chlorine, bromine, or iodine then enter into other combinations. It will be remarked that these residues represent the saturated hydrocarbons from which one atom of hydrogen has been removed.

$$CH^3 = CH^3Br - Br, \text{ or } CH^4 - H$$
$$C^2H^5 = C^2H^5Br - Br, \text{ or } C^2H^6 - H$$
$$C^5H^{11} = C^5H^{11}Br - Br, \text{ or } C^5H^{12} - H$$

The atoms of carbon contained in these residues, CH^3, C^2H^5, and C^5H^{11}, are no longer entirely saturated, since Cl, Br, I, or H has been removed, elements which satisfied one atomicity. Therefore, these residues are capable of entering other combinations, but as they possess only one free atomicity, they can only saturate one when they combine. This is expressed by saying that they play the part of *monatomic* or *univalent radicals.* The chlorides, bromides, and iodides from which they are derived contain but one atom of the halogen.

Alcohols.—The neutral hydroxides corresponding to the preceding chlorides, bromides, and iodides, are called alcohols.

If ethyl iodide be heated for a sufficiently long time with potassium hydroxide, potassium iodide will be formed, and the alkaline liquid will contain alcohol which may be separated.

This body is ethyl hydroxide, and is formed according to the following reaction:

$$\underset{\text{Ethyl iodide.}}{C^2H^5I} + KOH = KI + \underset{\text{Ethyl hydroxide.}}{C^2H^5.OH}$$

It is formed, as is seen, by double decomposition. The potassium having removed the iodine from the ethyl iodide, the monatomic residue C^2H^5 combines with the monatomic residue OH. Alcohol is then the hydroxide which corresponds to the iodide, C^2H^5I, and to the hydrocarbon, C^2H^6. Analogous hydroxides correspond to the other hydrocarbons of the same series; they constitute the series of monohydric alcohols, and may be defined as derived from the saturated hydrocarbons by the substitution of the group hydroxyl for one atom of hydrogen. The alcohols now known are numerous: the following are some of them:

$CH^3.OH$	methyl hydroxide, or methyl alcohol.
$C^2H^5.OH$	ethyl hydroxide, or ethyl alcohol.
$C^3H^7.OH$	propyl hydroxide, or propyl alcohol.
$C^4H^9.OH$	butyl hydroxide, or butyl alcohol.
$C^5H^{11}.OH$	amyl hydroxide, or amyl alcohol.
$C^6H^{13}.OH$	hexyl hydroxide, or hexyl alcohol.
$C^7H^{15}.OH$	heptyl hydroxide, or heptyl alcohol.
$C^8H^{17}.OH$	octyl hydroxide, or octyl alcohol.

Each member of this series differs from that which follows by $—CH^2$. All are allied by analogous properties. These two conditions characterize homologous bodies. The alcohols of which the general formula is $C^nH^{2n+1}OH$, form one of the most important series of homologues.

If one of these alcohols be heated with hydrochloric, hydrobromic, or hydriodic acid, water will be formed and the alcohol will be converted into a monatomic chloride, bromide, or iodide. In this reaction the hydroxyl, OH, is replaced by chlorine, bromine, or iodine.

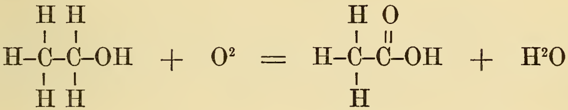
$$\underset{\text{Ethyl hydroxide.}}{C^2H^5.OH} + HCl = H^2O + \underset{\text{Ethyl chloride.}}{C^2H^5Cl}$$

The bodies thus formed are the monatomic chlorides, bromides, or iodides before considered. These experiments show the relations which exist between the latter compounds and the corresponding hydroxides, which are the alcohols.

Monobasic Acids.—Acetic acid, which exists in vinegar, is a derivative of alcohol, of which it is one of the products of oxidation. It is formed under many conditions, one of which is the oxidation of alcohol vapor on contact with platinum black and the air.

$$\underset{\text{Alcohol.}}{C^2H^5.OH} + O^2 = \underset{\text{Acetic acid.}}{C^2H^3O.OH} + H^2O$$

In this reaction an atom of oxygen removes two atoms of hydrogen to form water, and the place of these two atoms of hydrogen is filled by another atom of oxygen. The group ethyl, C^2H^5, thus becomes the group acetyl, C^2H^3O, and if alcohol be the hydroxide of ethyl, acetic acid is the hydroxide of acetyl. We can account for this reaction by developing the formulæ of alcohol and acetic acid according to the principles before explained.



$$\underset{\text{Alcohol.}}{\begin{array}{c} \text{H}\ \ \text{H} \\ |\ \ \ | \\ \text{H–C–C–OH} \\ |\ \ \ | \\ \text{H}\ \ \text{H} \end{array}} + O^2 = \underset{\text{Acetic acid.}}{\begin{array}{c} \text{H}\ \ \text{O} \\ |\ \ \ \| \\ \text{H–C–C–OH} \\ | \\ \text{H} \end{array}} + H^2O$$

Alcohol. Acetic acid.

In alcohol, the second carbon atom is combined with two atoms of hydrogen and with one group hydroxyl, while in acetic acid it is combined with an atom of oxygen and a group hydroxyl.

Acetic acid contains two atoms of carbon united together, and combined, the one with H^3, the second with O and OH. It is thus formed of a group CH^3 united to a group CO–OH $= CO^2H$. There exist many other acids analogous to acetic acid, and derived, like it, by oxidation of the monatomic alcohols of the series $C^nH^{2n+1}OH$. All of these acids contain a hydrocarbon group analogous to methyl, combined with the group $CO^2H = CO–OH$. The hydrogen of the latter group can be readily replaced by an equivalent quantity of metal. This hydrogen is said to be strongly basic, and all of the organic acids which contain a single group, CO^2H, united to a hydrocarbon group, are *monobasic* like acetic acid. The homologues of the latter form the following series:

$CH^2O^2 = H-CO^2H$ formic acid.
$C^2H^4O^2 = CH^3-CO^2H$ acetic acid.
$C^3H^6O^2 = C^2H^5-CO^2H$ propionic acid.
$C^4H^8O^2 = C^3H^7-CO^2H$ butyric acid.
$C^5H^{10}O^2 = C^4H^9-CO^2H$ valeric acid.
$C^6H^{12}O^2 = C^5H^{11}-CO^2H$ caproic acid.
$C^7H^{14}O^2 = C^6H^{13}-CO^2H$ œnanthic acid.
$C^8H^{16}O^2 = C^7H^{15}-CO^2H$ caprylic acid.
$C^9H^{18}O^2 = C^8H^{17}-CO^2H$ pelargonic acid.
$C^{10}H^{20}O^2 = C^9H^{19}-CO^2H$ capric acid, etc.

The first series of formulæ indicates simply the nature and number of atoms contained in the acids of the series $C^nH^{2n}O^2$. They are *empirical* formulæ. The second series gives certain indications upon the relations existing between these atoms. They are *rational* formulæ, and when developed so as to express the relations between all of the atoms, they become *constitutional* formulæ.

Compound Ethers.—The compound ethers are combinations which represent acids of which the hydrogen has been replaced by a hydrocarbon group.

If one of the alcohols of the preceding series, ordinary alcohol, for example, be heated for a long time with acetic acid, water will be formed, and a volatile, neutral liquid possessing an agreeable odor may be separated from the product; this substance is ethyl acetate, or acetic ether. It is formed according to the following reaction:

$$\underset{\text{Alcohol.}}{C^2H^5.OH} + \underset{\text{Acetic acid.}}{C^2H^3O.OH} = \underset{\text{Ethyl acetate.}}{C^2H^5O(C^2H^3O)} + H^2O$$

On comparing this compound with alcohol, we find that it is formed by substitution of the group C^2H^3O, the existence of which is admitted in acetic acid, and which is called acetyl, for one atom of hydrogen in alcohol; and this atom of hydrogen which is replaceable by acetyl is that which is united to the oxygen in alcohol,—that which forms a part of the hydroxyl group. The other atoms of hydrogen, those which constitute part of the group C^2H^5, cannot be replaced by acetyl.

All of the acids can form with alcohol, and indeed with all of the alcohols, compounds analogous to ethyl acetate, and these combinations are called *compound ethers*, or *ethereal salts.* The property possessed by the alcohols of etherifying acids is general and characteristic of this class of compounds. Alcohols which require for etherification but a single molecule of an acid analogous to acetic acid are called monohydric. Many exist which are not included in the preceding series.

Aldehydes.—Acetic acid is not the only product of the oxidation of alcohol. There is another compound intermediate between these two; it results from the action of a single atom of oxygen upon the molecule of alcohol, which thus loses two atoms of hydrogen without other change. The new compound is *aldehyde.*

$$\underset{\text{Alcohol.}}{C^2H^6O} + O = H^2O + \underset{\text{Aldehyde.}}{C^2H^4O}$$

It is a very volatile liquid having a great tendency to become oxidized and converted into acetic acid. It forms crystalline combinations with the alkaline acid-sulphites. To the other alcohols of the series $C^nH^{2n+2}O$, and other acids of the series $C^nH^{2n}O^2$, correspond compounds analogous to aldehyde by their composition and by their properties. They form the following series:

C^2H^4O	aldehyde or acetaldehyde.
C^3H^6O	propionic aldehyde.
C^4H^8O	butyric aldehyde.
$C^5H^{10}O$	valeric aldehyde, etc.

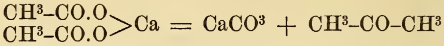
Ketones.—When calcium acetate is submitted to dry distillation a neutral, volatile liquid is obtained, having a peculiar aromatic odor, and known by the name *acetone.*

$$\underset{\text{Calcium acetate.}}{Ca''\left\{\begin{matrix} C^2H^3O^2 \\ C^2H^3O^2 \end{matrix}\right.} = \underset{\text{Acetone.}}{C^3H^6O} + \underset{\text{Calcium carbonate.}}{CaCO^3}$$

To the other acids of the acetic acid series correspond bodies analogous to acetone, and forming with it a homologous series. These ketones are related by properties and composition to the aldehydes. Like the latter, they form crystalline combinations with the alkaline acid-sulphites. It may be considered that while aldehyde is the hydride of acetyl, acetone is the methylide of acetyl, and that in general the ketones are derived by the substitution of a hydrocarbon group, analogous to methyl, for an atom of hydrogen in the aldehydes considered as hydrides.

$$\underset{\text{Aldehyde (acetyl hydride).}}{CH^3\text{–}CO\text{–}H} \qquad \underset{\text{Acetone (acetyl methylide).}}{CH^3\text{–}CO\text{–}CH^3}$$

Hence, acetone contains two methyl groups united to a group, CO (carbonyl). Its mode of formation justifies this conclusion, as shown in the following equation, in which the constitutional formula of acetic acid is employed:



$$\left.\begin{matrix}CH^3\text{–}CO.O\\CH^3\text{–}CO.O\end{matrix}\right>Ca = CaCO^3 + CH^3\text{–}CO\text{–}CH^3$$

Calcium acetate. Calcium carbonate. Acetone.

Diketones.—*Free acid radicals.*—Like the methyl group, the radicals of the monobasic acids cannot exist alone, but only in combination with other atoms or groups. Just as two methyl groups unite to form dimethyl or ethane, so two acetyl groups are combined in diacetyl. Such compounds containing two carbonyl groups are called diketones.

$CH^3CO.COCH^3$ diacetyl

$CH^3CO.COC^2H^5$ acetyl propionyl, etc.

Chlorides of Acid Radicals.—A compound is known in which the acetyl group is united with chlorine. Acetyl chloride, $C^2H^3O.Cl$, is a monatomic chloride, like ethyl chloride C^2H^5Cl, from which it is distinguished by the strongly electronegative nature of its radical.

If acetyl chloride be poured into water, it disappears in a short time with development of heat and the formation of acetic and hydrochloric acids.

$$C^2H^3O.Cl + H^2O = C^2H^3O.OH + HCl$$

Acetyl chloride. Acetic acid.

To acetyl chloride correspond other chlorides which contain radicals of acids analogous to acetic acid. When they are treated with water they yield hydrochloric acid and the acids corresponding to their radicals.

$C^3H^5O.Cl$ Propionyl chloride.	$C^3H^5O.OH$ Propionic acid.
$C^4H^7O.Cl$ Butyryl chloride.	$C^4H^7O.OH$ Butyric acid.

Amides.—If acetyl chloride be treated with ammonia, ammonium chloride will be formed, together with a solid, neutral, nitrogenized body called acetamide.

$$C^2H^5O.Cl + 2NH^3 = NH^4Cl + C^2H^3O.NH^2$$

Acetyl chloride. Acetamide.

There are many other compounds similar to acetamide, and known by the name *amides.* They are formed by the action of ammonia upon organic halides analogous to acetyl chloride. They are also formed by the action of heat upon the ammoniacal salts of the monobasic acids. The latter compounds then lose one molecule of water, and are converted into amides.

$$C^5H^9O.ONH^4 = C^5H^9O.NH^2 + H^2O$$

Ammonium valerate. Valeramide.

Acetamide may be regarded as ammonia in which an atom of hydrogen has been replaced by the radical acetyl.

$$\underset{\text{Ammonia.}}{N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.}\qquad\underset{\text{Acetamide.}}{N\left\{\begin{matrix}C^2H^3O\\H\\H\end{matrix}\right.}\qquad\underset{\text{Valeramide.}}{N\left\{\begin{matrix}C^5H^9O\\H\\H\end{matrix}\right.}$$

Compound Ammonias, or Amines.—If ethyl iodide be heated with ammonia, one of the products of the reaction will be the hydriodide of a base derived from ammonia by the substitution of an ethyl group for an atom of hydrogen.

$$\underset{\text{Ethyl iodide.}}{C^2H^5I} + NH^3 = \underset{\text{Ethylamine hydriodide.}}{(C^2H^5)NH^2.HI}$$

In this reaction, other ethylated bases are formed, independently of ethylamine, among which must be mentioned diethylamine and triethylamine. All present the most striking analogy to ammonia. They may be regarded as ammonia in which one, two, or three atoms of hydrogen have been replaced by one, two, or three ethyl groups.

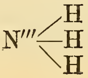
$$\underset{\text{Ammonia.}}{\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N}\qquad\underset{\text{Ethylamine.}}{\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N}\qquad\underset{\text{Diethylamine.}}{\left.\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right\}N}\qquad\underset{\text{Triethylamine.}}{\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}N}$$

The other alkyl groups, C^nH^{2n+1}, can in the same manner replace one or more atoms of hydrogen in ammonia. The products are bases having constitutions analogous to those of the ethyl bases. They are called *amines*, or *compound ammonias.*

It is necessary that the signification of the formulæ above given and those that are to follow shall be clearly understood. They are examples of typical notation, and indicate the relations of the compounds with the type ammonia.

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

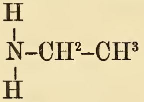
The brace joining the three hydrogen atoms signifies that the whole three are united to a single atom of triatomic nitrogen, with which each exchanges one atomicity; this may be expressed by writing the formula for ammonia thus:



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

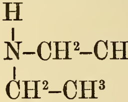
What, then, takes place when one or more atoms of hydrogen are replaced by a group like ethyl? The latter exchanges one atomicity with the nitrogen atom, precisely as the hydrogen atom did, and combines with the nitrogen by one of the atoms of carbon of the group ethyl, $CH^3{-}CH^2$, which requires the satisfaction of one atomicity.

This is clearly expressed in the following graphic formulæ:



$$\begin{matrix}H\\|\\N{-}CH^2{-}CH^3\\|\\H\end{matrix}$$

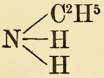
Ethylamine.



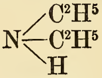
$$\begin{matrix}H\\|\\N{-}CH^2{-}CH^3\\|\\CH^2{-}CH^3\end{matrix}$$

Diethylamine.

However, such formulæ would be too cumbrous for ordinary use, and our formulæ must be more condensed.



Ethylamine.



Diethylamine.

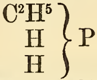
$N(C^2H^5)^3$

Triethylamine.

Phosphines.—Arsines.—Stibines.—There exist several series of combinations belonging to the same type as the compound ammonias, but in which the nitrogen is replaced by phosphorus, arsenic, or antimony. These compounds are derived from the hydrogen compounds of phosphorus, arsenic, and antimony by the substitution of one or more alkyl groups for one or more atoms of hydrogen.

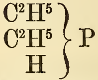
$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$$

Hydrogen phosphide.



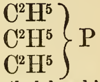
$$\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}P$$

Ethylphosphine.



$$\left.\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right\}P$$

Diethylphosphine.

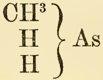


$$\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P$$

Triethylphosphine.

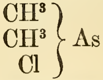
$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}As$$

Hydrogen arsenide.



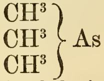
$$\left.\begin{matrix}CH^3\\H\\H\end{matrix}\right\}As$$

Methylarsine.



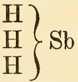
$$\left.\begin{matrix}CH^3\\CH^3\\Cl\end{matrix}\right\}As$$

Dimethylarsine chloride.



$$\left.\begin{matrix}CH^3\\CH^3\\CH^3\end{matrix}\right\}As$$

Trimethylarsine.



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

Hydrogen antimonide.

——

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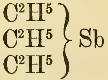
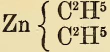


$$\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}Sb$$

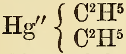
Triethylstibine.

Organo-metallic Compounds.—Ethyl and its congeneric radicals, methyl, amyl, etc., can enter into combination not only with nitrogen, phosphorus, arsenic, etc., of which they saturate one or more atomicities, but with a large number of metals. Thus, zinc, which is diatomic, can combine with two ethyl groups to form zinc ethyl.



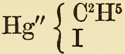
$$\mathrm{Zn}\left\{\begin{array}{l}C^2H^5\\C^2H^5\end{array}\right.$$

Mercury, also diatomic, can unite with one or two ethyl or methyl groups, etc. In the second case, the new combination is saturated; in the first, it is monatomic, $(Hg''C^2H^5)'$, and requires for saturation an atom of a monatomic element, or a monatomic group, iodine, for example.



$$\mathrm{Hg}''\left\{\begin{array}{l}C^2H^5\\C^2H^5\end{array}\right.$$

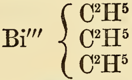
Mercur-ethyl.



$$\mathrm{Hg}''\left\{\begin{array}{l}C^2H^5\\I\end{array}\right.$$

Mercur-monethyl iodide.

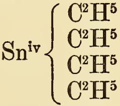
Bismuth, which is triatomic, can fix three ethyl groups.



$$\mathrm{Bi}'''\left\{\begin{array}{l}C^2H^5\\C^2H^5\\C^2H^5\end{array}\right.$$

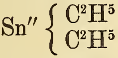
Bismuth-ethyl.

Stanno-tetrethyl is formed by the union of four ethyl groups with one atom of tetratomic tin.



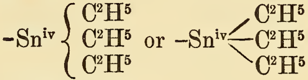
$$\mathrm{Sn}^{iv}\left\{\begin{array}{l}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5\end{array}\right.$$

If the four atomicities of tin be not all satisfied, non-saturated compounds may be formed.



$$\mathrm{Sn}''\left\{\begin{array}{l}C^2H^5\\C^2H^5\end{array}\right.$$

Stanno-diethyl.



$$-\mathrm{Sn}^{iv}\left\{\begin{array}{l}C^2H^5\\C^2H^5\\C^2H^5\end{array}\right. \text{ or } -\mathrm{Sn}^{iv}\begin{array}{l}\diagup C^2H^5\\-C^2H^5\\\diagdown C^2H^5\end{array}$$

Stanno-triethyl.

Stanno-diethyl is known in the free state, but stanno-triethyl doubles its molecule as soon as it is set at liberty, combining with itself, as it can combine with iodine.

$ISn^{iv}(C^2H^5)^3$ Stanno-triethyl iodide.

$(C^2H^5)^3Sn^{iv}-Sn^{iv}(C^2H^5)^3 = Sn^2(C^2H^5)^6.$ Sesquistannethyl.

Non-saturated compounds are apt to combine with other elements or radicals. Stanno-tetrethyl, which is saturated, does not possess this faculty.

The bodies just mentioned belong to the class of *organo-metallic compounds*. Their study is of great importance in the history of the atomicity of the metals, that is, their power of saturation. The theoretical considerations concerning them have been discussed by Frankland, Baeyer, and Cahours.

Monatomic Radicals.—From the preceding summary may be understood the position occupied in organic chemistry by certain groups containing carbon, groups that are distinguished as monatomic because they can manifest but a single atomicity. Only a single monatomic atom or group is wanting that all of the carbon atoms contained in these groups may be entirely saturated. These groups of atoms or radicals cannot exist in the state of liberty, but they can pass from one compound to another, replacing a single atom of hydrogen or other monatomic element, and consequently playing the part of that element in the new combination. This is expressed by saying that these groups act as monatomic radicals.

To indicate the constitution of the combinations containing such groups, and especially the metamorphoses that they may undergo by exchanging these radicals by double decomposition, it is convenient to designate the latter by expressions written separately in the formula and distinct from those for the other elements. The composition of all of the bodies which have just been reviewed may be represented by very simple formulæ, by comparing them to hydrogen compounds, such as free hydrogen, or hydrochloric acid, water, and ammonia. The notation then assumes a *typical* form, exceedingly clear for the interpretation of the majority of reactions.

The following are the typical formulæ for the combinations that have been considered:

TYPE HH.	TYPE $\left.\begin{matrix}H\\H\end{matrix}\right\}O$.	TYPE $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$.
$(C^2H^5)Cl$ **Ethyl chloride.**	$\left.\begin{matrix}(C^2H^5)\\H\end{matrix}\right\}O$ **Ethyl hydrate.**	$\left.\begin{matrix}(C^2H^5)\\H\\H\end{matrix}\right\}N$ **Ethylamine.**
$(C^2H^3O)Cl$ **Acetyl chloride.**	$\left.\begin{matrix}(C^2H^5)\\(C^2H^5)\end{matrix}\right\}O$ **Ethyl hydroxide.**	$\left.\begin{matrix}(C^2H^5)\\(C^2H^5)\\H\end{matrix}\right\}N$ **Diethylamine.**
$(C^2H^3O)H$ **Aldehyde.**	$\left.\begin{matrix}(C^2H^3O)\\H\end{matrix}\right\}O$ **Acetic acid.**	$\left.\begin{matrix}(C^2H^5)\\(C^2H^5)\\(C^2H^5)\end{matrix}\right\}N$ **Triethylamine.**
$(C^2H^3O)(CH^3)$ **Acetone.**	$\left.\begin{matrix}(C^2H^3O)\\(C^2H^5)\end{matrix}\right\}O$ **Ethyl acetate.**	$\left.\begin{matrix}(C^2H^3O)\\H\\H\end{matrix}\right\}N$ **Acetamide.**

POLYATOMIC RADICALS.

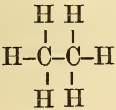
If chlorine and olefiant gas, or ethylene, be mixed in equal volumes, both gases disappear and are converted into an oily substance, which was formerly called Dutch liquid. This body results from the combination of a molecule of ethylene with a molecule (two atoms) of chlorine. It is ethylene chloride.

$$\underset{\text{Ethylene.}}{C^2H^4} + Cl^2 = \underset{\text{Ethylene chloride.}}{C^2H^4Cl^2}$$

If the constitution of ethylene gas, C^2H^4, be compared with that of the saturated hydrocarbon ethane, C^2H^6, which like the former contains two atoms of carbon, it will be noticed that it contains two atoms of hydrogen less.

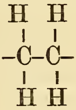
$$C^2H^6 - H^2 = C^2H^4$$

In ethylene the six atomicities of the pair of carbon atoms are not saturated. Hence that gas can absorb directly two atoms of chlorine or bromine to form a saturated compound.



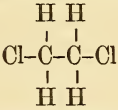
$$\begin{array}{c} H\ \ H \\ |\ \ \ | \\ H{-}C{-}C{-}H \\ |\ \ \ | \\ H\ \ H \end{array}$$

Ethane.



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

Ethylene.



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

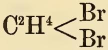
Ethylene chloride.

It is a diatomic radical, or alkylene, and it can exist in the free state because until other atoms are presented to satisfy the atomicities of the two atoms of carbon those two atoms are bound together by a double affinity. Thus, $H^2C{=}CH^2$. One of these bonds is loosed when the ethylene manifests its affinities and enters directly into combination, because the affinity of carbon for chlorine or such an element is greater than its affinity for carbon Ethylene is the first of a numerous class. The following bodies form with it the homologous series C^nH^{2n}:

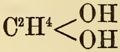
C^2H^4	ethylene.
C^3H^6	propylene.
C^4H^8	butylene.
C^5H^{10}	amylene.
C^6H^{12}	hexylene.
C^7H^{14}	heptylene.
C^8H^{16}	octylene.
C^9H^{18}	nonylene.
$C^{10}H^{20}$	decylene, etc.

All of these bodies are able to fix directly two atoms of chlorine or bromine. When they enter into combination, they take the place of two atoms of hydrogen. They can pass by double decomposition from one compound to another, and their combinations may undergo various metamorphoses analogous to those already indicated.

Dihydric Alcohols, or Glycols.—The glycols are compounds in which the two atomicities of the alkylenes are saturated by two hydroxyl groups. The two atoms of bromine in ethylene bromide, $C^2H^4Br^2$, may be replaced by two hydroxyl groups (OH), and the resulting combination is ethylene hydroxide.



$$C^2H^4<\begin{matrix}Br\\Br\end{matrix}$$



$$C^2H^4<\begin{matrix}OH\\OH\end{matrix}$$

The two atoms of hydrogen united to the oxygen in the hydroxyl groups in glycol may both be replaced by acid radicals analogous to acetyl, just as the single atom of hydrogen in the single hydroxyl group of a monatomic alcohol may be replaced by an acid radical. This is characteristic of a *dihydric alcohol.*

To ethylene hydroxide, or ordinary glycol, correspond the hydroxides of the other hydrocarbons homologous with ethylene. The following glycols are known:

$$C^2H^4\left\{\begin{matrix}OH\\OH\end{matrix}\right. \text{ glycol.}$$

$$C^3H^6\left\{\begin{matrix}OH\\OH\end{matrix}\right. \text{ propyleneglycol.}$$

$$C^4H^8\left\{\begin{matrix}OH\\OH\end{matrix}\right. \text{ butyleneglycol.}$$

$$C^5H^{10}\left\{\begin{matrix}OH\\OH\end{matrix}\right. \text{ amyleneglycol.}$$

$$C^6H^{12}\left\{\begin{matrix}OH\\OH\end{matrix}\right. \text{ hexyleneglycol, etc.}$$

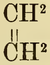
Around each of these bodies are grouped a great number of derivatives, among which we can only consider the *ethers*, *acids*, and *compound ammonias.*

Ethers of the Glycols.—The ethers of the glycols result from the substitution of alcoholic or acid radicals for the hydrogen of the groups OH. One or both of these hydrogens may be thus replaced, and the following examples will illustrate the constitution of the compounds so formed:

$$C^2H^4\left\{\begin{matrix}O.C^2H^5\\OH\end{matrix}\right. \qquad C^2H^4\left\{\begin{matrix}O.C^2H^5\\O.C^2H^5\end{matrix}\right. \qquad C^2H^4\left\{\begin{matrix}O.C^2H^3O\\OH\end{matrix}\right. \qquad C^2H^4\left\{\begin{matrix}O.C^2H^3O\\O.C^2H^3O\end{matrix}\right.$$

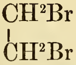
Monethylic glycol. Diethylic glycol. Glycol monacetate. Glycol diacetate.

Hydroxy-acids and **dibasic acids** result from the oxidation of the glycols. Their formation and constitution may be understood by developing the formulæ of the hydrocarbons which constitute the radicals of these glycols. Ordinary glycol may yield two acids by oxidation, the first resulting from the substitution of an atom of oxygen for two atoms of hydrogen, the second from the substitution of two atoms of oxygen for four atoms of hydrogen. The following formulæ express the constitution and derivation of these compounds:



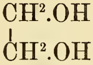
$$\begin{array}{c}CH^2\\ \|\\ CH^2\end{array}$$

Ethylene.



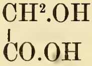
$$\begin{array}{c}CH^2Br\\ |\\ CH^2Br\end{array}$$

Ethylene bromide.



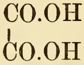
$$\begin{array}{c}CH^2.OH\\ |\\ CH^2.OH\end{array}$$

Glycol.



$$\begin{array}{c}CH^2.OH\\ |\\ CO.OH\end{array}$$

Glycollic acid.



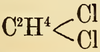
$$\begin{array}{c}CO.OH\\ |\\ CO.OH\end{array}$$

Oxalic acid.

Glycollic acid and oxalic acid are, therefore, both derived from the same dihydric alcohol; but the former is monobasic because it contains but a single atom of hydrogen that can be replaced by a metal. The second is dibasic, for it contains two atoms of hydrogen that are replaceable by an equivalent quantity of metal. This basic hydrogen is that which forms part of the group CO^2H. Oxalic acid is composed simply of two groups $-CO^2H$; it is dibasic. Glycollic acid contains but one, and it is consequently monobasic. The hydrogen united to the oxygen in the group $-CH^2.OH$ is called alcoholic hydrogen; it may be replaced by an acid radical, but it cannot be easily replaced by a metal. All bodies containing a group $CH^2.OH$ are alcohols, and all bodies containing a group $CO.OH$ are acids. The alcohols and acid are thus defined by their constitution. Glycollic acid is at the same time an alcohol and an acid,—an hydroxy-acid,—for it contains both a group $CH^2.OH$ and a group $CO.OH$.

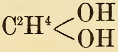
There exists a series of acids homologous with glycollic acid, and another series homologous with oxalic acid. Both series are derived from the higher dihydric alcohols.

Diatomic Ammonias, or Diamines.—Compounds exist which hold the same relation to the dihydric alcohols as ethylamine and its homologues to the monohydric alcohols. Such a compound is ethylene-diamine. Its relations with ethylene chloride and glycol are expressed by the following formulæ:



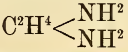
$$C^2H^4\begin{array}{l}\diagup Cl\\ \diagdown Cl\end{array}$$

Ethylene chloride.



$$C^2H^4\begin{array}{l}\diagup OH\\ \diagdown OH\end{array}$$

Glycol.



$$C^2H^4\begin{array}{l}\diagup NH^2\\ \diagdown NH^2\end{array}$$

Ethylene-diamine.

Trihydric and Polyhydric Alcohols.—There are alcohols containing three or more hydroxyl groups; glycerol, for example, is a *trihydric alcohol.* It contains a radical, C^3H^5, which is triatomic, since it is derived from the saturated hydrocarbon C^3H^8 by the subtraction of three atoms of hydrogen. Erythritol is a *tetrahydric alcohol;* it contains the tetratomic radical $C^4H^6 = C^4H^{10} - H^4$. Lastly, the sweet, sugar-like substance derived from manna, and known as mannitol, is a *hexahydric alcohol.* There are many analogous bodies containing three or more hydroxyl groups, but in no case does the number of these groups exceed that of the carbon atoms in the molecule. The following formulæ represent the composition and the functions of the *polyhydric alcohols* that have been mentioned:

$C^3H^{5'''}(OH)^3$	$C^4H^{6\text{iv}}(OH)^4$	$C^6H^{8\text{vi}}(OH)^6$
Glycerol.	Erythritol.	Mannitol.

Around these bodies are grouped the numerous corresponding derivatives, ethers, acids, etc.

The above considerations show that the neutral hydroxides, called alcohols, are highly important in themselves and on account of the derivatives which attach to them. Hence the elements of a natural classification of organic compounds are deduced.

COMPOUNDS OF CYANOGEN.

Gay-Lussac gave the name cyanogen to the radical of prussic or hydrocyanic acid, which was discovered by Scheele in 1782. This radical is composed of one atom of carbon and one atom of nitrogen. In hydrocyanic acid it is united with hydrogen; in the cyanides it is combined with the metals.

$H(CN)'$	$K(CN)'$	$Hg''(CN)^2$
Hydrocyanic acid.	Potassium cyanide.	Mercury cyanide.

The preceding compounds may be compared with the corresponding chlorides:

HCl	KCl	$HgCl^2$
Hydrochloric acid.	Potassium chloride.	Mercuric chloride.

It is somewhat remarkable that potassium cyanide is isomorphous with potassium chloride.

In the preceding compounds, cyanogen, which is composed of an atom of carbon and an atom of nitrogen, plays a part analogous to that of chlorine. It is a monatomic radical; nitrogen, which is triatomic, can saturate only three of the four atomicities which reside in an atom of carbon. Hence there remains one free atomicity, and cyanogen can act as a monatomic radical, $-C\equiv N$.

All of the compounds of cyanogen are prepared from potassium ferrocyanide, or yellow prussiate of potash, which is described on page 468.

CYANOGEN.

$$(CN)^2 = Cy^2$$

Formation.—Cyanogen occurs in small quantities in the gases from blast-furnaces. Nitrogen and carbon combine together with difficulty, but their direct union takes place in presence of potassium or potassium carbonate at a high temperature. When nitrogen gas is passed over an incandescent mixture of carbon and potassium carbonate, potassium cyanide is formed. A larger yield of cyanide is obtained if the nitrogen is replaced by ammonia gas. Also, if ammonia gas is passed over incandescent charcoal in a porcelain tube, ammonium cyanide is formed, and may be condensed in crystals in a cooled receiver (Kuhlmann).

$$C + 2NH^3 = \underset{\text{Ammonium cyanide.}}{NH^4.CN} + H^2$$

Cyanogen is also formed by the dehydration of ammonium oxalate, when that salt is treated with phosphoric anhydride. This reaction allows cyanogen gas to be regarded as the *nitrile* of oxalic acid. A nitrile is a cyanide which may be converted into an acid by hydration, with elimination of ammonia, by the action of an alkaline hydroxide.

$$\underset{\text{Ammonium oxalate.}}{\begin{array}{l}CO.ONH^4\\ |\\ CO.ONH^4\end{array}} = \underset{\text{Cyanogen.}}{\begin{array}{l}CN\\ |\\ CN\end{array} + 4H^2O}$$

Preparation.—Mercury cyanide is heated in a small retort fitted with a delivery-tube. The mercury volatilizes, and a gas is disengaged which may be collected over mercury. This is a free cyanogen. It has separated from the mercury, which is condensed in the dome of the retort. There remains in the retort a solid brown mass which possesses the same composition as cyanogen, and is known as *paracyanogen.*

$$Hg(CN)^2 = (CN)^2 + Hg$$

Composition and Properties.—Cyanogen is a colorless gas, possessing a strong odor of bitter almonds. It may be easily liquefied by a pressure of 4 atmospheres or a temperature of —25°. Its density is 1.8064 compared to air, or 26 compared to hydrogen.

In the cyanide of mercury the metal was combined with two groups (CN), which unite together when they separate from the mercury, and remain combined together in the gas which is disengaged. The latter contains CN combined with CN. Its formula is:

$$NC{-}CN = (CN)^2 = Cy^2$$

2 volumes of this gas contain two atoms of carbon and two atoms of nitrogen.

This composition may be demonstrated by eudiometric analysis.

2 volumes of cyanogen and 4 volumes of oxygen are introduced into a mercury eudiometer. On the passage of an electric spark there is a flash of blue light, and the volume of the gas is not changed. If a solution of potassium hydrate be now passed into the eudiometer, the six volumes of gas will be reduced to two.

4 volumes of CO^2 are formed;
2 volumes of N remain.

2 volumes of cyanogen then contain the carbon contained in $2CO^2$, that is, C^2, and N^2.

This is expressed by saying that the formula of cyanogen, $C^2N^2 = Cy^2$, corresponds to 2 volumes.

On contact with flame, cyanogen takes fire and burns in the air with a purple flame, yielding carbon dioxide and nitrogen.

Water dissolves four and one-half times its volume of cyanogen. When this solution is left to itself it deposits brown flakes. It then contains in solution urea, ammonium carbonate, ammonium cyanide, and ammonium oxalate.

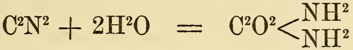
$$\underset{\text{Cyanogen.}}{C^2N^2} + 4H^2O = \underset{\text{Ammonium oxalate.}}{(NH^4)^2C^2O^4}$$

$$\underset{\text{Cyanogen.}}{C^2N^2} + H^2O = \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Cyanic acid.}}{\left.\begin{matrix}CO\\H\end{matrix}\right\rangle N}$$

$$\underset{\text{Cyanic acid.}}{\left.\begin{matrix}CO\\H\end{matrix}\right\rangle N} + H^2O = CO^2 + \underset{\text{Ammonia.}}{NH^3}$$

The ammonia formed by the latter reaction combines with the cyanic acid to form ammonium cyanate, which becomes converted into urea, as will be seen shortly.

It is a curious fact that in the presence of a small quantity of aldehyde, the decomposition of an aqueous solution of cyanogen yields, almost entirely, but one product,—oxamide.



$$C^2N^2 + 2H^2O = C^2O^2 < \begin{matrix} NH^2 \\ NH^2 \end{matrix}$$

Oxamide.

If a fragment of potassium be heated in cyanogen gas, a brilliant flash of light takes place; in combining with cyanogen potassium becomes incandescent. Potassium cyanide is formed.

$$(CN)^2 + K^2 = 2KCN$$

In this reaction, cyanogen combines directly with a metal. It acts like an element, such as chlorine.

Paracyanogen, which has been mentioned before, is a polymeride of cyanogen. When it is quickly heated to redness, it is entirely transformed into cyanogen gas.

HYDROCYANIC ACID.

(PRUSSIC ACID.)

$$HCN = HCy$$

Preparation.—Gay-Lussac prepared hydrocyanic acid by heating mercury cyanide with hydrochloric acid.

An easier process consists in decomposing prussiate of potash (potassium ferrocyanide) with sulphuric acid. 8 parts of the salt in fine powder are heated in a retort with 9 parts of sulphuric acid, previously diluted with 14 parts of water.

The neck of the retort is inclined upwards, so that the aqueous vapors are condensed and run back into the retort, while the vapor of prussic acid, which is very volatile, is dried by passage through a tube containing calcium chloride, and condensed in a receiver placed in a freezing mixture of ice and salt.

Properties.—This acid is a colorless, limpid, and very volatile liquid, having a penetrating odor resembling that of bitter almonds. Its density at 7° is 0.7058. It boils at 26.5°, and solidifies to a crystalline mass at —15°.

It scarcely reddens blue litmus-paper. On contact with an incandescent body, it takes fire and burns with a pale violet flame.

It does not keep long in the pure state. It becomes brown, and is finally converted into a solid, brown mass.

It dissolves in water in all proportions. A solution containing 2 per cent. is used in medicine.

When hydrocyanic acid is mixed with its own volume of concentrated hydrochloric acid, the mixture gets hot and soon deposits abundant crystals of ammonium chloride. The solution contains formic acid.

$$\underset{\text{Hydrocyanic acid.}}{HCN} + 2H^2O = \underset{\text{Formic acid.}}{CH^2O^2} + NH^3$$

In reactions with the hydracids, hydrocyanic acid can function like a compound ammonia, $N(CH)'''$ (*formonitrile*). It unites with elevation of temperature with hydrochloric, hydrobromic, and hydriodic acids to form compounds, such as $N(CH)'''.HCl$ and $N(CH)'''.HI$, that may be compared to the ammonium salts. In these crystalline compounds, the anhydrous bases can displace the hydrocyanic acid, as they displace ammonia in the ammoniacal salts; thus,

$$N(CH)HCl + NH^3 = NH^4Cl + HCN$$

Cupric oxide displaces hydrocyanic acid in the same manner in the hydrobromide of formonitrile.

The oxidized organic acids unite only with difficulty with hydrocyanic acid, and at an elevated temperature (Arm. Gautier).

Hydrocyanic acid is one of the most rapid and most dangerous of poisons. A single drop placed upon the eye of a rabbit is sufficient to kill the animal in a few instants, and after violent convulsions.

Hydrocyanic acid may be detected by the following tests:

1. It gives a white precipitate of silver cyanide with silver nitrate, and this precipitate does not darken on exposure to light. When properly dried and heated, silver cyanide disengages cyanogen.

2. If a drop of hydrocyanic acid be added to a mixed solution of ferrous and ferric sulphates, and an excess of potassium hydrate be added, a thick, dark-colored precipitate is formed. If this be treated with an excess of hydrochloric acid, the ferrous and ferric oxides precipitated will be dissolved, and Prussian blue will remain, strongly coloring the liquid.

3. If a drop of hydrocyanic acid be mixed with a drop of ammonium sulphide, and then evaporated to dryness, ammonium

sulphocyanate is formed, and a blood-red color is produced when the spot is touched with a drop of ferric chloride slightly acidulated with hydrochloric acid.

METALLIC CYANIDES.

We will only consider the two more important metallic cyanides, those of potassium and mercury.

Potassium Cyanide, KCy = KCN.—This compound is prepared by heating well-dried potassium ferrocyanide to redness in stoneware retorts. After cooling, the black mass is exhausted with alcohol; this solvent leaves a black deposit, consisting of charcoal and iron, and the solution evaporated in vacuo deposits the potassium cyanide as a white, crystalline mass.

This body crystallizes in cubes. It has a caustic taste and an after-taste of bitter almonds. It is very poisonous. It is quite soluble in water, only sparingly soluble in absolute alcohol. When the aqueous solution is boiled, it disengages ammonia, and is converted into potassium formate. This reaction takes place slowly in the cold, and is analogous to that which has before been described.

When potassium cyanide is heated with sulphur, it is converted into potassium sulphocyanate. Iodine dissolves abundantly in a solution of potassium cyanide; potassium iodide is formed, and cyanogen iodide is deposited in crystals.

Solution of potassium cyanide dissolves the cyanides of many metals, such as zinc, silver, and gold, forming soluble double cyanides. This property is utilized in the extraction of gold from its ores.

Mercury Cyanide, $HgCy^2 = Hg(CN)^2$.—This compound is prepared by dissolving finely-powdered mercuric oxide in an aqueous solution of hydrocyanic acid until the odor of the latter has entirely disappeared, being careful to avoid an excess of the oxide. After concentration and cooling, colorless, anhydrous prisms are obtained, which are unaltered by air and light. This is mercury cyanide. It is very poisonous.

It possesses a nauseous metallic taste, and dissolves in 8 parts of cold water.

It is decomposed by heat into mercury and cyanogen; paracyanogen is formed at the same time. The solution of mercury cyanide dissolves mercuric oxide, and forms with it a compound more soluble than the cyanide, crystallizing in colorless scales.

FERROCYANIDES.

By this name are designated compounds containing cyanogen and iron intimately combined together and forming a complex radical capable of passing from one compound to another by double decomposition. This radical, which is called *ferrocyanogen*, contains one atom of diatomic iron combined with six cyanogen groups, CN. As each of the latter represents one atomicity, it is evident that the group $(Cy^6{=}Fe)^{iv}$, in which but two atomicities are saturated between the Fe and 2Cy, must be tetratomic. Hence ferrocyanogen can combine with four atoms of a monatomic metal such as potassium. The important compound known as potassium ferrocyanide, or yellow prussiate of potash, has such a composition.

Potassium Ferrocyanide, $K^4Cy^6Fe + 3H^2O$.—This salt is obtained by calcining animal matters, such as blood, horn, the débris of skin, leather, etc., in closed iron vessels with potassium carbonate. The sintered mass, which contains potassium cyanide, is exhausted with boiling water, and ferrous sulphate is added to the solution, which is then evaporated to crystallization; or the solution is boiled with metallic iron, which dissolves with evolution of hydrogen. The iron may also be added to the mixture of animal matter and potassium carbonate before calcination; after cooling, the mass is pulverized and exhausted with boiling water. The solution contains ferrocyanide.

When sufficiently concentrated, it deposits the salt in yellow crystals, which are derived from a square octahedron. They are unaltered by the air, but lose 12.8 per cent. of water at 100°. The anhydrous salt is white.

Potassium ferrocyanide dissolves in 2 parts of boiling, and in 4 parts of cold water. It is insoluble in alcohol. When heated with bodies rich in oxygen, such as manganese dioxide, it is converted into potassium cyanate, the iron itself being oxidized to peroxide. It is not poisonous.

When fused with sulphur, it is converted into potassium sulphocyanate.

When heated with concentrated sulphuric acid, it yields pure carbon monoxide, and a residue consisting of sulphates of iron, potassium, and ammonium.

Potassium ferrocyanide precipitates many metallic solutions. The following are some of these precipitates:

Zinc ferrocyanide	Zn^2Cy^6Fe,	white.
Copper ferrocyanide	Cu^2Cy^6Fe,	mahogany color.
Lead ferrocyanide	Pb^2Cy^6Fe,	white.
Silver ferrocyanide	Ag^4Cy^6Fe,	white.

Potassium ferrocyanide forms a bluish-white precipitate with ferrous salts. This precipitate contains:

$$Cy^6Fe\left\{\begin{matrix}Fe''\\ K^2\end{matrix}\right.$$

It is identical with the bluish-white deposit which is formed when potassium ferrocyanide is heated with dilute sulphuric acid.

Prussian Blue, $(Fe^2)^2(Cy^6Fe)^3$.—This is the dark-blue precipitate obtained when a solution of potassium ferrocyanide is poured into a ferric salt.

$$\underset{\text{Ferric chloride.}}{4FeCl^3} + \underset{\text{Potassium ferrocyanide.}}{3K^4Cy^6Fe} = 12KCl + \underset{\substack{\text{Ferric ferrocyanide.}\\ \text{(Prussian blue.)}}}{Fe^4(Cy^6Fe)^3}$$

When calcined in contact with the air, it leaves a residue of peroxide of iron. It is insoluble in water, alcohol, and in the weaker acids. Oxalic acid dissolves it, and the solution is employed as a blue ink.

POTASSIUM FERRICYANIDE.

(RED PRUSSIATE OF POTASH.)

K^3Cy^6Fe

This beautiful salt, discovered by Leopold Gmelin, is formed when a current of chlorine is passed into a solution of potassium ferrocyanide. Potassium chloride and potassium ferricyanide are formed, and the latter gives to the liquid a deep green-brown color. On evaporation it deposits the new salt, which is purified by a second crystallization. Potassium chloride remains in the mother-liquor.

$$\underset{\text{Potassium ferrocyanide.}}{2K^4(Cy^6Fe)} + Cl^2 = 2KCl + \underset{\text{Potassium ferricyanide.}}{2K^3Cy^6Fe}$$

Potassium ferricyanide forms magnificent monoclinic prisms of a ruby-red color. These crystals are anhydrous.

It is believed that this salt contains a triad radical, Cy^6Fe, which is called *ferricyanogen.*

Potassium ferricyanide dissolves in 3.8 parts of cold water, and in a less quantity of boiling water. The solution has a dark yellow-brown color. It does not precipitate the ferric salts. In solutions of the ferrous salts it gives a blue precipitate analogous to Prussian blue, and which is called *Turnbull's blue.*

$$\underset{\substack{\text{Potassium}\\\text{ferricyanide.}}}{2K^3Cy^6Fe} + \underset{\text{Ferrous sulphate.}}{3FeSO^4} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{3K^2SO^4} + \underset{\substack{\text{Ferrous ferricyanide.}\\\text{(Turnbull's blue.)}}}{Fe^3(Cy^6Fe)^2}$$

In alkaline solution potassium ferricyanide acts as an energetic oxydizing agent, thus:

$$2K^3Cy^6Fe + 2KOH = 2K^4Cy^6Fe + H^2O + O$$

NITROFERROCYANIDES.

These salts, which were discovered by Playfair, are formed by the action of nitric acid upon certain alkaline ferrocyanides. The best known is *sodium nitroferrocyanide*, or, as it is ordinarily called, *sodium nitroprusside.*

It is prepared by oxidizing potassium ferrocyanide with dilute nitric acid. After filtration and evaporation, crystals of potassium nitrate and a deposit of oxamide are obtained. The mother-liquor is saturated with sodium carbonate, and on evaporation yields sodium nitroprusside, which may be purified by recrystallization.

Sodium nitroferrocyanide crystallizes in large right rhombic prisms of a ruby-red color. Its composition is represented by the formula $Na^2Cy^5(NO)Fe + 2H^2O$. Its aqueous solution has a red-brown color, and gives a very intense but evanescent purple color with solutions of the alkaline sulphides.

CHLORIDES OF CYANOGEN.

There are two chlorides of cyanogen known, a chloride, CyCl, which is liquid below 15.5°, and a solid chloride, Cy^3Cl^3. These two chlorides present a curious instance of polymerism.

Liquid Cyanogen Chloride, CyCl = CNCl.—This compound is prepared by passing chlorine gas over mercury cyanide, or better, into an aqueous solution of hydrocyanic acid, which is maintained at 0°. Hydrochloric acid and cyanogen chloride are formed.

$$HCN + Cl^2 = CNCl + HCl$$

When the solution is saturated with chlorine, it is gently heated, and the cyanogen chloride which is disengaged is passed through a tube containing calcium chloride, and condensed in a well-cooled receiver.

When properly purified, cyanogen chloride is a colorless liquid, having a penetrating odor, which is very irritating to the eyes. It boils at 15.5° and solidifies at about 5°. When pure, it can be preserved without alteration, but if it contain a trace of chlorine, it soon becomes converted into the solid chloride.

Solid Cyanogen Chloride, $Cy^3Cl^3 = C^3N^3Cl^3$.—This body results from the polymeric transformation which the liquid chloride undergoes spontaneously under certain circumstances. It can also be obtained by exposing hydrocyanic acid to the action of chlorine in direct sunlight.

It crystallizes in brilliant, yellow needles or plates. It melts at 140° and boils at 190°. It has a peculiar, irritating odor. Boiling water immediately decomposes it into hydrochloric and cyanuric acids.

$$\underset{\text{Cyanogen chloride.}}{C^3N^3Cl^3} + 3H^2O = \underset{\text{Cyanuric acid.}}{\left.\begin{matrix}(CO)^3\\ H^3\end{matrix}\right\}N^3} + 3HCl$$

Cyanogen Bromide and Iodide.—The bromide and iodide of cyanogen correspond in constitution to the liquid chloride. They are obtained by the action of bromine or iodine upon mercury cyanide. These elements decompose mercury cyanide with formation of bromide or iodide of mercury, the excess of bromine or iodine combining with the cyanogen to form cyanogen bromide or iodide.

Cyanogen bromide, CNBr, is solid and crystallizes in brilliant cubes.

Cyanogen iodide, CNI, sublimes spontaneously in beautiful colorless needles when a mixture of iodine and mercury cyanide is placed in the bottom of a flask, mercuric iodide being formed. Cyanogen iodide has a penetrating odor; it is very volatile, and, like the chloride and bromide, is very poisonous.

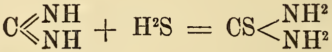
AMIDO DERIVATIVES OF CYANOGEN.

Cyanamide, $CN^2H^2 = C\genfrac{}{}{0pt}{}{\lll NH}{\lll NH}$.—This compound is formed by the action of cyanogen chloride or bromide on an ethereal solution of ammonia. It is also obtained by the action of mercuric oxide or silver oxide upon sulpho-urea (page 483).

$$CS{<}\begin{matrix}NH^2\\NH^2\end{matrix} + HgO = HgS + H^2O + C{\ll}\begin{matrix}NH\\NH\end{matrix}$$

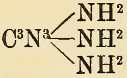
Sulpho-urea. Cyanamide.

It forms crystals fusible at 40°, soluble in water, alcohol, and ether. Ammoniacal silver nitrate precipitates from its solution a yellow silver compound containing CN^2Ag^2. By the action of acids it combines with the elements of water, forming urea (page 478). Hydrogen sulphide reconverts it into sulpho-urea.

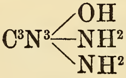


$$C{\ll}\begin{matrix}NH\\NH\end{matrix} + H^2S = CS{<}\begin{matrix}NH^2\\NH^2\end{matrix}$$

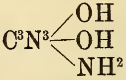
Melamine, $C^3N^6H^6$.—When cyanamide is heated to 150°, it becomes polymerized, and converted into tricyanuramide. This substance is known as *melamine*. It crystallizes in brilliant right-rhombic octahedra, soluble in hot water, insoluble in alcohol and ether. It unites with acids, forming salts. When heated with dilute alkalies or with acids, it is converted successively by the action of one, two, or three molecules of water, and elimination of one, two, or three molecules of ammonia, into ammeline, ammelide, and cyanuric acid.



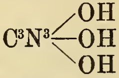
Melamine.



Ammeline.



Ammelide.



Cyanuric acid.

Cyanuric acid, which is formed according to the following equation, will be described farther on.

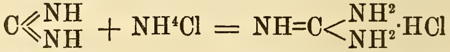
$$C^3N^3(NH^2)^3 + 3H^2O = C^3N^3(OH)^3 + 3NH^3$$

GUANIDINE.

CH^5N^3

This body is related to the amides of cyanogen. It was first obtained by the oxidation of guanine, derived from guano; hence its name. Since then it has been formed synthetically by the following reactions.

1. When an alcoholic solution of either cyanogen iodide or cyanamide is heated to 100° with ammonium chloride:



$$C{\ll}\begin{matrix}NH\\NH\end{matrix} + NH^4Cl = NH{=}C{<}\begin{matrix}NH^2\\NH^2\end{matrix}\cdot HCl$$

Cyanamide. Hydrochloride of guanidine.

If cyanogen iodide be employed, cyanamide is first formed.

2. By the action of carbonyl chloride on ammonia (G. Bouchardat).

3. By the action of ammonia on either ethyl orthocarbonate or chloropicrin (page 491).

$$\underset{\text{Ethyl orthocarbonate.}}{C(OC^2H^5)^4} + 3NH^3 = \underset{\text{Guanidine.}}{CN^3H^5} + \underset{\text{Alcohol.}}{4C^2H^5.OH}$$

4. The method generally employed for the preparation of guanidine consists in heating for a long time ammonium sulphocyanate (page 482) to a temperature of 180° or 190°. Sulpho-urea is formed, and decomposed into hydrogen sulphide and guanidine sulphocyanate.

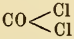
$$\underset{\text{Sulpho-urea.}}{2CSN^2H^4} = H^2S + \underset{\text{Guanidine sulphocyanate.}}{CN^3H^5.CNSH}$$

Properties.—Guanidine forms deliquescent crystals, very soluble in water and alcohol. It has a strong alkaline reaction, and absorbs carbonic acid gas from the air. With acids it forms crystallizable salts. The nitrate, $CN^3H^5.HNO^3$, precipitates in plates when nitric acid is added to an aqueous solution of guanidine. The carbonate $(CN^3H^5)^2.H^2CO^3$, crystallizes in quadratic prisms the solution of which has an alkaline reaction.

CARBONYL COMPOUNDS.

Carbon monoxide plays the part of a diatomic radical. It is capable of uniting with one atom of oxygen to form carbonic acid gas, or with two atoms of chlorine to form carbonyl chloride.

It can also unite with two residues, NH^2, which are monatomic since they represent ammonia less one atom of hydrogen; lastly, it may unite with NH, which is diatomic since it represents ammonia minus two atoms of hydrogen. The compounds thus formed have the following constitutions:

$CO.O$	carbon dioxide.
 $CO<\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$	carbonyl chloride.
 $CO<\begin{smallmatrix}NH^2\\NH^2\end{smallmatrix}$	urea.
$CO(NH)''$	isocyanic acid.

The last two compounds can be considered as derived from the ammonia type.

Isocyanic acid is derived from one molecule of ammonia by the substitution of the diatomic radical CO, which is called *carbonyl*, for two atoms of hydrogen.

$$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. \qquad\qquad N\left\{\begin{matrix}CO''\\H\end{matrix}\right. \text{ isocyanic acid.}$$

Urea is derived from two molecules of ammonia by the substitution of the radical carbonyl for two atoms of hydrogen.

$$N^2\left\{\begin{matrix}H^2\\H^2\\H^2\end{matrix}\right. \qquad\qquad N^2\left\{\begin{matrix}CO''\\H^2\\H^2\end{matrix}\right. \text{ urea.}$$

Urea is then *carbonyl diamide ;* or more simply, *carbamide.*

ISOCYANIC ACID.

CONH

Liebig and Wöhler obtained this acid by the dry distillation of cyanuric acid. One molecule of the latter, which is polymeric with isocyanic acid, then breaks up into three molecules of the latter body.

$$\underset{\text{Cyanuric acid.}}{C^3O^3N^3H^3} = \underset{\text{Isocyanic acid.}}{3CONH}$$

The latter acid condenses at a few degrees below 0° to a colorless liquid having a strong and irritating odor. It is very unstable. As soon as it is removed from the freezing mixture in which it is condensed, and its temperature rises to a few degrees above 0°, it produces a crackling noise and little explosions, and is converted by a molecular transformation into an amorphous white mass called cyamelide. The latter body is also formed at the same time as isocyanic acid by the dry distillation of cyanuric acid.

Potassium Isocyanate, CONK.—This salt is prepared by heating to dull redness in a flat sheet-iron dish an intimate mixture of 2 parts of potassium ferrocyanide and 1 part of manganese dioxide, both in fine powder and perfectly dry. The mixture must be continually stirred; it blackens and enters into semi-fusion; after cooling, it is reduced to powder and exhausted with hot alcohol of 80 per cent. On cooling, the filtered alcoholic solution deposits potassium isocyanate in laminated, transparent crystals which are anhydrous. This salt is very soluble in water, and but slightly soluble in cold concentrated alcohol. If hydrochloric acid be added to an aqueous solution of potassium isocyanate, carbonic acid gas is disengaged with brisk effervescence. The liquid contains ammonium chloride.

$$CONH + H^2O = CO^2 + NH^3$$

Potassium Cyanate.—There is a compound isomeric with potassium isocyanate; it is formed by the action of cyanogen chloride upon potassium hydroxide (Bannow).

$$CN.Cl + 2KOH = KCl + H^2O + KCNO$$

Cyanogen chloride. Potassium cyanate.

The hydrate corresponding to this potassium salt would be the true cyanic acid, of which the ethers were discovered by Cloëz. The compound formerly known by the name cyanic acid does not merit that name. It is not a compound of cyanogen, but a combination of oxide of carbon; it is *carbimide*. It is the *isocyanic acid* which we have just described. The following formulæ will explain this curious isomerism.

$H{-}O{-}C{\equiv}N$ Cyanic acid.	$H{-}N{=}C{=}O$ Isocyanic acid.
$K{-}O{-}C{\equiv}N$ Potassium cyanate (Bannow).	$K{-}N{=}C{=}O$ Potassium isocyanate (ordinary cyanate).
$C^2H^5{-}O{-}C{\equiv}N$ Ethyl cyanate (Cloëz).	$C^2H^5{-}N{=}C{=}O$ Ethyl isocyanate. (Cyanic ether of Wurtz.)

Ammonium Isocyanate.—This is formed when vapor of isocyanic acid is passed into a flask containing ammonia gas. It is a solid, white mass, very soluble in water. When its aqueous solution is treated with hydrochloric acid, it disengages carbon dioxide like the solution of potassium isocyanate. If its aqueous solution be boiled, or even left to itself for several days, ammonium isocyanate becomes transformed into urea.

$$(\overset{v}{N}H^4)CON = CO{<}\begin{matrix}NH^2\\NH^2\end{matrix}$$

Ammonium isocyanate. Urea.

CYANURIC ACID.

$$C^3N^3H^3O^3 = C^3N^3(OH)^3$$

Cyanuric acid is formed by the action of water upon the solid cyanogen chloride, by the action of heat on urea, or by that of dilute acetic acid on a solution of potassium isocyanate; in the last case, potassium acid cyanurate, $C^3N^3H^2KO^3$, is precipated after a time, and liberates cyanuric acid when treated with hydrochloric acid.

Preparation.—Small quantities of urea are heated in an oil-bath until ammonia is no longer disengaged. The gray mass remaining is pulverized and dissolved in dilute potassium hydrate: when the filtered solution is treated with hydrochloric acid, cyanuric acid is obtained as a white precipitate.

Another process consists in decomposing urea by a stream of dry chlorine at a temperature of 130° or 140°. Nitrogen and hydrochloric acid are disengaged, and there remains a mixture of cyanuric acid and ammonium chloride which may be separated by cold water. The residue consisting of cyanuric acid is exhausted with boiling water, which, on cooling, deposits the acid in crystals.

$$\underset{\text{Urea.}}{3\mathrm{CON^2H^4}} + \mathrm{Cl^3} = \underset{\text{Cyanuric acid.}}{\mathrm{C^3N^3H^3O^3}} + 2\mathrm{NH^4Cl} + \mathrm{HCl} + \mathrm{N}$$

Properties.—Cyanuric acid occurs in small white crystals, soluble in forty parts of cold water, very soluble in boiling water and in alcohol. It separates from its boiling aqueous solution in orthorhombic prisms containing two molecules of water of crystallization. When strongly heated it yields isocyanic acid. Phosphorus pentachloride converts it into solid cyanogen chloride.

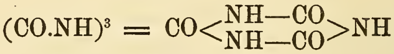
$$\mathrm{C^3N^3(OH)^3} + 3\mathrm{PCl^5} = 3\mathrm{POCl^3} + \mathrm{C^3N^3Cl^3} + 3\mathrm{HCl}$$

By this reaction, and by its formation from cyanogen chloride, cyanuric acid is related to the cyanogen compounds, and the relation is expressed by the formula $\mathrm{C^3N^3(OH)^3}$.

When it is boiled with strong acids, cyanuric acid is decomposed into carbon dioxide and ammonia.

$$\mathrm{C^3N^3H^3O^3} + 3\mathrm{H^2O} = 3\mathrm{CO^2} + 3\mathrm{NH^3}$$

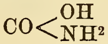
This reaction recalls the analogous decomposition of isocyanic acid (page 474), and relates cyanuric acid to carbimide. From this point of view, cyanuric acid would be tricarbimide,—that is, three molecules of carbon monoxide (carbonyl) united by the intervention of three imidogen groups (NH).



$$(\mathrm{CO.NH})^3 = \mathrm{CO}{<}\begin{matrix}\mathrm{NH{-}CO}\\ \mathrm{NH{-}CO}\end{matrix}{>}\mathrm{NH}$$

It is, then, possible that there may be two isomeric modifications of cyanuric acid. There are certainly two isomerides of its ethers: the trimethylic ether of the true cyanuric acid, $\mathrm{C^3N^3(OCH^3)^3}$, is formed by the action of cyanogen chloride on sodium methylate; and, on the other hand, there are ethers of tricarbimide or isocyanuric acid, which will be described farther on.

CARBAMIC ACID.

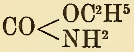


$$\mathrm{CO}<\begin{matrix}\mathrm{OH}\\ \mathrm{NH^2}\end{matrix}$$

This acid is not known in the free state. Its ammonium salt is commonly known as anhydrous ammonium carbonate; its ether, urethane, or ethyl carbamate, is described on page 515.

$$\mathrm{CO}<\begin{matrix}\mathrm{ONH^4}\\ \mathrm{NH^2}\end{matrix}$$

Ammonium carbamate.



$$\mathrm{CO}<\begin{matrix}\mathrm{OC^2H^5}\\ \mathrm{NH^2}\end{matrix}$$

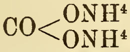
Urethane.

When two volumes of ammonia gas and one volume of carbon dioxide are mixed over the mercury trough, a white mass is obtained; this exists in the ammonium carbonate of commerce, and constitutes ammonium carbamate. At 60°, it is dissociated and resolved into its constituent gases, one molecule of ammonium carbamate yielding four volumes of ammonia and two volumes of carbon dioxide. Water converts it into ammonium carbonate.

$$\mathrm{CO}<\begin{matrix}\mathrm{ONH^4}\\ \mathrm{NH^2}\end{matrix} + \mathrm{H^2O} = \mathrm{CO}<\begin{matrix}\mathrm{ONH^4}\\ \mathrm{ONH^4}\end{matrix}$$

Ammonium carbamate. Ammonium carbonate.

Ammonium carbamate is intermediate between urea and ammonium carbonate.



$$\mathrm{CO}<\begin{matrix}\mathrm{ONH^4}\\ \mathrm{ONH^4}\end{matrix}$$

Ammonium carbonate.

$$\mathrm{CO}<\begin{matrix}\mathrm{ONH^4}\\ \mathrm{NH^2}\end{matrix}$$

Ammonium carbamate.

$$\mathrm{CO}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix}$$

Urea.

UREA OR CARBAMIDE.

$$\mathrm{CO(NH^2)^2}$$

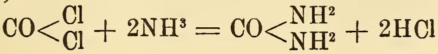
This body, discovered by Rouelle in 1773, is the most abundant of the solid constituents of urine. Wöhler was the first to obtain urea artificially by heating an aqueous solution of ammonium isocyanate.

$$\mathrm{CONNH^4} = \mathrm{CO(NH^2)^2}$$

This discovery was the first instance of the synthesis of an organic body.

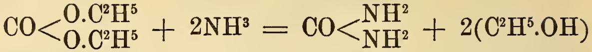
Urea is also formed by many other reactions.

1. By the action of carbonyl chloride upon ammonia (Natanson).



$$\mathrm{CO}<\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix} + \mathrm{2NH^3} = \mathrm{CO}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix} + \mathrm{2HCl}$$

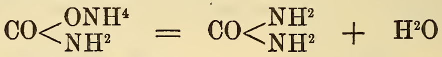
2. By the action of ammonia on ethyl carbonate.



$$\mathrm{CO}<\begin{matrix}\mathrm{O.C^2H^5}\\ \mathrm{O.C^2H^5}\end{matrix} + 2\mathrm{NH^3} = \mathrm{CO}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix} + 2(\mathrm{C^2H^5.OH})$$

Ethyl carbonate. Urea. Alcohol.

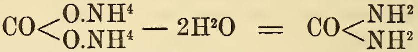
3. When ammonium carbamate is heated to 130° or 140° under pressure in sealed tubes.



$$\mathrm{CO}<\begin{matrix}\mathrm{ONH^4}\\ \mathrm{NH^2}\end{matrix} = \mathrm{CO}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix} + \mathrm{H^2O}$$

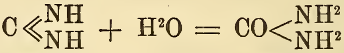
Ammonium carbamate.

These reactions show clearly that urea is the amide corresponding to carbonic acid,—that is, carbamide. Indeed, it represents neutral ammonium carbonate, less two molecules of water.



$$\mathrm{CO}<\begin{matrix}\mathrm{O.NH^4}\\ \mathrm{O.NH^4}\end{matrix} - 2\mathrm{H^2O} = \mathrm{CO}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix}$$

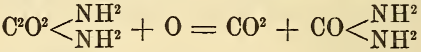
4. Urea is formed by the action of small quantities of acids on cyanamide.



$$\mathrm{C}\ll\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix} + \mathrm{H^2O} = \mathrm{CO}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix}$$

Cyanamide. Urea.

5. When oxamide is heated with mercuric oxide (Williamson).



$$\mathrm{C^2O^2}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix} + \mathrm{O} = \mathrm{CO^2} + \mathrm{CO}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix}$$

Oxamide.

Preparation.—1. Urea may be obtained from urine by the following process. The urine is evaporated to a syrupy consistence on a water-bath. It is allowed to cool, and an excess of cold nitric acid is added; a mass of crystals are formed, which ordinarily have a brown color. They are drained, washed with a little ice-water, redissolved in hot water, and animal charcoal which has been washed with hydrochloric acid is added. The whole is heated on a water-bath for a few minutes and then filtered. Colorless crystals of urea nitrate are obtained on cooling.

They are dissolved in water, and barium carbonate is added until all effervescence ceases. Carbon dioxide is disengaged, and barium nitrate is formed, while the urea is set free. The filtered liquor is evaporated to dryness on the water-bath, and the residue exhausted with absolute alcohol, which dissolves the urea, while the barium nitrate remains. The alcoholic solution is concentrated, and urea crystallizes out.

2. Potassium isocyanate is prepared by heating 28 parts of well-dried potassium ferrocyanide with 14 parts of manganese dioxide, as has been already indicated. The cooled mass is coarsely powdered, and exhausted with cold water, which dissolves the potassium isocyanate. 20 parts of ammonium sulphate are added to the filtered liquid, which is then evaporated to dryness on a water-bath. The residue is exhausted with boiling alcohol, which dissolves the urea and leaves potassium sulphate.

In this operation the potassium isocyanate and ammonium sulphate undergo double decomposition, with formation of potassium sulphate, and ammonium isocyanate which is transformed into urea.

Properties.—Urea separates from its aqueous solution in long, flattened, and striated prisms. It sometimes deposits from its alcoholic solution in square prisms.

The crystals are colorless and possess a cooling taste. They dissolve in their own weight of water at 15°, and in 5 parts of cold alcohol of specific gravity 0.816. They are but slightly soluble in ether.

If a solution of urea be added to a concentrated solution of chloride of lime, there is an abundant disengagement of gas, which is a mixture of nitrogen and carbon dioxide. The urea is entirely destroyed.

$$CH^4N^2O + H^2O + 3Cl^2 = CO^2 + N^2 + 6HCl$$

This reaction serves for the estimation of urea in urine. The volume of nitrogen disengaged when a given volume of the urine is treated with sodium hypobromite, is measured, and the corresponding quantity of urea is calculated.

An aqueous solution of chlorine produces the same decomposition.

Nitrous anhydride instantly destroys urea, with formation of water, carbon dioxide, and nitrogen.

$$CH^4N^2O + N^2O^3 = CO^2 + 2H^2O + 2N^2$$

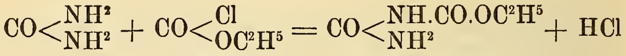
When an aqueous solution of urea is heated to 140° in a sealed tube, it absorbs the elements of water, and is converted into ammonia and carbon dioxide.

$$CH^4N^2O + H^2O = CO^2 + 2NH^3$$

This conversion of urea into carbonate of ammonia takes place spontaneously in stale urine, under the influence of a peculiar ferment (Van Tieghem, Musculus).

Urea fuses at 132°. When it is rapidly heated to a higher temperature, it disengages ammonia and leaves a white residue, which consists principally of cyanuric acid (page 475). There are also formed ammelide and biuret (page 481).

When urea is heated with ethyl chlorocarbonate (page 516), ethyl allophanate is formed.



$$CO<\begin{matrix}NH^2\\NH^2\end{matrix} + CO<\begin{matrix}Cl\\OC^2H^5\end{matrix} = CO<\begin{matrix}NH.CO.OC^2H^5\\NH^2\end{matrix} + HCl$$

Ethyl chlorocarbonate. Ethyl allophanate.

Liebig, who discovered this compound, obtained it by passing vapor of isocyanic acid into absolute alcohol. Ethyl allophanate crystallizes in brilliant prisms, soluble in alcohol and in boiling water, and fusible at 190°–191°. It is a substituted urea, one atom of hydrogen in the latter being replaced by the group $CO.OC^2H^5$.

Compounds of Urea with Acids.—If nitric acid be added to a concentrated solution of urea, the liquid becomes a white, crystalline, laminated mass, composed of crystals of urea nitrate, $CH^4N^2O.HNO^3$, which are only slightly soluble in nitric acid. These crystals are soluble in water and alcohol. They strongly redden litmus solution. They decompose at 140°, disengaging a large quantity of gas.

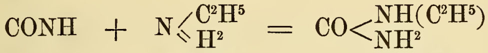
The hydrochloride of urea, $CH^4N^2O.HCl$, and the oxalate, $(CH^4N^2O)^2C^2H^2O^4$, are known. The latter salt precipitates in small, colorless, granular crystals when a concentrated solution of oxalic acid is added to a concentrated solution of urea.

Compounds of Urea with Oxides and with Salts.—There are several compounds of urea with mercuric oxide. They are formed either by the direct action of mercuric oxide upon urea, which dissolves that oxide, or by the reaction of mercuric chloride or nitrate upon urea, which is precipitated by both of these salts. A solution of urea converts recently-precipitated silver oxide into a gray powder, which is a compound of urea and oxide of silver. Among the compounds of urea with the various salts, that which it forms with sodium chloride is the most important. It crystallizes in colorless, oblique rhombic prisms, containing $CH^4N^2O.NaCl + H^2O$.

Among the bodies closely related to urea there is an interesting isomeride, *isuret*, which is formed by the action of hydrocyanic acid on hydroxylamine; also hydroxyl urea, $CO<^{NH.OH}_{NH^2}$, which is formed by the action of isocyanic acid on hydroxylamine.

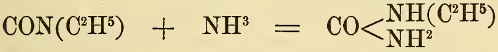
COMPOUND UREAS.

The compounds which are derived from urea by the substitution of the various alkyl groups for hydrogen are called *compound ureas.* They are obtained either by the action of cyanic acid upon the compound ammonias, or by treating the cyanic ethers with ammonia or with the compound ammonias (Ad. Wurtz).



$$CONH + N\begin{cases}C^2H^5\\H^2\end{cases} = CO<^{NH(C^2H^5)}_{NH^2}$$

Cyanic acid. Ethylamine. Ethylurea.



$$CON(C^2H^5) + NH^3 = CO<^{NH(C^2H^5)}_{NH^2}$$

Ethyl cyanate. Ethylurea.

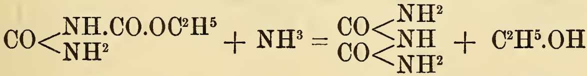
The following is the nomenclature and composition of some of the principal compound ureas:

CH^4N^2O urea.
$CH^3(CH^3)N^2O$ methylurea.
$CH^3(C^2H^5)N^2O$ ethylurea.
$CH^2(C^2H^5)^2N^2O$ diethylurea.
$CH(C^2H^5)^3N^2O$ triethylurea.
$CH^3(C^5H^{11})N^2O$ amylurea.
$CH^3(C^6H^5)N^2O$ phenylurea.
$CH^2(C^6H^5)^2N^2O$ diphenylurea.

BIURET.

$C^2H^5N^3O^2$

Biuret is the amide of allophanic acid, the ethyl compound of which is described on the preceding page, and is formed when allophanic ether is heated to 100° with aqueous ammonia.



$$CO<^{NH.CO.OC^2H^5}_{NH^2} + NH^3 = \begin{matrix}CO<^{NH^2}_{NH}\\CO<_{NH^2}\end{matrix} + C^2H^5.OH$$

Ethyl allophanate. Biuret. Alcohol.

It is also formed by the action of heat on urea.

$$2CON^2H^4 = C^2O^2N^3H^5 + NH^3$$

Biuret crystallizes in delicate needles, or in little masses, containing one molecule of water of crystallization. In the presence of potassium hydroxide its aqueous solution dissolves cupric oxide with the production of a violet-red color.

Closely related to the compounds of carbon monoxide are the following bodies, in which the radical sulphocarbonyl, CS, replaces the analogous radical carbonyl CO.

POTASSIUM THIOCYANATE (SULPHOCYANATE).

KCSN

This salt, which was formerly called potassium sulphocyanide, corresponds to the isocyanate, in which the oxygen is replaced by sulphur.

It is prepared by heating a mixture of two parts of potassium ferrocyanide and one part of sublimed sulphur to redness in a covered crucible. After cooling, the mass is dissolved in water, the solution filtered, and potassium carbonate added to the liquor as long as a precipitate of ferrous carbonate is formed. The solution is again filtered, evaporated to dryness, the residue exhausted with alcohol, and the alcoholic solution allowed to evaporate spontaneously.

Potassium thiocyanate crystallizes in long striated prisms resembling potassium nitrate, or in needles terminated by four-faced points. It is deliquescent and very soluble in water and alcohol.

Solution of potassium thiocyanate produces an intense blood-red color with the ferric salts, due to the formation of ferric thiocyanate.

Ammonium Thiocyanate, NH^4CSN.—This body corresponds to ammonium isocyanate. It occurs in the water from the purification of coal-gas. When heated to 170°, it is converted into *sulpho-urea* (Reynolds).

The sulphocyanates present an isomerism exactly like that which has been mentioned for the cyanates: there is a series of compounds derived from a thiocyanic acid, $N\equiv C{-}SH$, and another series derived from an isothiocyanic acid, $(CS)''NH$. To the latter series belong the ordinary thiocyanates, examples of which have just been described.

SULPHO-UREA, OR SULPHOCARBAMIDE.

$$\mathrm{CS}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix}$$

Sulpho-urea, which was discovered by Reynolds, is formed by a molecular metamorphosis of ammonium sulphocyanate, as urea is formed by the metamorphosis of ammonium isocyanate.

$$\mathrm{CS{-}N'''{-}N^{v}H^4} \text{ becomes } \mathrm{CS}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix}$$

It is also formed by the direct combination of hydrogen sulphide and cyanamide (page 472).

It crystallizes sometimes in fine, silky needles, sometimes in large orthorhombic prisms. It is very soluble in water and alcohol, slightly soluble in ether. It has a bitter taste and a neutral reaction. It melts at 149°, and if heated with water to 140° is reconverted into ammonium sulphocyanate. With acids it forms crystallizable salts. When treated with mercuric oxide, it yields cyanamide.

MONOHYDRIC ALCOHOLS AND THEIR DERIVATIVES.

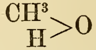
These compounds form part of the great class of alcohols. They are neutral hydroxides, derived from hydrocarbons by the substitution of the radical hydroxyl OH for an atom of hydrogen. Among these bodies, the more important are those which belong to the same series, as ordinary alcohol, or ethyl hydroxide, which has been indicated on page 450. Wood-spirit, or methyl hydroxide, is the simplest term of the series. While studying its combinations, in 1835, Dumas and Peligot were the first to call attention to the function "alcohol."

METHYL COMPOUNDS.

In these compounds we assume the existence of a radical, CH^3, to which the name methyl is given. Wood-spirit is its hydroxide; marsh gas, or methane, its hydride. To this hydride correspond a chloride, a bromide, and an iodide. Chloroform is dichloro-methyl chloride, or trichloromethane. Around methyl hydroxide are grouped the salts of methyl, or methylic ethers, resulting from the action of the acids upon that body, and which bear the same relations to methyl hydroxide as the potassium salts do to potassium hydroxide. They are the compound methyl ethers. The following formulæ indicate the relations which exist between these bodies:

CH^3H

Methane, or methyl hydride.

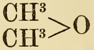


$$\left.\begin{matrix}CH^3\\H\end{matrix}\right>O$$

Methyl hydroxide.

CH^3Cl

Methyl chloride.

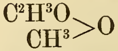


$$\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right>O$$

Methyl oxide.

$CHCl^3$

Chloroform.



$$\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right>O$$

Methyl acetate.

These compounds will be but briefly described.

METHANE.

(MARSH GAS.)

CH^4

The inflammable gas which is disengaged from the mud of marshes is impure methane. The same gas is frequently evolved in the galleries of coal mines, and constitutes the *fire-damp* of miners. It is produced artificially by the action of an excess of alkali upon acetic acid (Persoz, Dumas).

Preparation.—Methane is most conveniently prepared in the pure state by strongly heating in a glass flask or retort a mixture of 1 part of sodium acetate, 1 part of potassium hydroxide, and 1½ parts of lime; the lime is added to prevent the action of the potassium hydroxide upon the glass. The gas may be collected over water.

$$\underset{\text{Sodium acetate.}}{NaC^2H^3O^2} + NaOH = \underset{\text{Methane.}}{CH^4} + Na^2CO^3$$

Properties.—Methane is a colorless, odorless gas. Its density is 0.559; it is but slightly soluble in water, somewhat more so in alcohol. It burns in the air with a pale, almost non-luminous flame. A mixture of methane and oxygen explodes violently on the application of flame or the passage of an electric spark.

If two volumes of methane and four volumes of oxygen be introduced into an eudiometer and the spark be passed, a bright flash is visible. After the combustion, the mercury rises in the tube, and it is found that the volume of gas is reduced to one-third of the original volume (to 2 volumes); if a solution of caustic potash be introduced, the whole of the remaining gas will be absorbed. 2 volumes of methane produce in burning 2 volumes of carbon dioxide, and require 4 volumes of oxygen. This experiment establishes the molecular composition of methane.

2 volumes of carbon dioxide contain 2 volumes of oxygen combined with 1 volume (1 atom) of carbon; consequently one molecule of marsh gas contains one atom of carbon.

The other 2 volumes of oxygen consumed have combined with 4 volumes of hydrogen, contained in 2 volumes of methane; that is, the molecule of methane contains 4 atoms (=2 molecules) of hydrogen.

Hence it follows that a molecule of methane contains 1 atom of carbon and 4 atoms of hydrogen.

A mixture of chlorine and methane explodes when exposed to direct sunlight. In diffused daylight, the action is less violent, especially if an inert gas, such as carbon dioxide, be added. In this case, methyl chloride is formed, and in presence of an excess of chlorine, methylene chloride, chloroform, and finally carbon tetrachloride.

$CH^4 + Cl^2 = HCl + CH^3Cl$ methyl chloride.
$CH^4 + 2Cl^2 = 2HCl + CH^2Cl^2$ methylene chloride.
$CH^4 + 3Cl^2 = 3HCl + CHCl^3$ chloroform.
$CH^4 + 4Cl^2 = 4HCl + CCl^4$ carbon tetrachloride.

It is seen that in these reactions the chlorine is substituted for hydrogen, atom for atom.

Inversely, when these substitution products are submitted to the action of nascent hydrogen, an inverse substitution is effected: they are reconverted into methane. This may be accomplished by putting the chlorine compounds in contact with sodium amalgam and water. The latter is decomposed by the sodium, and constitutes a source of hydrogen (Melsens).

$$CHCl^3 + 3H^2 = 3HCl + CH^4$$

METHYL HYDROXIDE, OR METHYL ALCOHOL.

(WOOD-SPIRIT.)

$$CH^4O = CH^3\text{–}OH$$

The products of the dry distillation of wood contain about one per cent. of a spirituous liquid, which was discovered in

1812 by Taylor, and named wood-spirit. It is separated by several distillations and rectifications over lime; for, being more volatile than the other products, it passes over first.

The methyl alcohol of commerce is always impure, and cannot be purified by fractional distillation, as it contains a considerable proportion of acetone, of which the boiling-point (56°) is very near that of methyl alcohol. The impurities may be removed by treating the impure alcohol with calcium chloride, with which it forms a crystalline compound, $CaCl^2 + 4CH^3.OH$. The crystals are drained, dried between folds of blotting-paper, and distilled with water, when they yield dilute methyl alcohol. This is rectified by repeated distillation, and finally dehydrated over quick-lime.

To obtain the alcohol perfectly pure, an ether of methyl is prepared and freed from all impurities by either crystallization or distillation. The ether is then decomposed with an alkaline hydroxide, and the methyl alcohol formed is distilled off and dehydrated over lime. Thus, methyl oxalate is prepared by treating the still impure methyl alcohol with oxalic acid, and is purified by crystallization.

$$\underset{\text{Methyl hydroxide.}}{2CH^3.OH} + \underset{\text{Oxalic acid.}}{C^2O^4H^2} = \underset{\text{Methyl oxalate.}}{(CH^3)^2.C^2O^4} + 2H^2O$$

The methyl oxalate is boiled with potassium hydroxide, and the methyl alcohol which distils is rectified over quick-lime.

$$(CH^3)^2.C^2O^4 + 2KOH = 2CH^3.OH + C^2O^4K^2$$

It is a mobile, colorless liquid, having an alcoholic odor. It boils at 66.5°. Its density at 0° is 0.8142.

It is inflammable and burns with an almost colorless flame. It is miscible with water, alcohol, and ether in all proportions. It dissolves caustic baryta, forming a definite combination.

Potassium and sodium react energetically upon methyl hydroxide; the metal dissolves with disengagement of hydrogen and formation of an alkaline methylate or methoxide.

$$\underset{\text{Methyl hydroxide.}}{CH^3\text{–}OH} \qquad \underset{\text{Potassium methylate.}}{CH^3\text{–}OK}$$

If methyl alcohol be placed under a bell-jar containing also some watch-glasses filled with platinum black, so that the vapor of the wood-spirit mixed with air may come in contact with the finely-divided metal, it is found that the liquid soon becomes strongly acid. By the slow oxidation of the wood-spirit under these conditions, formic acid and formaldehyde are produced.

$$\underset{\text{Methyl hydroxide.}}{CH^3\text{–}OH} + O^2 = \underset{\text{Formic acid.}}{CHO\text{–}OH} + H^2O$$

$$2CH^3\text{–}OH + O^2 = \underset{\text{Formaldehyde.}}{2H\text{–}CHO} + 2H^2O$$

METHYL OXIDE, OR METHYL ETHER.

$(CH^3)^2O$

When methyl alcohol is heated with twice its weight of concentrated sulphuric acid, a colorless gas is disengaged, which is methyl oxide.

$$\underset{\text{Methyl hydroxide.}}{2CH^3.OH} = \underset{\text{Methyl oxide.}}{(CH^3)^2O} + H^2O$$

This gas is formed by the dehydration of methyl alcohol and the linking together of two methyl groups by an atom of oxygen. Methyl ether is readily absorbed by water, and is even more soluble in alcohol and ether. It liquefies at —23°.

CHLORIDE, BROMIDE, AND IODIDE OF METHYL.

These compounds may be regarded as marsh gas in which one atom of hydrogen is replaced by an atom of chlorine, bromine, or iodine.

They are formed by the action of hydrochloric, hydrobromic, and hydriodic acids upon methyl alcohol.

$$CH^3.OH + HCl = CH^3Cl + H^2O$$

Hence they are considered as derived from the hydracids by the substitution of the group methyl for the atom of hydrogen.

$$\underset{\text{Hydrochloric acid.}}{HCl} \qquad \underset{\text{Methyl chloride.}}{(CH^3)Cl}$$

Methyl chloride is a colorless gas, having an agreeable odor. When exposed to intense cold, it condenses to a liquid which boils at —22°. When heated for a considerable time with a concentrated solution of potassium hydroxide, it is converted into methyl alcohol. Liquid methyl chloride is employed industrially in the production of cold, and large quantities are consumed in the manufacture of dye-stuffs.

Methyl iodide, CH^3I, boils at 43°; its density at 0° is 2.1992.

It is made by gradually adding iodine to a mixture of methyl alcohol and amorphous phosphorus, and distilling. The distilled liquid is mixed with water, which precipitates the iodide; the dense liquid is separated, dried with calcium chloride, and distilled.

METHYLENE CHLORIDE.

CH^2Cl^2

This compound may be prepared by the action of chlorine on methane, or on methyl chloride, or by the reduction of chloroform by nascent hydrogen. The latter method is the more convenient. An alcoholic solution of chloroform is treated with zinc in a flask connected with a condenser, and hydrochloric acid is introduced in small portions. Methylene chloride and unaltered chloroform distil over, and towards the close of the operation the distillation is continued by the aid of heat. The distillate is then washed, dried, and submitted to fractional distillation.

Methylene chloride is a mobile liquid, having an odor resembling that of chloroform, and boiling at 40°. Its density at 0° is 1.36.

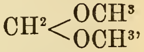
METHYLENE IODIDE,

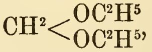
CH^2I^2,

is made by the action of hydriodic acid on chloroform or iodoform in sealed tubes at a temperature of 150°.

$$CHCl^3 + 4HI = CH^2I^2 + 3HCl + I^2$$

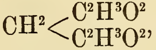
It is also formed by the action of sodium ethylate on iodoform. It is a yellow, highly refracting liquid, having a density of 3.342 at 5°, and solidifying at 2°. It boils at 182°, with partial decomposition.

Methylal, or the dimethylic ether of methylene,  $CH^2<\begin{matrix}OCH^3\\OCH^3\end{matrix}$, is obtained by the action of sulphuric acid and manganese dioxide on methyl alcohol. It is a limpid liquid, boiling at 42°. Its reactions are identical with those of formaldehyde (p. 545).

Methylene diethylate,  $CH^2<\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}$, the ether intermediary between methyl-ethyl oxide (p. 502) and Kay's ether (p. 489), may be obtained by the action of sodium ethylate on methylene chloride (Greene).

$$CH^2Cl^2 + 2C^2H^5ONa = 2NaCl + CH^2(OC^2H^5)^2$$

It is an ethereal liquid, having a pleasant, penetrating odor. Its density at 0° is 0.851, and it boils at 89°.



Methylene diacetate, $CH^2{<}\substack{C^2H^3O^2\\C^2H^3O^2}$, is formed by the action at 100° of silver acetate on methylene iodide in presence of acetic acid (Boutlerow). It is an aromatic liquid, which when heated with lead oxide is decomposed into lead acetate and oxymethylene (p. 545).

$$\underset{\text{Methylene diacetate.}}{3CH^2(C^2H^3O^2)^2} + 3PbO = \underset{\text{Lead acetate.}}{3Pb(C^2H^3O^2)^2} + \underset{\text{Trioxymethylene.}}{C^3H^6O^3}$$

CHLOROFORM.

$CHCl^3$

This important substance was discovered in 1831 by Soubeiran and Liebig. It is made by distilling either dilute alcohol or acetone with bleaching powder (chloride of lime). The distilled liquid separates in two layers, of which the lower is impure chloroform. It is separated, washed first with water and then with a solution of potassium carbonate, and rectified over calcium chloride.

Chloroform is a colorless, very mobile liquid, having an agreeable, ethereal odor. Its density at 0° is 1.525, and it boils at 60.8°. It does not take fire on contact with flame.

It is but slightly soluble in water, but dissolves readily in alcohol and ether. It dissolves sulphur, phosphorus, fats, resins, a great number of the alkaloids, and in general, organic matters rich in carbon.

By the prolonged action of chlorine, it is converted into *carbon tetrachloride*, CCl^4, a colorless liquid boiling at 77°.

A boiling alcoholic solution of potassium hydroxide converts it into formate and chloride.

$$\underset{\text{Chloroform.}}{CHCl^3} + 4KOH = 2H^2O + 3KCl + \underset{\text{Potassium formate.}}{KCHO^2}$$

When chloroform is boiled with an alcoholic solution of ethylate of sodium, sodium chloride is formed, together with an ethereal compound, $CH(OC^2H^5)^3$, in which 3 oxethyl groups, OC^2H^5, replace the 3 chlorine atoms of chloroform (Kay).

$$\underset{\text{Chloroform.}}{CHCl^3} + \underset{\text{Sodium ethylate.}}{3NaO.C^2H^5} = 3NaCl + \underset{\text{Kay's ether.}}{CH(OC^2H^5)^3}$$

Chloroform, heated to 180° with aqueous or alcoholic ammonia, yields ammonium cyanide and sal-ammoniac. This reaction takes place at 100°, in presence of potassium hydroxide.

$$CHCl^3 + 5NH^3 = NH^4CN + 3NH^4Cl$$

Chloroform acts in a remarkable manner upon the phenols in presence of an alkali such as soda or potassa, forming aromatic aldehydes. This reaction, discovered by Reimer, will be described farther on (see Phenol).

When heated with an alcoholic solution of ethylamine in presence of potassium hydroxide, chloroform yields ethylcarbylamine (page 509). A similar reaction occurs with other bases analogous to ethylamine, such as aniline. This reaction characterizes the primary amines (Hofmann).

Chloroform is much employed in surgery as an anæsthetic. The inhalation of its vapor produces insensibility and loss of muscular action, and apparently without any danger, provided the preparation is free from impurities.

BROMOFORM.

$CHBr^3$

Bromoform may be made by the action of bromine on a solution of an alkaline hydroxide in alcohol or acetone. Potassium or sodium hydroxide is dissolved in its own weight of crude methyl alcohol, and to the solution, which is cooled in ice-water, bromine is added in small portions until the liquid begins to assume a permanent color. The product of the reaction is agitated with water, and the oily liquid which separates is washed, dried, and rectified.

Bromoform is an oily liquid, having an agreeable odor, resembling that of chloroform. Its density is 2.77, and it boils at about 150°. Insoluble in water, it dissolves readily in alcohol and ether. Its reactions are similar to those of chloroform.

IODOFORM.

CHI^3

Iodoform is formed by the simultaneous action of iodine and an alkaline hydroxide on alcohol and many other organic substances. It is prepared by dissolving two parts of crystallized sodium carbonate in ten parts of water and one part of alcohol; the solution is heated to 80°, and one part of iodine is added in small portions. Iodoform separates in yellow scales. If alcohol and potassium hydroxide be added to the mother liquid and chlorine be passed through, an additional quantity of iodoform may be obtained.

Iodoform crystallizes in brilliant yellow, hexagonal scales, which sometimes assume large dimensions.

It has a peculiar odor, recalling that of saffron. It melts at 119°, and cannot be distilled, but at 100° its tension of vapor is sufficient to allow it to volatilize with the vapor of water. Insoluble in water, it dissolves in alcohol and ether. By the aid of heat, hydriodic acid converts it into methylene iodide with separation of iodine.

$$CHI^3 + HI = CH^2I^2 + I^2$$

This reduction by hydriodic acid is only one example of the action of that acid on carbon compounds generally. The extent of the reduction depends upon the temperature at which the reaction takes place. Iodine is always set free in these cases.

Owing to its antiseptic properties, iodoform is extensively used in surgery.

NITROFORM.

$CH(NO^2)^3$

This compound is trinitromethane,—that is, methane, CH^4, in which three atoms of hydrogen are replaced by three nitryl groups, NO^2. It is formed in small quantity by the action of nitric acid on various organic compounds. It is also formed when trinitroacetonitrile (p. 493) is boiled with water.

$$\underset{\text{Trinitroacetonitrile.}}{C(NO^2)^3\text{–}CN} + 2H^2O = \underset{\text{Ammonia compound of nitroform.}}{CH(NO^2)^3.NH^3} + CO^2$$

From the ammonia compound formed in this reaction, sulphuric acid separates nitroform as a thick, colorless oil, which below 15° solidifies in cubical crystals.

Nitroform is soluble in water; when rapidly heated it explodes. It plays the part of an energetic acid; the single atom of hydrogen which it contains is strongly basic, by reason of its proximity to the three nitryl groups. There is a potassium salt $C(NO^2)^3K$.

CHLOROPICRIN.

$CCl^3(NO^2)$

Chloropicrin, which has long been known, represents chloroform in which the hydrogen atom is replaced by the group NO^2.

It is formed by the action of nitric acid on many chlorine organic compounds, such as chloral. On the other hand, it may be obtained by the reaction of chlorine or chlorinated lime on nitrogenized organic compounds, such as picric acid, mercuric fulminate, etc. It is prepared by distilling a milk of chlorinated lime with a saturated solution of picric acid. Chloropicrin then distils with the vapor of water.

It is a colorless liquid, having a very irritating odor and exciting tears. Its density is 1.665. It boils at 112°, but explodes when heated suddenly. Nascent hydrogen, produced by the action of acetic acid and iron, converts it into methylamine.

$$\underset{\text{Chloropicrin.}}{CCl^3(NO^2)} + 6H^2 = \underset{\text{Methylamine.}}{CH^3.NH^2} + 3HCl + 2H^2O$$

There is a *bromopicrin*, $CBr^3(NO^2)$, prepared by a reaction analogous to that which yields chloropicrin, which it resembles in its general properties.

CARBON TETRACHLORIDE.

CCl^4

Carbon tetrachloride, or tetrachloromethane, is obtained by the prolonged action of chlorine on chloroform in direct sunlight, or by passing through a red-hot porcelain tube a mixture of chlorine and vapor of carbon disulphide. In the latter reaction sulphur chloride is also formed, and must be removed by agitating the product with a solution of potassium hydroxide.

Carbon tetrachloride is a colorless liquid, having an agreeable odor like that of chloroform. Its density at 0° is 1.629. It boils at 77°. When its vapor is passed through a red-hot tube it is decomposed, yielding the chlorides C^2Cl^4 and C^2Cl^6.

When heated with aluminium iodide, AlI^3, carbon tetrachloride is converted into carbon tetraiodide, CI^4, which separates from its ethereal solution in dark-red regular octahedra (Gustavson).

METHYL CYANIDE, OR ACETONITRILE.

$C^2H^3N = CH^3.CN$

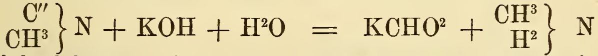
This body may be obtained by distilling a mixture of potassium methylsulphate and potassium cyanide, or by distilling acetamide with phosphoric anhydride, which removes one molecule of water from the former body.

$$\underset{\text{Acetamide.}}{C^2H^3O.NH^2} - H^2O = \underset{\text{Methyl cyanide, or acetonitrile.}}{C^2H^3N}$$

Methyl cyanide is a colorless liquid, having a disagreeable odor; it boils at 81.3°. A boiling solution of potassium hydroxide decomposes it into ammonia and potassium acetate.

$$\underset{\text{Methyl cyanide.}}{CH^3\text{–}CN} + 2H^2O = \underset{\text{Acetic acid.}}{CH^3\text{–}CO.OH} + NH^3$$

Gautier has discovered an isomeride of methyl cyanide, *methyl carbylamine*. This body is formed, together with methyl cyanide, when a mixture of potassium methylsulphate and potassium cyanide is distilled. Under the influence of alkalies, it decomposes into formic acid and methylamine.



$$\left.\begin{matrix}C''\\CH^3\end{matrix}\right\}N + KOH + H^2O = KCHO^2 + \left.\begin{matrix}CH^3\\H^2\end{matrix}\right\}N$$

Methyl carbylamine. Potassium formate. Methylamine.

The trinitro-derivative of methyl cyanide, $C(NO^2)^3CN$, is called *trinitro-acetonitrile*. It is a white, camphor-like mass, melting at 41.5°, and exploding at 200°.

METHYL NITRATE.

$CH^3.NO^3$

This substance, which represents nitric acid in which the basic hydrogen is replaced by methyl, is an example of a compound methyl ether.

It is prepared by introducing into a retort 50 grammes of powdered potassium nitrate, and adding a mixture of 100 grammes of sulphuric acid and 50 grammes of wood-spirit. The reaction begins in the cold, but must be finished by distilling on a water-bath. The liquid condensed in the receiver is washed with water, and rectified several times over a mixture of massicot and calcium chloride.

It is a colorless, neutral liquid; density, 1.182; boiling-point, 66°. Its vapor explodes violently when heated above 150°.

Methyl nitrate dissolves in ammonia, producing ammonium nitrate and methylamine.

$$CH^3.NO^3 + 2NH^3 = NH^4.NO^3 + CH^3(NH^2)$$

METHYL NITRITE AND NITROMETHANE.

These two compounds present a remarkable instance of isomerism in very simple combinations.

The first, $CH^3O.NO$, which represents nitrous acid, HNO^2, in which the hydrogen is replaced by methyl, is obtained when methyl alcohol is heated with nitric acid in presence of copper. It is a liquid boiling at about —12°.

The second, called also *nitrocarbol*, represents methane, in which an atom of hydrogen is replaced by the group $(NO^2)'$.

$$\underset{\text{Methane.}}{CH^4} \qquad\qquad \underset{\text{Nitromethane.}}{CH^3(NO^2)}$$

It is obtained by the action of potassium nitrite upon potassium monochloracetate (Kolbe).

$$\underset{\substack{\text{Potassium mono-}\\\text{chloracetate.}}}{CH^2Cl.CO^2K} + \underset{\substack{\text{Potassium}\\\text{nitrite.}}}{KNO^2} + H^2O = KCl + \underset{\text{Nitromethane.}}{CH^3(NO^2)} + KHCO^3$$

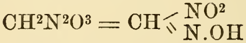
It is also produced by the action of silver nitrite on methyl iodide (V. Meyer).

Nitromethane is a liquid boiling between 101 and 102°. It has an acid character, and one of its hydrogen atoms may be replaced by sodium.

Nitromethane is clearly distinguished from methyl nitrite by the following property: nascent hydrogen transforms nitromethane into methylamine, a reaction which does not take place with its isomeride.

$$\underset{\text{Nitromethane.}}{CH^3(NO^2)} + 3H^2 = \underset{\text{Methylamine.}}{CH^3.NH^2} + 2H^2O$$

METHYLNITROLIC ACID.



$$CH^2N^2O^3 = CH\left\langle\begin{matrix}NO^2\\N.OH\end{matrix}\right.$$

This remarkable combination has been obtained by V. Meyer by the action of nitrous acid upon nitromethane.

$$CH^3(NO^2) + NO.OH = CH\left\langle\begin{matrix}NO^2\\N{-}OH\end{matrix}\right. + H^2O$$

It is seen that in this compound two atoms of hydrogen of the methyl group CH^3, are removed by an atom of oxygen of the nitrous acid, and replaced by the residue (N.OH).

Methylnitrolic acid is prepared by dissolving 5 grammes of nitromethane in water, and adding first a dilute solution of potassium nitrite cooled to 0°, then dilute sulphuric acid also cooled to 0°, and finally dilute solution of potassium hydrate as long as the red color persists. At this moment, sulphuric acid is again added until the liquid is decolorized; the solution is then saturated with calcium carbonate, and agitated with ether, which dissolves the methylnitrolic acid.

After the evaporation of the ether, the acid remains as large, transparent, colorless prisms, fusible at 54°, but decomposing at the same time into formic acid and nitrogen. Dilute sulphuric acid decomposes methylnitrolic acid into formic acid and nitrogen monoxide.

$$CH^2N^2O^3 = \underset{\text{Formic acid.}}{CH^2O^2} + \underset{\text{Nitrogen monoxide.}}{N^2O}$$

The crystals decompose spontaneously in a few days.

FULMINATES OF MERCURY AND SILVER.

Among the important compounds related to the more simple organic combinations are those explosive salts known as *fulminates of mercury and silver.*

They are obtained by dissolving mercury or silver in nitric acid and adding alcohol to the still hot solution. In a few minutes a brisk effervescence takes place, and fulminate of mercury or of silver is deposited as a white, crystalline precipitate. When dry, these bodies explode violently by either heat or percussion. Fulminate of mercury is the basis of percussion-caps.

The composition of these salts is interesting. They are derived from *fulminic acid*, a body which is isomeric with cyanic acid (Liebig, Gay-Lussac). According to Kekulé, fulminic acid is *nitro-acetonitrile*, $CH^2(NO^2).CN$, that is methane in which one hydrogen atom is replaced by the monatomic group NO^2, and a second one by the cyanogen group (CN). More recent investigations by Nef and others make it appear probable, however, that it is *carbyloxime*, $C = NOH$, in which a diatomic carbon atom is united with the group $N = OH$, which characterizes a large and important class of carbon compounds known as the *oximes* (page 554).

In fulminate of mercury one atom of metal replaces two atoms of hydrogen in two molecules of the acid, while in the silver salt the metal replaces hydrogen atom for atom: the formula of mercury fulminate is $2C^2N^2O^2Hg + H^2O$, and that of the silver salt $C^2N^2O^2Ag^2$.

Free fulminic acid results when these compounds are decomposed by strong acids. Its odor resembles that of hydrocyanic acid, and, like the latter, it is very poisonous. Upon heating with hydrochloric acid, it yields formic acid and hydroxylamine.

CACODYL, OR DIMETHYLARSINE.

$As^2(CH^3)^4$

This interesting compound has long been known in an impure state, having been first obtained in 1760 by Cadet as a product of the distillation of a mixture of potassium acetate and white arsenic (arsenious oxide). He collected in the receiver an oily liquid, having an extremely offensive odor, and producing dense white fumes in the air. Hence the name *fuming liquor of Cadet.*

Bunsen's investigation into the chemistry of this body and its combinations has become classic. According to his researches, the fuming liquor of Cadet is a mixture of two bodies, one of which, containing only carbon, hydrogen, and arsenic, plays the part of a radical: it is cacodyl; the other body is the oxide of this radical.

To obtain cacodyl in the pure state, the crude product is treated with hydrochloric acid, which converts the oxide of cacodyl into chloride.

$$\underset{\text{Dimethylarsine oxide.}}{As^2(CH^3)^4O} + 2HCl = \underset{\text{Dimethylarsine chloride.}}{2As(CH^3)^2Cl} + H^2O$$

This chloride, separated by distillation, and treated with zinc at 100° in sealed tubes, furnishes free cacodyl.

The latter is a dense liquid boiling at 170°, and having a penetrating arsenical odor. It is very poisonous. It produces dense white fumes in the air, even taking fire spontaneously. Its vapor density is 7.101.

According to this vapor density, free cacodyl is diarsenic tetramethyl, $As^2(CH^3)^4 = (CH^3)^2As\text{–}As(CH^3)^2$.

Arsenic being either triatomic or pentatomic it is seen that cacodyl is not saturated; hence it can directly fix chlorine, oxygen, etc., yielding two series of compounds. Thus, one molecule of cacodyl, $As^2(CH^3)^4$, can fix 1 or 3 molecules of chlorine, forming the two chlorides:

$$As^2(CH^3)^4 + Cl^2 = 2As(CH^3)^2Cl$$
$$As^2(CH^3)^4 + 3Cl^2 = 2As(CH^3)^2Cl^3$$

To the two chlorides correspond the bromides, iodides, oxides, sulphides, etc. The oxides are

Cacodyl oxide $[As(CH^3)^2]^2O$
Cacodylic acid $As(CH^3)^2O.OH$

Independently of the cacodyl compounds, other combinations of arsenic and methyl are known,—the *methylarsines* and the compounds of methylarsonium.

These bodies form two series, which were discovered and studied by Baeyer, and which belong to the type AsX^3 and AsX^5. The compounds of the first kind are not saturated, and can combine with Cl^2, or the equivalent of Cl^2, passing into the state of the saturated compounds of the series AsX^5.

Series AsX^3	*Series* AsX^5
$As(CH^3)^3$ Trimethylarsine.	$As(CH^3)^4Cl$ Tetramethylarsonium chloride.
$As(CH^3)^2Cl$ Dimethylarsine monochloride.	$As(CH^3)^3Cl^2$ Trimethylarsine dichloride.
$As(CH^3)Cl^2$ Monomethylarsine dichloride.	$As(CH^3)^2Cl^3$ Dimethylarsine trichloride.
$AsCl^3$ Arsenic trichloride.	$As(CH^3)Cl^4$ Monomethylarsine tetrachloride.
	[$AsCl^5$]

It is worthy of remark that the trichloride of arsenic is incapable of fixing Cl^2, and passing into the state of pentachloride, although the corresponding fluoride, AsF^5, is known.

These compounds need not be described. It may only be mentioned that trimethylarsine, $As(CH^3)^3$, is formed, together with cacodyl, by the action of methyl iodide on sodium arsenide. It is a liquid boiling below 100°.

ETHYL COMBINATIONS.

The monatomic residue $(C^2H^5)' = C^2H^6 - H$, which is the radical of ordinary alcohol, is called ethyl. Numerous compounds are known into which the radical enters.

When combined with hydrogen, it forms a gas, C^2H^6, which is ethyl hydride or *ethane*. The chloride, bromide, iodide, and cyanide of ethyl were formerly designated as *simple ethers*.

C^2H^5Cl	ethyl chloride.
C^2H^5Br	ethyl bromide.
C^2H^5I	ethyl iodide.
$C^3H^5.CN$	ethyl cyanide.

Ordinary alcohol is the hydroxide, ether is the oxide of ethyl.

$C^2H^5\text{–}OH$ ethyl hydroxide (alcohol).
$C^2H^5\text{–}O\text{–}C^2H^5 = (C^2H^5)^2O$ ethyl oxide (ether).

The *neutral compound ethers* are derived from the corresponding acids by the substitution of the radical C^2H^5 for their basic hydrogen.

$C^2H^3O\text{-}OH$ Acetic acid.	$C^2H^3O\text{-}OC^2H^5$ Ethyl acetate.
$C^2O^2 \left\{ \begin{matrix} OH \\ OH \end{matrix} \right.$ Oxalic acid.	$C^2O^2 \left\{ \begin{matrix} O.C^2H^5 \\ O.C^2H^5 \end{matrix} \right.$ Ethyl oxalate.
$PO \left\{ \begin{matrix} OH \\ OH \\ OH \end{matrix} \right.$ Phosphoric acid.	$PO \left\{ \begin{matrix} O.C^2H^5 \\ O.C^2H^5 \\ O.C^2H^5 \end{matrix} \right.$ Phosphoric ether (triethyl phosphate).

Free Ethyl, or Butane, C^4H^{10}.—When it is sought to obtain free ethyl by heating ethyl iodide to 150° with zinc in sealed tubes, the radical combines with itself, its molecule being doubled (Frankland).

$$2C^2H^5I + Zn = ZnI^2 + (C^2H^5)^2$$

A gas is thus formed which liquefies at +1°. It was formerly named free ethyl, but is the hydride of butyl, or butane. Indeed, it is incapable of regenerating ethyl compounds containing the simple radical (C^2H^5). When treated with bromine, it yields hydrobromic acid and a bromide $C^4H^8Br^2$, which, according to Carius, is identical with butylene bromide.

Ethyl Hydride, Ethane, or Dimethyl, $C^2H^6 = CH^3\text{-}CH^3$.—Frankland obtained this gas by treating zinc-ethyl with water.

$$\underset{\text{Zinc ethyl.}}{Zn(C^2H^5)^2} + 2H^2O = \underset{\text{Ethane.}}{2C^2H^6} + \underset{\text{Zinc hydrate.}}{Zn(OH)^2}$$

It is likewise formed when methyl iodide is heated with sodium in closed tubes.

$$2CH^3I + 2Na = C^2H^6 + 2NaI$$

It is a colorless gas, burning with a slightly blue, luminous flame. When treated with chlorine, it yields ethyl chloride and hydrochloric acid.

ETHYL HYDROXIDE, OR ALCOHOL.

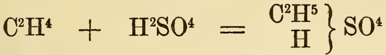
$$C^2H^6O = CH^3\text{-}CH^2.OH$$

Alcohol is the product of the fermentation of solutions which contain glucose, or a substance capable of transformation into glucose.

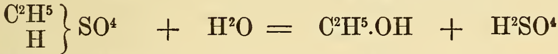
It may be formed synthetically in various manners:

1. By passing ethylene gas into sulphuric acid (Hennell and

Faraday) and boiling the ethylsulphuric acid so formed (Berthelot).



$$\underset{\text{Ethylene.}}{C^2H^4} + H^2SO^4 = \underset{\text{Ethylsulphuric acid.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4}$$



$$\underset{\text{Ethylsulphuric acid.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4} + H^2O = \underset{\text{Alcohol.}}{C^2H^5.OH} + H^2SO^4$$

2. By heating ethylene gas with hydriodic acid and decomposing the ethyl iodide so formed with potassium hydroxide (Berthelot).

$$C^2H^4 + HI = C^2H^5I$$
$$C^2H^5I + KOH = C^2H^5.OH + KI$$

3. By bringing aldehyde in contact with sodium amalgam in presence of water. The nascent hydrogen formed in this case fixes upon the aldehyde, converting it into alcohol (A. Wurtz).

$$\underset{\text{Aldehyde.}}{C^2H^4O} + H^2 = \underset{\text{Alcohol.}}{C^2H^6O}$$

Preparation and Purification of Alcohol.—Alcohol is manufactured by distilling fermented liquors, such as wine, fermented juice of beet-roots, and the product obtained from the fermentation of malt, which is saccharified barley, corn, or other grain. The apparatus now used for this operation has reached such a degree of excellence that alcohol of 95 per cent. may be obtained immediately by one distillation.

Absolutely pure alcohol is obtained by rectifying the alcohol of commerce over hygroscopic substances, such as anhydrous potassium carbonate, quick-lime, or caustic baryta. The last portions of water are removed, and *absolute* alcohol obtained by redistilling the rectified alcohol with caustic baryta. Or some sodium may be dissolved in the alcohol, which may then be rectified on a water-bath.

Properties.—Alcohol is a colorless, mobile liquid, having an agreeable, spirituous odor. Density at 0°, 0.8095. Boiling-point, 78.4° at the normal pressure. It freezes at —130°.

Alcohol mixes with water and ether in all proportions. Its mixture with water takes place with elevation of temperature and contraction of volume. The maximum contraction takes place when the two bodies are mixed in the proportion of one molecule of alcohol (46 parts) to three molecules of water (54 parts).

Alcohol absorbs moisture when exposed to the air. It dissolves many gases, liquids, and solids. *Tinctures* are solutions of various medicinal substances in alcohol.

Among the simple bodies which are soluble in alcohol may be mentioned iodine. Potassium and sodium hydroxides dissolve in it readily, and the same is true of many of the mineral acids. Many of the chlorides are soluble in alcohol; such are those of calcium, strontium, zinc, and cadmium, ferric, cupric, mercuric, and auric chlorides.

Alcohol dissolves the natural alkaloids, the essential oils, resins, and fatty bodies, the latter, however, less readily than ether.

Decompositions.—When vapor of alcohol is passed through a red-hot porcelain tube, it is decomposed into water, carbon monoxide, hydrogen, methane, and ethylene. Besides this, carbon is deposited in the porcelain tube, and a small quantity of naphthalene is produced (Th. de Saussure), as well as benzene and phenol (Berthelot). The principal products of the decomposition of alcohol at a dull-red heat are methane, hydrogen, and carbon monoxide.

$$C^2H^6O = CO + CH^4 + H^2$$

On the application of a burning body, alcohol takes fire and burns with a slightly luminous, bluish flame. On contact with platinum black, alcohol vapor mixed with air undergoes a slow combustion, which produces successively aldehyde and acetic acid.

$$\underset{\text{Alcohol.}}{C^2H^6O} + O = \underset{\text{Aldehyde.}}{C^2H^4O} + H^2O$$

$$\underset{\text{Aldehyde.}}{C^2H^4O} + O = \underset{\text{Acetic Acid.}}{C^2H^4O^2}$$

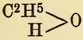
Acetic ether and a small quantity of a volatile, neutral body, called acetal, are at the same time formed as accessory products (Stas).

The lamp without flame of Döbereiner depends upon the slow combustion of alcohol. The wick of an ordinary spirit-lamp is surmounted by a spiral of platinum wire, so that when the lamp is lighted the spiral is heated to incandescence. If then the flame be extinguished, by covering it for an instant with a test-tube, the alcohol vapor continues to rise with the air around the still hot spiral, and undergoes a slow combustion. But the latter develops heat, and the spiral rapidly becomes heated to incandescence, and if the current of air be regulated by a small glass chimney, the experiment may continue as long as the wick emits vapor of alcohol in sufficient quantity.

Bodies rich in oxygen oxidize alcohol at ordinary temperatures; such are chloric and chromic acids. If a little alcohol be poured upon some chromic acid placed upon a brick, the liquid is immediately inflamed and the chromic acid reduced to chromium oxide.

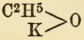
Chlorine attacks alcohol with great energy, the final product of the reaction being a body which has received the name *chloral* (Liebig, Dumas).

If a small piece of potassium or sodium be thrown into pure alcohol, the metal soon melts, and then dissolves with disengagement of hydrogen. The product of the reaction is a crystalline, solid matter which is ethylate of potassium or sodium, that is, a body derived from alcohol by the substitution of an atom of an alkaline metal for an atom of hydrogen.



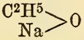
$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right>O$$

Alcohol.



$$\left.\begin{matrix}C^2H^5\\K\end{matrix}\right>O$$

Potassium ethylate.



$$\left.\begin{matrix}C^2H^5\\Na\end{matrix}\right>O$$

Sodium ethylate.

Uses of Alcohol.—Alcohol is used as a combustible in spirit-lamps. In the arts, it is employed in the manufacture of ether, chloroform, perfumeries, and many other products. It is largely used in the laboratory, and in pharmacy, as a solvent; it serves for the preservation of anatomical specimens. In France and England, alcohol employed for certain industrial uses is exempted from part of the tax, when it has previously been mixed with about one-tenth of wood-spirit and a few per cent. of mineral oils and resin. Such a mixture is unfit for the manufacture of brandy and liquors, but its usefulness as a solvent is in most cases unimpaired.

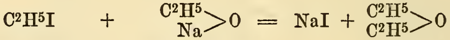
Alcohol exists in fermented liquors, such as wine, cider, and beer. It is contained in much larger quantities in brandies, whiskeys, and spirits. These are products of the distillation of various alcoholic liquids. They are more or less rich in alcohol. Brandy is prepared by the distillation of wine, cider, or the products of fermentation of cherry-juice (cherry-brandy), sugar-cane (rum), beet-root molasses (beet-brandy). Whiskey is distilled from fermented starchy materials, such as corn, rye, potatoes, etc., the starch being first saccharified. The richness of these materials in alcohol is indicated by the degrees of an alcoholometer. The following table gives the strength of some of these liquors. (For wine, beer, etc., see page 648).

	BAUMÉ'S HYDROMETER.	SPECIFIC GRAVITY.	PERCENTAGE OF ALCOHOL BY VOLUME.
Weak brandy	16°	0.9605	37.9
Proof spirits	19°	0.9420	50.1
Strong brandy	22°	0.9241	59.2
Ordinary alcohol	34°	0.8588	85.1
Rectified alcohol (strongest commercial)	40°	0.8295	95.
Absolute alcohol	46°	0.8095	100.

ETHYL OXIDE, OR ETHER.

$$(C^2H^5)^2O = CH^3\text{–}CH^2\text{–}O\text{–}CH^2\text{–}CH^3$$

If ethyl iodide be added to an alcoholic solution of ethylate of sodium and a gentle heat be applied, a deposit of sodium iodide is formed and vapors are disengaged which may be condensed in a cooled receiver into an ethereal liquid. It is oxide of ethyl.



$$\underset{\text{Ethyl iodide.}}{C^2H^5I} + \underset{\text{Sodium ethylate.}}{\begin{matrix}C^2H^5\\ Na\end{matrix}\!\!>O} = NaI + \underset{\text{Ethyl oxide.}}{\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\!\!>O}$$

Ethyl iodide. Sodium ethylate. Ethyl oxide.

If, in the preceding experiment, the ethyl iodide be replaced by methyl iodide, an extremely volatile liquid will be formed, which is the double oxide of methyl and ethyl.

$$\underset{\text{Methyl iodide.}}{CH^3I} + \begin{matrix}C^2H^5\\ Na\end{matrix}\!\!>O = NaI + \underset{\text{Oxide of methyl and ethyl.}}{\begin{matrix}C^2H^5\\ CH^3\end{matrix}\!\!>O}$$

Methyl iodide. Oxide of methyl and ethyl.

These classic experiments, due to Williamson, show that the oxide of ethyl contains two ethyl groups. It may be regarded as alcohol in which the hydrogen atom of the group hydroxyl is replaced by ethyl.

$H\text{–}O\text{–}H$	$C^2H^5\text{–}O\text{–}H$	$C^2H^5\text{–}O\text{–}C^2H^5$
Water.	Alcohol.	Ethyl oxide.

Ether may also be obtained by the action of ethyl iodide on silver oxide.

Preparation.—Ether is prepared in the arts by the action of sulphuric acid on alcohol. A mixture of 9 parts of concentrated sulphuric acid and 5 parts of alcohol of 90 per cent. is heated in a flask, A (Fig. 126), and a small, continuous stream of alcohol is allowed to flow into this mixture through the funnel-tube *a*. The temperature of the liquid, indicated by the thermometer *t*, should not exceed 140 or 145°. The vapor disengaged is condensed in a Liebig's condenser, B, through which a stream of cold water flows continually. Under these conditions, a mixture of ether and water collects in the receiver D, together with a little alcohol, and towards the close of the operation, a small quantity of sulphurous acid gas is disengaged. The product is purified by washing with milk of lime, and then with pure water, after which it is rectified over calcium chloride on a water-bath. Fig. 126 represents the apparatus used for public demonstration; in the arts, the operation is conducted on a large scale in apparatus of an analogous construction.

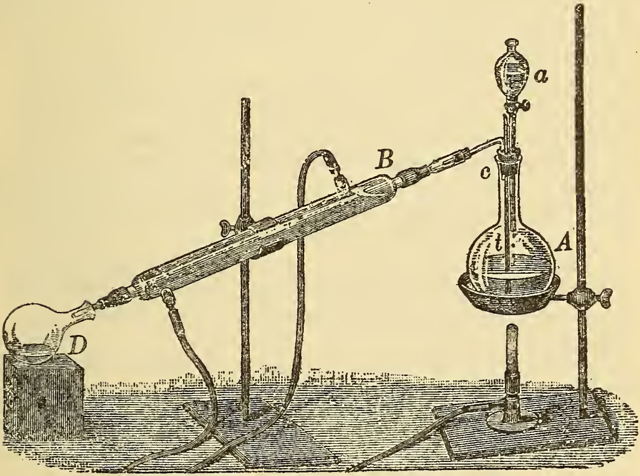


FIG. 126.

Theory of Etherification.—The transformation of alcohol into ether is a true dehydration, brought about by the sulphuric acid.

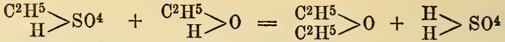
$$2(C^2H^5.OH) = (C^2H^5)^2O + H^2O$$

Williamson clearly proved that it is effected in two distinct phases; in the first, ethylsulphuric acid and water are formed.

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right> O \quad + \quad \left.\begin{matrix}H\\H\end{matrix}\right> SO^4 \quad = \quad \left.\begin{matrix}C^2H^5\\H\end{matrix}\right> SO^4 \quad + \quad H^2O$$

Alcohol. Sulphuric acid. Ethylsulphuric acid.

In the second, another molecule of alcohol reacts with the ethylsulphuric acid; ether is formed and sulphuric acid is regenerated.



$$\underset{\text{Ethylsulphuric acid.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right>SO^4} + \underset{\text{Alcohol.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right>O} = \underset{\text{Ether.}}{\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right>O} + \underset{\text{Sulphuric acid.}}{\left.\begin{matrix}H\\H\end{matrix}\right>SO^4}$$

Hence the ether and water collected in the receiver are products of two distinct phases of the reaction. Ethylsulphuric acid is continually formed and as continually decomposed, regenerating sulphuric acid ready to act upon new portions of alcohol. However, although the operation is continuous, it cannot go on indefinitely: the mixture blackens; while the acid is being diluted continually with water formed in the first phase of the reaction, it is also in part reduced by the alcohol, sulphur dioxide being formed.

Properties of Ether.—Ether is a colorless, very mobile liquid; its taste is at first burning, then cooling; its odor is suave and agreeable, and is called ethereal. Density at 0°, 0.7366. Boiling-point under the normal pressure, 34.5°.

It is but slightly miscible with water, on the surface of which it forms a separate layer. 9 parts of water dissolve 1 part of ether; 36 parts of ether dissolve 1 part of water. Ether dissolves in all proportions in alcohol and in methyl alcohol.

It slightly dissolves sulphur and phosphorus, and notable quantities of bromine, iodine, ferric, mercuric, and auric chlorides, and many organic bodies, such as the oils, fats, resins, alkaloids, etc.

In 1846, Dr. William T. G. Morton, of Boston, discovered the fact that ether vapor when inhaled produces unconsciousness and anæsthesia. This discovery has been of inestimable value in surgery, and while other anæsthetics, such as chloroform, have been introduced, ether still seems to have the general preference.

It is very inflammable and burns with a quite luminous flame. Its vapor explodes violently when mixed with air or oxygen and ignited.

If a heated spiral of platinum wire be suspended in a glass jar containing a little ether, in such a manner that the lower extremity of the wire is but a little distance from the surface of the liquid, the wire will soon become brightly incandescent and will ignite the ether. This effect is due to the ether vapor, which, coming in contact with the platinum, and being mixed with air, undergoes a slow combustion. Heat is thus developed, and the wire becomes incandescent.

Chlorine acts on ether with extreme energy. If the action be moderated, various products of substitution are obtained, among which the following have been well studied:

Monochlorether	$\begin{matrix}C^2H^4Cl\\C^2H^5\end{matrix}>O$	liquid boiling at 98–99°.
Dichlorether	$\begin{matrix}C^2H^3Cl^2\\C^2H^5\end{matrix}>O$	liquid boiling at 140–147°.
Tetrachlorether	$\begin{matrix}C^2H^3Cl^2\\C^2H^3Cl^2\end{matrix}>O$	liquid, density 1.5.
Perchlorether	$\begin{matrix}C^2Cl^5\\C^2Cl^5\end{matrix}>O$	colorless crystals, fusible at 69°.

The last is a solid body, crystallizing in octahedra. By the action of heat it is decomposed into carbon sesquichloride and perchloraldehyde (Malaguti).

$$\underset{\text{Perchlorether.}}{\begin{matrix}C^2Cl^5\\C^2Cl^5\end{matrix}>O} = \underset{\text{Carbon sesquichloride.}}{C^2Cl^6} + \underset{\text{Perchloraldehyde.}}{C^2Cl^4O}$$

When two parts of bromine are added to one part of ether, and the mixture is cooled, a garnet-colored compound of bromine and ether, $(C^2H^5)^2O.Br^2$, separates. It crystallizes in thin plates, fusible at 22°, and is easily decomposed (Schützenberger).

HYDROSULPHIDE AND SULPHIDE OF ETHYL.

Two bodies are known which are intimately related, as regards their constitutions, with alcohol and ether. They are the *hydrosulphide* and the *sulphide of ethyl.* The first, formerly known as *mercaptan*, represents alcohol containing an atom of sulphur instead of an atom of oxygen; the second represents ether in which the oxygen atom is replaced by sulphur.

$$\underset{\text{Ethyl hydroxide.}}{C^2H^5.OH} \qquad \underset{\text{Ethyl oxide.}}{(C^2H^5)^2O}$$

$$\underset{\text{Ethyl hydrosulphide.}}{C^2H^5.SH} \qquad \underset{\text{Ethyl sulphide.}}{(C^2H^5)^2S}$$

Ethyl hydrosulphide is obtained by distilling a concentrated aqueous solution of potassium hydrosulphide with a solution of potassium ethyl sulphate.

It may also be prepared by passing vapor of ethyl chloride into an alcoholic solution of potassium hydrosulphide. The liquid is distilled as soon as it is saturated with ethyl chloride, and water is added to the distillate. Ethyl hydrosulphide separates.

$$\underset{\text{Potassium hydrosulphide.}}{KSH} + \underset{\text{Ethyl chloride.}}{C^2H^5Cl} = KCl + \underset{\text{Ethyl hydrosulphide.}}{C^2H^5.SH}$$

Ethyl hydrosulphide is a transparent, colorless liquid, very mobile, and having a fetid odor. Density at 21°, 0.835. Boiling-point, 36.2° (Liebig).

It reacts energetically with mercuric oxide, forming water and a white, crystalline body which represents ethyl hydrosulphide in which the hydrogen is replaced by mercury. Hence the name *mercaptan* (mercurium captans) given to the hydrosulphide of ethyl by Zeise. This mercuric compound is insoluble in water; it contains $(C^2H^5S)^2Hg''$.

Ethyl sulphide is obtained, like the hydrosulphide, by double decomposition. Vapor of ethyl chloride is passed into an alcoholic solution of potassium monosulphide.

$$\underset{\text{Potassium sulphide.}}{K^2S} + \underset{\text{Ethyl chloride.}}{2C^2H^5Cl} = 2KCl + \underset{\text{Ethyl sulphide.}}{(C^2H^5)^2S}$$

Ethyl sulphide is a colorless liquid, having a garlicky odor. It boils at 91°. It is insoluble in water.

ETHYL CHLORIDE.

C^2H^5Cl

This body is prepared by saturating alcohol with hydrochloric acid gas and distilling on a water-bath. Ethyl chloride is disengaged, and should be passed first through a wash-bottle and then through a tube containing calcium chloride, after which it may be condensed in a receiver placed in a freezing mixture.

Below 12.5°, its boiling-point, ethyl chloride is a mobile, colorless liquid, having a penetrating and agreeable odor. It is inflammable, and burns with a flame tinged with green.

If some solution of silver nitrate be agitated in a jar containing vapor of ethyl chloride, no precipitate will be formed; but if the agitation be continued after the vapor has been ignited, an abundant precipitate of silver chloride will be formed, owing to decomposition of the silver nitrate by the hydrochloric acid produced by combustion of the ethyl chloride.

Ethyl chloride produces a precipitate of silver chloride when passed into an alcoholic solution of silver nitrate.

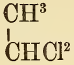
Chlorinated Derivatives of Ethyl Chloride.—When ethyl chloride is submitted to the action of chlorine, various compounds are successively formed by the substitution of chlorine for hydrogen, atom for atom. The following is the nomenclature and composition of these chlorinated compounds, which were discovered by V. Regnault.

C^2H^5Cl	ethyl chloride.
$C^2H^4Cl^2$	dichlorethane (ethylidene chloride)—boils at 57.5°.
$C^2H^3Cl^3$	trichlorethane—boils at 75°.
$C^2H^2Cl^4$	tetrachlorethane—boils at 127.5°.
C^2HCl^5	pentachlorethane—boils at 158°.
C^2Cl^6	hexachlorethane (sesquichloride of carbon).

It will be noticed that the second of these compounds is isomeric with ethylene chloride, or Dutch liquid, of which the description will be found farther on. It may be obtained by treating aldehyde with phosphorus pentachloride.

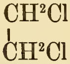
$$\underset{\text{Aldehyde.}}{CH^3\text{–}CHO} + PCl^5 = \underset{\text{Dichlorethane.}}{CH^3\text{–}CHCl^2} + \underset{\text{Phosphorus oxychloride.}}{POCl^3}$$

This mode of formation indicates its constitution, which is expressed by the formula



$$\begin{array}{l} CH^3 \\ | \\ CHCl^2 \end{array}$$

To distinguish it from its isomeride ethylene chloride,



$$\begin{array}{l} CH^2Cl \\ | \\ CH^2Cl \end{array}$$

it is named dichlorethane or ethylidene chloride.

In the sesquichloride of carbon, C^2Cl^6, the hydrogen atoms are all replaced by chlorine. Carbon sesquichloride is a crystalline solid, melting at 187°, and boiling at 200°–210°

ETHYL BROMIDE.

C^2H^5Br

Ethyl bromide is prepared by distilling a mixture of alcohol, bromine, and amorphous phosphorus, or a mixture of potassium bromide, alcohol, and sulphuric acid diluted with its own volume of water. In either case the distillate is washed with water, and the oily ethyl bromide separated and dried with potassium carbonate.

It is a colorless, refracting liquid, having an odor resembling that of chloroform, and a burning taste. It mixes in all proportions with alcohol and ether, but is insoluble in water. Its density at 15° is 1.4189, and it boils at 40.7°.

It has been employed to a limited extent as an anæsthetic.

ETHYL IODIDE.

C^2H^5I

This important compound is prepared by the action of alcohol on iodine in presence of amorphous phosphorus. Phosphorus iodide is formed, and reacts upon the alcohol, yielding ethyl iodide and an acid of phosphorus. The former distils into the receiver, together with the alcohol which escapes the reaction. Water is added, and the lower layer of liquid is separated, dried with calcium chloride, and rectified on a water-bath.

Ethyl iodide is a colorless liquid, but becomes brown when long kept, especially when exposed to light. Density at 0°, 1.9753. Boiling-point, 72.2°.

It can exchange its iodine by double decomposition, as can potassium iodide. If ethyl iodide be added to an alcoholic solution of silver nitrate, a yellow precipitate of silver iodide is at once formed, while ethyl nitrate remains in solution.

$$\underset{\text{Ethyl iodide.}}{C^2H^5I} + \underset{\text{Silver nitrate.}}{AgNO^3} = AgI + \underset{\text{Ethyl nitrate.}}{(C^2H^5)NO^3}$$

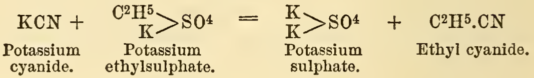
ETHYL CYANIDE.

$C^3H^5N = CH^3\text{–}CH^2\text{–}CN$

This compound is formed when ammonium propionate is distilled with phosphoric anhydride.

$$\underset{\text{Ammonium propionate.}}{(NH^4)C^3H^5O^2} = \underset{\text{Ethyl cyanide.}}{C^3H^5N} + 2H^2O$$

From this mode of formation, ethyl cyanide is sometimes called *propionitrile*. The same body exists in the product of the distillation of a mixture of potassium cyanide and potassium ethylsulphate.



$$\underset{\substack{\text{Potassium}\\\text{cyanide.}}}{KCN} + \underset{\substack{\text{Potassium}\\\text{ethylsulphate.}}}{\begin{matrix}C^2H^5\\K\end{matrix}\!\!>SO^4} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{\begin{matrix}K\\K\end{matrix}\!\!>SO^4} + \underset{\text{Ethyl cyanide.}}{C^2H^5.CN}$$

But this product, which is liquid and has a variable boiling-point, contains, independently of the true cyanide of ethyl, an isomeride of that body, whose existence was foreseen by Meyer, and discovered by Gautier in the product of the action of ethyl iodide on silver cyanide.

Ethyl cyanide is a colorless liquid, having a penetrating and pleasant odor. It boils at 96.7°.

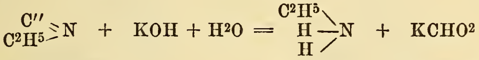
When it is boiled with potassium hydroxide, potassium propionate is formed and ammonia is disengaged (Dumas, Malaguti, and Le Blanc).

$$\underset{\text{Ethyl cyanide.}}{C^3H^5N} + KOH + H^2O = \underset{\text{Potassium propionate.}}{KC^3H^5O^2} + NH^3$$

When ethyl cyanide is brought into contact with dilute sulphuric acid and zinc, it fixes 4 atoms of hydrogen and is converted into propylamine (Mendius).

$$\underset{\text{Ethyl cyanide.}}{C^3H^5N} + H^4 = \underset{\text{Propylamine.}}{C^3H^9N}$$

Ethylcarbylamine.—This name was given by Gautier to the isomeride of ethyl cyanide already mentioned. It is a colorless liquid, having a very penetrating and intensely offensive odor. It boils at 79°. With potassium hydroxide it yields potassium formate and ethylamine.



$$\left.\begin{matrix}C''\\C^2H^5\end{matrix}\right\rangle N + KOH + H^2O = \left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\rangle N + KCHO^2$$

Ethylcarbylamine. Ethylamine. Potassium formate.

ETHYL NITRITE, OR NITROUS ETHER.

$C^2H^5.O\text{–}NO$

This compound is obtained by the action of nitric acid on alcohol. The reaction is very violent, and abundant red vapors are evolved. After passing through a wash-bottle, they are conducted into a well-cooled receiver, where the ethyl nitrite condenses.

It is a yellowish, very volatile liquid, whose odor recalls that of apples. It boils at 18°. It is but slightly soluble in water. Hot water immediately decomposes it into alcohol and nitrous acid, the latter being itself decomposed into nitric acid and nitric oxide.

NITROETHANE AND ITS DERIVATIVES.

$C^2H^5\text{–}NO^2$

This isomeride of ethyl nitrite represents ethane, C^2H^6, in which one atom of hydrogen is replaced by the group $(NO^2)'$. It is the higher homologue of nitromethane.

It is obtained, together with a certain quantity of ethyl nitrite, when ethyl iodide is treated with silver nitrite.

$$\underset{\text{Ethyl iodide.}}{C^2H^5I} + \underset{\text{Silver nitrite.}}{AgNO^2} = \underset{\text{Nitrethane.}}{C^2H^5(NO^2)} + AgI$$

It is a liquid having a peculiar, ethereal odor and boiling at 113–114°. Density at 13°, 1.0582 (V. Meyer).

With nascent hydrogen, it furnishes pure ethylamine.

$$C^2H^5(NO^2) + 3H^2 = C^2H^5(NH^2) + 2H^2O$$

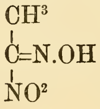
All of the homologues of nitroethane thus yield the corresponding amines. It is a general character of the *nitro* compounds, and one which is not possessed by their isomerides, the *nitrous ethers*. In constitution and properties, nitroethane approaches nitrobenzene, as will be seen by the following comparison of their formulæ:

$C^6H^5.H$ Ethane.	$C^6H^5.H$ Benzene.
$C^2H^5(NO^2)$ Nitroethane.	$C^6H^5(NO^2)$ Nitrobenzene.
$C^2H^5(NH^2)$ Ethylamine.	$C^6H^5(NH^2)$ Phenylamine (aniline).

The presence of the group (NO^2) confers acid properties upon nitroethane. Its sodium compound, $C^2H^4{<}^{NO^2}_{Na}$, is formed either by the action of an alcoholic solution of sodium hydrate on nitroethane, or by the direct action of sodium on the same body; in the latter case hydrogen is disengaged. Sodium-nitroethane is very explosive (V. Meyer and Stuber).

When it is sought to prepare potassium-nitroethane by the action of alcoholic potassium hydrate on nitroethane, the latter body is decomposed, yielding, among other products, potassium nitrite. Now, the latter salt exerts a remarkable action on nitroethane, giving rise to a new body of complex composition, *potassium ethylnitrolate.*

Ethylnitrolic acid may be obtained by a process analogous to that which has been described for the preparation of methylnitrolic acid. Ethylnitrolic acid contains



$$\begin{array}{l} CH^3 \\ | \\ C{=}N.OH \\ | \\ NO^2 \end{array}$$

It crystallizes in light-yellow, transparent prisms, possessing a feeble bluish fluorescence and a very sweet taste. It decomposes without violence at 81–82° into nitrogen, nitrous vapors, and acetic acid. When boiled with dilute sulphuric acid, it decomposes into acetic acid and nitrogen monoxide.

$$\underset{\text{Ethylnitrolic acid.}}{C^2H^4N^2O^3} = \underset{\text{Acetic acid.}}{C^2H^4O^2} + N^2O$$

ETHYL NITRATE, OR NITRIC ETHER.

$$(C^2H^5)NO^3$$

This is obtained by the action of nitric acid upon alcohol in presence of a small quantity of urea. The latter body prevents the reduction of the nitric acid to nitrous acid. Nitric ether condenses in the receiver. It is washed with water, dehydrated with calcium chloride, and rectified. It is a liquid, having an agreeable, ethereal odor. It boils at 86°. Density at 0°, 1.1322.

Potassium hydroxide decomposes it, like all compound ethers, forming potassium nitrate and alcohol.

$$(C^2H^5)NO^3 + KOH = C^2H^5.OH + KNO^3$$

It dissolves in ammonia, especially if the latter be warm, yielding ammonium nitrate and ethylamine. The reaction is analogous to that of ammonia upon methyl nitrate.

ETHYL SULPHATES.

Ethylsulphuric or Sulphovinic Acid.—$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4 = \begin{matrix}C^2H^5O\\HO\end{matrix}\!>\!SO^2$. This body is an example of an acid ether. It results from the substitution of a single ethyl group for one atom of hydrogen in sulphuric acid, which is dibasic.

$$\left.\begin{matrix}H\\H\end{matrix}\right\}SO^4$$

$$\begin{matrix}C^2H^5\\H\end{matrix}\!>\!SO^4$$

It is formed by the action of sulphuric acid upon alcohol. The mixture of the two bodies becomes hot, and if after cooling the liquid be diluted and saturated with barium carbonate, an abundant precipitate of barium sulphate will be formed, and a soluble salt of barium, the ethylsulphate, will remain in solution. A solution of ethylsulphuric acid may be obtained by exactly decomposing this salt with dilute sulphuric acid.

By boiling, ethylsulphuric acid is decomposed into sulphuric acid and alcohol.

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4 + \left.\begin{matrix}H\\H\end{matrix}\right\}O = \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO^4$$

The ethylsulphates are beautiful salts; they are crystallizable and soluble in water.

Ethyl Sulphate.—$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}SO^4 = \begin{matrix}C^2H^5.O\\C^2H^5.O\end{matrix}{>}SO^2$. This body, which represents sulphuric acid in which the two atoms of hydrogen are replaced by two ethyl groups, is formed when silver sulphate is warmed with ethyl iodide; double decomposition takes place, thus:

$$Ag^2SO^4 + 2C^2H^5I = (C^2H^5)^2SO^4 + 2AgI$$

It is an oily liquid having an acrid taste. Its density is 1.184. It boils at 208°, with partial decomposition.

ETHYLSULPHONIC ACID AND ETHYL SULPHITE.

When mercaptan, $C^2H^5.SH$, is oxidized by nitric acid, a thick, very acid liquid is obtained, which in a vacuum solidifies to a crystalline mass. It is ethylsulphonic acid, which concentrated nitric acid oxidizes and converts into ethylsulphuric acid. Unlike the latter, ethylsulphonic acid is very stable. It is not decomposed by boiling with potassium hydrate: when fused with the latter, it yields potassium sulphite and alcohol.

$$C^2H^5.SO^3K + KOH = C^2H^5.OH + K^2SO^3$$

Phosphorus pentachloride converts it into *ethylsulphonic chloride*, $C^2H^5\text{–}SO^2.Cl$, a liquid boiling at 173°.

Ethylsulphonic acid is analogous in its properties and constitution to phenylsulphonic acid, and its analogues, which will be described farther on. Ethylsulphonic acid is the sulphonic derivative of ethane.

C^2H^6 ethane.	C^6H^6 benzene.
$C^2H^5.SO^3H$ ethylsulphonic acid.	$C^6H^5.SO^3H$ phenylsulphonic acid.

The sulphonic acids may be considered as derivatives of a hypothetical acid, $H.SO^2.OH$, to which the name unsymmetrical sulphurous acid has been given. The hydrogen atom in direct combination with the sulphur is replaceable by ethyl, phenyl, etc., and the sulphonates result from the replacement of the remaining hydrogen by metals or alcohol radicals.

There is possible another sulphurous acid, symmetrical sulphurous acid HO.SO.OH, and derivatives of this acid are also known: they are the sulphites of the alcohol radicals, and present the structure $SO(OR)^2$.

1. If silver sulphite and ethyl iodide be heated together, a double decomposition takes place, yielding silver iodide and ethyl sulphonate.

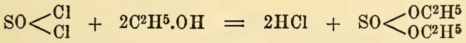
$$\underset{\text{Silver sulphite.}}{AgSO^2.OAg} + \underset{\text{Ethyl iodide.}}{2C^2H^5I} = 2AgI + \underset{\text{Ethyl sulphonate.}}{C^2H^5.SO^2.OC^2H^5}$$

This is the ether of the ethylsulphonic acid which has been described. It may be obtained by the action of ethylsulphonic chloride on sodium ethylate.

$$C^2H^5.SO^2.Cl + C^2H^5.ONa = NaCl + C^2H^5.SO^2.OC^2H^5$$

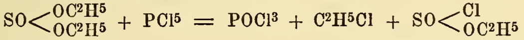
It is a liquid, boiling at 208°, and having at 0° a density of 1.47.

2. By the action of thionyl (sulphuryl) chloride on absolute alcohol, ethyl sulphite is obtained isomeric with the preceding.



$$\underset{\text{Thionyl chloride.}}{SO<\begin{matrix}Cl\\Cl\end{matrix}} + 2C^2H^5.OH = 2HCl + \underset{\text{Symmetric ethyl sulphite.}}{SO<\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}}$$

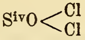
This ether corresponds to ethyl sulphate. When heated with water it is decomposed into sulphurous acid and alcohol. Phosphorus pentachloride converts it into *ethylsulphurous chloride*, boiling at 122°.



$$\underset{\text{Ethyl sulphite.}}{SO<\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}} + PCl^5 = POCl^3 + C^2H^5Cl + \underset{\text{Ethylsulphurous chloride.}}{SO<\begin{matrix}Cl\\OC^2H^5\end{matrix}}$$

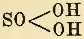
When it is treated with an equivalent quantity of potassium hydroxide in alcoholic solution, potassium ethylsulphite separates in brilliant scales.

We have, therefore, two distinct series of compounds, viz.:



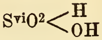
$$S^{iv}O<\begin{matrix}Cl\\Cl\end{matrix}$$

Thionyl chloride.



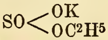
$$SO<\begin{matrix}OH\\OH\end{matrix}$$

Sulphurous acid (unknown).



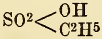
$$S^{vi}O^2<\begin{matrix}H\\OH\end{matrix}$$

Unsymmetrical sulphurous acid (unknown).



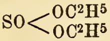
$$SO<\begin{matrix}OK\\OC^2H^5\end{matrix}$$

Potassium ethylsulphite.



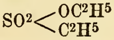
$$SO^2<\begin{matrix}OH\\C^2H^5\end{matrix}$$

Ethylsulphonic acid.



$$SO<\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}$$

Ethyl sulphite.



$$SO^2<\begin{matrix}OC^2H^5\\C^2H^5\end{matrix}$$

Ethyl sulphonate.

PHOSPHORIC ETHERS.

Orthophosphoric acid forms three ethyl ethers, and in general three series of ethers corresponding to the three series of orthophosphates.

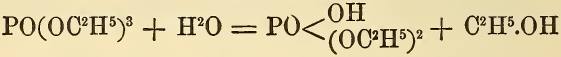
$PO(OH)^2(OC^2H^5)$	$PO(OH)(OC^2H^5)^2$	$PO(OC^2H^5)^3$
Monethylphosphoric acid.	Diethylphosphoric acid.	Triethylphosphate.

We can only describe triethylphosphate, which may be obtained by the action of anhydrous ether on phosphoric anhydride, or by the action of phosphorus oxychloride on sodium ethylate.

$$POCl^3 + 3C^2H^5.ONa = 3NaCl + PO(OC^2H^5)^3$$

De Clermont has obtained it by the reaction of ethyl iodide with silver phosphate.

It is a syrupy liquid, soluble in water, alcohol and ether. Its density at 12° is 1.072. It boils at 215°. It is readily decomposed by water into alcohol and diethylphosphoric acid.



$$PO(OC^2H^5)^3 + H^2O = PO{<}\begin{matrix}OH\\(OC^2H^5)^2\end{matrix} + C^2H^5.OH$$

NORMAL ETHYL BORATE.

$B(OC^2H^5)^3$

Triethyl borate, corresponding to boron trichloride, BCl^3, is obtained by distilling borax with potassium ethylsulphate. It is also formed, independently of other boric ethers, by the action of boron trichloride on absolute alcohol. It is a colorless, limpid liquid, boiling at 119°. Density, 0.885. It burns with a green flame. Water decomposes it into boric acid and alcohol.

ETHYL SILICATES.

Ebelmen has described several silicates of ethyl. To silicon tetrachloride, $SiCl^4$, there corresponds an ortho-silicic ether, $Si(OC^2H^5)^4$; to the chloride, Si^2Cl^6, there corresponds an ether, $Si^2(OC^2H^5)^6$. A metasilicic ether, $SiO(OC^2H^5)^2$, has also been described, but its existence is not certainly established.

Ethyl orthosilicate, $Si(OC^2H^5)^4$, is a colorless liquid, boiling at 165–168°, and having a density of 0.933. It burns with a brilliant white light, diffusing a smoke of silicic acid. It is insoluble in water, which gradually decomposes it into alcohol and silicic acid, the latter being deposited as a very hard, vitreous mass.

Ethyl disilicate, $Si^2(OC^2H^5)^6$, is formed by the action of silicon chloride on alcohol not absolutely free from water.

ETHYL ORTHOCARBONATE.

$C(OC^2H^5)^4$

Basset obtained this ether by causing sodium ethylate to react with chloropicrin.

$$C(NO^2)Cl^3 + 4C^2H^5.ONa = NaNO^2 + 3NaCl + C(OC^2H^5)^4$$

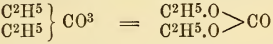
Chloropicrin. Sodium ethylate. Sodium nitrite. Ethyl orthocarbonate.

It is an ethereal liquid, boiling at 158–159°. Its conversion into guanidine by the action of ammonia has already been indicated (page 473).

Ethyl orthocarbonate corresponds to an unknown orthocarbonic acid which would be derived from carbon tetrachloride.

$$CCl^4 \qquad C(OH)^4 \qquad C(OC^2H^5)^4$$

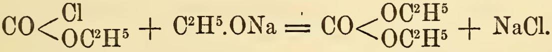
ETHYL CARBONATE.



$$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}CO^3 = \begin{matrix}C^2H^5.O\\C^2H^5.O\end{matrix}>CO$$

Ettling obtained this compound by introducing potassium or sodium little by little into ethyl oxalate heated to 130°. The metal dissolves, disengaging carbon monoxide. A brown mass is obtained, which must be distilled with water. The ethyl carbonate which passes over is dehydrated with calcium chloride and distilled.

It may also be obtained by double decomposition by heating ethyl iodide with silver carbonate (P. de Clermont), or by the action of ethylchlorocarbonate (page 516) on sodium ethylate.



$$CO<\begin{matrix}Cl\\OC^2H^5\end{matrix} + C^2H^5.ONa = CO<\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix} + NaCl.$$

Ethyl carbonate is a colorless liquid, having a pleasant, ethereal odor; its density at 0° is 0.9998, and it boils at 125°. In the cold, ammonia converts it into *ethyl carbamate*, or *urethane*, a body soluble in water and alcohol, and crystallizable in large tables fusible at 51–52°, and boiling at 180° (Dumas).

$$\begin{matrix}C^2H^5.O\\C^2H^5.O\end{matrix}>CO + NH^3 = \begin{matrix}NH^2\\C^2H^5.O\end{matrix}>CO + C^2H^5.OH$$

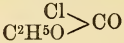
Ethyl carbonate. Ethyl carbamate.

It yields urea and alcohol when heated to 100° with ammonia.

$$\begin{matrix}C^2H^5.O\\C^2H^5.O\end{matrix}>CO + 2NH^3 = CO<\begin{matrix}NH^2\\NH^2\end{matrix} + 2C^2H^5.OH$$

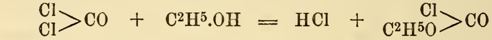
Ethyl carbonate. Urea.

ETHYL CHLOROCARBONATE.



$$\begin{matrix}Cl\\C^2H^5O\end{matrix}>CO$$

Dumas obtained this ether by passing carbonyl chloride into alcohol. Water is added to the product of the reaction, and the insoluble liquid is separated, dried, and distilled.



$$\begin{matrix}Cl\\Cl\end{matrix}>CO + C^2H^5.OH = HCl + \begin{matrix}Cl\\C^2H^5O\end{matrix}>CO$$

Carbonyl chloride. Ethyl chlorocarbonate.

It is a liquid having a pungent, ethereal odor. It boils at 94°. Hot water decomposes it. Ammonia converts it into ethyl carbamate, or urethane.

$$\begin{matrix}Cl\\C^2H^5.O\end{matrix}>CO + 2NH^3 = NH^4Cl + \begin{matrix}NH^2\\C^2H^5O\end{matrix}>CO$$

ETHYL ISOCYANATE.

$C^2H^5{-}N{=}CO$

This compound is prepared by distilling on an oil-bath a mixture of 2 parts of potassium ethylsulphate and 1 part of recently-prepared and well-dried potassium isocyanate. The product which condenses in the receiver is rectified on a water-bath (Wurtz). Ethyl isocyanate is a colorless liquid, having a very irritating odor. It boils at 60°. Potassium hydrate decomposes it into carbonic acid gas and ethylamine. It combines with ammonia, developing heat and producing ethylurea (page 481).

The bodies which were formerly known as cyanic acid and ethyl cyanate, are only isomerides of the oxygen compounds of cyanogen. They have been described as isocyanic acid and isocyanate of ethyl. The true cyanic ether, $(C^2H^5.O)CN$, or rather a polymeride of that body, has been obtained by Cloëz. It is formed by the action of cyanogen chloride on ethylate of sodium.

$$CNCl + Na.OC^2H^5 = CN.OC^2H^5 + NaCl$$

Cyanogen chloride. Sodium ethylate. Ethyl cyanate.

Potassium hydroxide decomposes the true ethyl cyanate, like all other compound ethers, into alcohol and the corresponding potassium salt (cyanate), or into the decomposition products of that body,—carbon dioxide and ammonia.

CYANURIC ETHERS.

When potassium isocyanate is distilled with ethyl sulphate, besides the ethyl isocyanate which has just been described, there is formed also the isocyanurate.

$$C^3O^3N^3\,(C^2H^5)^3 = (CO)^3{\equiv}(N.C^2H^5)^3$$

The latter condenses in a solid white mass which may be purified by recrystallization from boiling alcohol. It crystallizes in brilliant prisms, fusible at 95°; it boils at 276° (A. Wurtz). Boiling potassium hydroxide decomposes it, like the isocyanate, with disengagement of carbon dioxide, a reaction which justifies the constitution indicated by the preceding formula.

Its isomeride $C^3N^3(OC^2H^5)^3$, which corresponds to the normal cyanuric acid (page 474), melts at 29° and boils at 275°.

The mother liquor from which triethyl isocyanurate has deposited, contains diethyl isocyanurate, $C^3O^3N^3H(C^2H^5)^2$, which crystallizes in six-sided prisms, fusible at 173°.

Normal methyl cyanurate is formed by the action of cyanogen chloride on sodium methylate.

$$3CNCl + 3CH^3.ONa = 3NaCl + C^3N^3(OCH^3)^3$$

It crystallizes in needles fusible at 132°. It boils between 160 and 170°, and at this temperature is converted into its isomeride methyl isocyanurate, fusible at 175°, and boiling at 296°. By the action of boiling potassium hydroxide, it is decomposed into potassium cyanurate and methyl alcohol.

SERIES OF SATURATED HYDROCARBONS.

C^2H^{2n+2}

To methane and ethane, which have already been described, are related numerous hydrocarbons belonging to the same series, C^nH^{2n+2}. They are called *saturated* because no hydrocarbons are known in which the number of hydrogen atoms exceeds that indicated by the preceding formula. Again, the hydrocarbons in question can fix directly no other atoms. For example, in order that chlorine can enter into one of their molecules, hydrogen must first be removed, and this displacement is known to take place, atom for atom, according to the law of substitution. Thus, if chlorine be made to act upon the hydrocarbon C^6H^{14} (hexane), the compounds $C^6H^{13}Cl$, $C^6H^{12}Cl^2$, $C^6H^{11}Cl^3$, may be obtained successively. Let us consider the first of these compounds, $C^6H^{13}Cl$. The Cl may be replaced by the group OH, and the chloride is thus converted into an alcohol. For this purpose the chloride is caused to react with a silver salt, the acetate, for example, and hexyl acetate is formed by double decomposition.

$$\underset{\text{Hexlyl chloride.}}{C^6H^{13}Cl} + \underset{\text{Silver acetate.}}{AgC^2H^3O^2} = \underset{\text{Hexyl acetate.}}{C^6H^{13}.C^2H^3O^2} + AgCl$$

Boiling potassium hydroxide will transform this ether into hexyl hydroxide.

$$\underset{\text{Hexyl acetate.}}{C^6H^{13}.C^2H^3O^2} + KOH = \underset{\text{Potassium acetate.}}{KC^2H^3O^2} + \underset{\text{Hexyl hydroxide.}}{C^6H^{13}.OH}$$

This series of reactions permits of the successive transformation of any hydrocarbon of the saturated series into a chloride, an acetate, and a hydroxide, and the latter is the alcohol corresponding to the hydrocarbon. The following is the series of saturated hydrocarbons:

CH^4	methane.
C^2H^6	ethane.
C^3H^8	propane.
C^4H^{10}	butanes.
C^5H^{12}	pentanes.
C^6H^{14}	hexanes.
C^7H^{16}	heptanes.
C^8H^{18}	octanes.
C^9H^{20}	nonanes.
$C^{10}H^{22}$	decanes, etc.

All of these hydrocarbons, after the fourth of the series, up to the term $C^{16}H^{34}$, have been obtained from petroleum and the products of distillation of bitumen and peat. Towards the close of the distillation, when the temperature passes above 300°, the products which distil condense to a solid mass on cooling. When properly purified, this solid forms a colorless, translucent mass, which has received the name paraffin. It is probably a mixture of several hydrocarbons of the series C^nH^{2n+2}. Its point of fusion varies between 45 and 65°.

All of the compounds belonging to this series cannot be described here, but we may briefly consider their constitution.

The third member of the series, propane, C^3H^8, has the constitution indicated by the formula $CH^3–CH^2–CH^3$. It is a gas which liquefies at —17°.

Its higher homologue, butane, C^4H^{10}, has the constitution $CH^3{-}CH^2{-}CH^2{-}CH^3$, and can be obtained by the action of zinc or sodium on ethyl iodide.

$$2C^2H^5I + Na^2 = 2NaI + C^4H^{10}$$

It is a colorless gas, condensable at +1°. But we have here a remarkable instance of isomerism. There is another butane, isomeric with the preceding, and having the constitution expressed by the formula  $CH^3{-}CH{<}{\genfrac{}{}{0pt}{}{CH^3}{CH^3}}$. It is trimethyl-methane, $CH(CH^3)^3$, while normal butane is dimethyl-ethane, $C^2H^4(CH^3)^2$, or propyl-methane, $CH^3(C^3H^7)$. The signification of these words and formulæ is evident. Trimethyl-methane is methane, CH^4, in which three atoms of hydrogen are replaced by three methyl groups. The difference in the atomic grouping is attended by a difference in properties. Trimethyl-methane is a gas which condenses only at —17°.

The succeeding terms of the series present isomerisms of the same kind, but much more numerous as their molecular complication is greater. They need not be described here, since the same general principles apply to all.

PETROLEUM.

Petroleum, or rock oil, was known to the ancients, oil-springs existing in Persia, India, Italy and Russia. It was used by the American Indians, but until 1859 mineral oil was obtained only in small quantities, usually by the distillation of argillaceous rocks saturated with hydrocarbons, such as boghead coal. In 1859 the discovery of numerous and prolific oil-bearing soils in Northwestern Pennsylvania led to the method now employed of sinking deep wells, from which the oil either flows naturally, by reason of interior pressure, or is pumped by machinery. A single well has furnished two thousand barrels of oil a day.

Crude petroleum is usually dark brown in color, often having a greenish reflection. It is sometimes mobile, sometimes viscous like molasses. Its density varies from 0.75 to 0.92. By fractional distillation it can be separated into a large number of hydrocarbons, most of which are homologues of marsh gas. Schorlemmer, and Pelouze and Cahours, have thus succeeded in isolating from petroleum the whole saturated series from C^4H^{10} to $C^{16}H^{34}$. American petroleum consists almost entirely of hydrocarbons of the series C^nH^{2n+2}, while Russian petroleum contains considerable quantities of the naphthenes, a series of hydrocarbons related to benzene.

For commercial purposes the crude oil is subjected to fractional distillation; that is, it is heated, and the fractions passing over at different temperatures are collected separately. Under such circumstances, American petroleum at 70° gives off the volatile hydrocarbons, which constitute *petroleum ether; gasoline* distils between 70° and 90°, and the portion passing between 90° and 150° is known as *benzine*. Above 150°, and up to about 300°, refined petroleum, or *kerosene*, is collected. From the latter temperature up to 400° heavy oils of a density from 0.83 to 0.9, and valuable as lubricants, are obtained. Much *paraffine* distils towards the end of the operation, and a residue of coke remains in the retort.

Petroleum ether having a density of about 0.60 is used for the artificial production of cold, and as a solvent for fatty matters, and gasoline having a density of 0.63 serves for the manufacture of an illuminating gas. Benzine, which must not be confounded with benzene (page 671), is largely employed on account of its solvent powers for resins, fats, oils, etc., especially in cleaning and scouring.

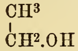
Kerosene, or illuminating oil, should contain no product whose boiling point is below 150°. The comparative safety of the oil is usually determined by slowly heating it, and observing by means of a thermometer the temperature at which it emits inflammable vapors, and that at which the oil itself ignites. A lighted match is passed over the surface of the warm oil until the flashing point and igniting point are attained. The former should not be below 60°, and the latter not lower than 65.5°.

SERIES OF ALCOHOLS.

Ethyl alcohol, of which the more important compounds have been briefly described, is not the only product of the fermentation of saccharine liquids. Other alcohols are formed in small quantity in this reaction, which is conducted on an extensive scale in the arts. Among these alcohols of fermentation are the following:

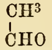
Propyl alcohol, or propyl hydroxide,	$C^3H^7.OH$
Butyl alcohol, or butyl hydroxide,	$C^4H^9.OH$
Amyl alcohol, or amyl hydroxide,	$C^5H^{11}.OH$
Hexyl alcohol, or hexyl hydroxide,	$C^6H^{13}.OH$
Heptyl alcohol, or heptyl hydroxide,	$C^7H^{15}.OH$

To each of these alcohols correspond numerous ethereal compounds in which the groups propyl, C^3H^7, butyl, C^4H^9, amyl, C^5H^{11}, etc., are substituted for the hydrogen of the hydracids and oxyacids. To each of these alcohols correspond also an aldehyde and an acid, just as ordinary aldehyde and acetic acid correspond to ordinary alcohol or ethyl hydroxide.



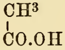
$$\begin{array}{l}CH^3\\ |\\ CH^2.OH\end{array}$$

Alcohol.



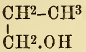
$$\begin{array}{l}CH^3\\ |\\ CHO\end{array}$$

Aldehyde.



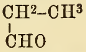
$$\begin{array}{l}CH^3\\ |\\ CO.OH\end{array}$$

Acetic acid.



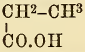
$$\begin{array}{l}CH^2\text{–}CH^3\\ |\\ CH^2.OH\end{array}$$

Propyl alcohol.



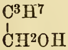
$$\begin{array}{l}CH^2\text{–}CH^3\\ |\\ CHO\end{array}$$

Propaldehyde.



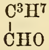
$$\begin{array}{l}CH^2\text{–}CH^3\\ |\\ CO.OH\end{array}$$

Propionic acid.



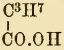
$$\begin{array}{l}C^3H^7\\ |\\ CH^2OH\end{array}$$

Butyl alcohol.



$$\begin{array}{l}C^3H^7\\ |\\ CHO\end{array}$$

Butaldehyde.

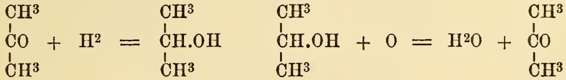


$$\begin{array}{l}C^3H^7\\ |\\ CO.OH\end{array}$$

Butyric acid.

All of these alcohols contain a group $CH^2.OH$ united to a group or radical, C^nH^{2n+1}. When they are converted by oxidation into aldehydes and acids, the group $CH^2.OH$ is transformed into a group CHO, characteristic of the aldehydes, or a group CO.OH, characteristic of the acids. These alcohols are said to be *primary*. Beginning with butyl alcohol, the primary alcohols may have several isomeric modifications, as will be seen shortly. Independently of the primary alcohols, there are others, isomeric with the preceding, but distinguished from them by the fact that they do not yield corresponding aldehydes and acids when oxidized. These *iso-alcohols* are divided into *secondary*, which contain the group CH.OH, and *tertiary*, which contain the group C.OH (Kolbe). Without entering into the details of this subject, we may cite two examples:

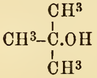
1. By the action of nascent hydrogen acetone yields secondary propyl alcohol, which oxidation reconverts into acetone.



$$\begin{array}{l}CH^3\\ |\\ CO\\ |\\ CH^3\end{array} + H^2 = \begin{array}{l}CH^3\\ |\\ CH.OH\\ |\\ CH^3\end{array} \qquad \begin{array}{l}CH^3\\ |\\ CH.OH\\ |\\ CH^3\end{array} + O = H^2O + \begin{array}{l}CH^3\\ |\\ CO\\ |\\ CH^3\end{array}$$

Acetone. Isopropyl alcohol.

2. Butlerow discovered an isomeride of butyl alcohol, and named it *tertiary butyl alcohol;* its constitution is thus expressed:



$$\begin{array}{r}CH^3\\ |\\ CH^3\text{–}C.OH\\ |\\ CH^3\end{array}$$

This alcohol contains, as is seen, the group C.OH. It yields neither aldehyde nor acid by oxidation.

In the primary alcohols, the OH is united to a C which is combined with only one other carbon atom; in the secondary alcohols, to a C united to two other carbon atoms; while in the tertiary alcohols, the C to which the hydroxyl is attached is joined to three other atoms of carbon.

In order to exactly designate the class of any alcohol by its name, Kolbe proposed to consider all alcohols as derived from methyl alcohol, which he named *carbinol*. The replacement of one of the hydrogen atoms in the CH^3 group by a hydrocarbon radical would yield a mono-substituted carbinol or primary alcohol; the disubstituted carbinols are secondary alcohols, while the tertiary alcohols are trisubstituted carbinols. This may be more clearly understood by the aid of the following formula:

$(C^2H^5)CH^2.OH$	$(C^2H^5)^2CH.OH$	$(CH^3)^3C.OH$
Ethyl carbinol.	Diethyl carbinol.	Trimethyl carbinol.
Primary propyl alcohol.	Secondary (iso) amyl alcohol.	Tertiary butyl alcohol.

PROPYL ALCOHOLS.

C^3H^8O

Normal Propyl Alcohol.—$CH^2–CH^2–CH^2.OH$.—This was discovered by Chancel in the oily liquid remaining after the distillation of brandy. It is a spirituous liquid, boiling at 98°. Its iodide, C^3H^7I, boils at 104.5°.

Isopropyl Alcohol, $CH^3–CH.OH–CH^3$, is prepared by the action of sodium amalgam upon acetone in aqueous solution, according to the reaction given on the previous page.

It boils at 81°. When propylene gas is heated with hydriodic acid, isopropyl iodide, C^3H^7I, is obtained, boiling at 92°.

$$\underset{\text{Propylene.}}{C^3H^6} + HI = \underset{\text{Isopropyl iodide.}}{C^3H^7I}$$

BUTYL ALCOHOLS.

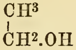
$C^4H^{10}O$

There are four butyl alcohols. The best known is the

Butyl Alcohol of Fermentation, or isopropylcarbinol.

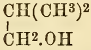
In 1852, Wurtz obtained it from the fusel-oil from the rectification of beet-root alcohol. It is a colorless liquid, having a penetrating odor analogous to that of amyl alcohol, but more spirituous. It dissolves in 10.5 times its volume of water. It boils at 109°, and yields on oxidation an acid isomeric with butyric acid and called *isobutyric*. Its density at 18° is 0.805.

It may be regarded as ordinary alcohol in which two atoms of hydrogen are replaced by two methyl groups.



$$\begin{array}{l} CH^3 \\ | \\ CH^2.OH \end{array}$$

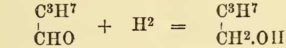
Alcohol.



$$\begin{array}{l} CH(CH^3)^2 \\ | \\ CH^2.OH \end{array}$$

Isobutyl alcohol.

Normal Butyl Alcohol is isomeric with the alcohol of fermentation, and by oxidation yields butyric aldehyde and butyric acid. Lieben obtained this alcohol by the action of sodium amalgam in presence of water on butaldehyde.



$$\begin{array}{l} C^3H^7 \\ | \\ CHO \end{array} + H^2 = \begin{array}{l} C^3H^7 \\ | \\ CH^2.OH \end{array}$$

Butaldehyde. Normal butyl alcohol.

Normal butyl alcohol is a liquid having a pleasant odor. It boils at 117°. Its density at 0° is 0.824.

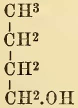
Fitz has obtained this alcohol, as well as ethyl alcohol and normal propyl alcohol, by the decomposition of glycerol under the influence of a peculiar organized ferment.

Secondary Butyl Alcohol was obtained by De Luynes by the reduction of erythritol (page 633). This alcohol is secondary, having the constitution $CH^3–CH^2–CH(OH)–CH^3$. It boils at 98–100°. Density at 0°, 0.85. The corresponding iodide, $CH^3–CH^2–CHI–CH^3$, boils at 118°. It is formed by the following reaction:

$$\underset{\text{Erythritol.}}{C^4H^{10}O^4} + 7HI = \underset{\text{Secondary butyl iodide.}}{C^4H^9I} + 4H^2O + 3I^2$$

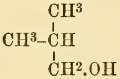
Tertiary Butyl Alcohol, discovered by Butlerow, has received the name *trimethylcarbinol*, on account of its constitution, which has already been indicated. It is a compound crystallizing in right-rhombic prisms, melting at 23°. It boils at 83–84°, and is soluble in all proportions of water.

In conclusion, four alcohols are known having the composition $C^4H^{10}O$, and presenting a remarkable instance of isomerism. Their constitutions are again indicated in the following formulæ:



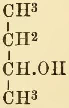
$$\begin{array}{l} CH^3 \\ | \\ CH^2 \\ | \\ CH^2 \\ | \\ CH^2.OH \end{array}$$

Normal primary butyl alcohol. (Lieben.)



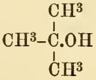
$$\begin{array}{r} CH^3 \\ | \\ CH^3–CH \\ | \\ CH^2.OH \end{array}$$

Primary isobutyl alcohol (fermentation). (Wurtz.)



$$\begin{array}{l} CH^3 \\ | \\ CH^2 \\ | \\ CH.OH \\ | \\ CH^3 \end{array}$$

Secondary butyl alcohol. (De Luynes.)



$$\begin{array}{c} CH^3 \\ | \\ CH^3–C.OH \\ | \\ CH^3 \end{array}$$

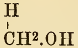
Tertiary butyl alcohol. (Boutlerow.)

AMYL ALCOHOLS.

$C^5H^{12}O$

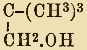
Theory predicts the existence of eight isomeric amyl alcohols:

1. Four primary alcohols which may be regarded as formed by the substitution of various alcoholic groups for one atom of hydrogen of the methyl group in methyl alcohol.



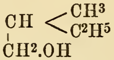
$$\begin{array}{l} H \\ | \\ CH^2.OH \end{array}$$

Methyl alcohol.



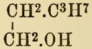
$$\begin{array}{l} C\text{–}(CH^3)^3 \\ | \\ CH^2.OH \end{array}$$

Tertiary-butylcarbinol.



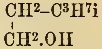
$$\begin{array}{l} CH < {}^{CH^3}_{C^2H^5} \\ | \\ CH^2.OH \end{array}$$

Active amyl alcohol.



$$\begin{array}{l} CH^2.C^3H^7 \\ | \\ CH^2.OH \end{array}$$

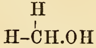
Normal amyl alcohol. Butyl carbinol.



$$\begin{array}{l} CH^2\text{–}C^3H^7i \\ | \\ CH^2.OH \end{array}$$

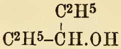
Amyl alcohol of fermentation. Isobutylcarbinol.

2. Three secondary alcohols, in which two atoms of hydrogen of the methyl group in methyl alcohol are replaced by alcoholic groups.



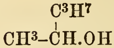
$$\begin{array}{c} H \\ | \\ H\text{–}CH.OH \end{array}$$

Methyl alcohol.



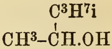
$$\begin{array}{c} C^2H^5 \\ | \\ C^2H^5\text{–}CH.OH \end{array}$$

Diethylcarbinol.



$$\begin{array}{c} C^3H^7 \\ | \\ CH^3\text{–}CH.OH \end{array}$$

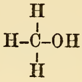
Propylmethylcarbinol.



$$\begin{array}{c} C^3H^7i \\ | \\ CH^3\text{–}CH.OH \end{array}$$

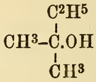
Isopropylmethylcarbinol.

3. One tertiary alcohol, in which one ethyl group and two methyl groups replace the three hydrogen atoms of the CH^3 in methyl alcohol.



$$\begin{array}{c} H \\ | \\ H\text{–}C\text{–}OH \\ | \\ H \end{array}$$

Methyl alcohol.



$$\begin{array}{c} C^2H^5 \\ | \\ CH^3\text{–}C.OH \\ | \\ CH^3 \end{array}$$

Dimethylethylcarbinol.

All of these eight isomerides are actually known.

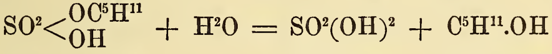
Normal Amyl Alcohol, $CH^3\text{–}CH^2\text{–}CH^2\text{–}CH^2\text{–}CH^2.OH$.—Lieben obtained this compound by the action of nascent hydrogen on valeral, the corresponding aldehyde. It is a liquid, almost insoluble in water, boiling at 137°. Its density at 0° is 0.829. Oxidizing agents convert it into normal valeric acid.

The corresponding chloride, $C^5H^{11}Cl$, boils at 106–107°. It may be prepared by the action of hydrochloric acid upon the normal alcohol, and has also been obtained by the action of chlorine on normal pentane, $CH^3\text{–}(CH^2)^3\text{–}CH^3$, as described on page 504.

Amyl Alcohol of Fermentation.—This consists in great part of inactive isobutyl carbinol, ${}^{CH^3}_{CH^3}{>}CH\text{–}CH^2\text{–}CH^2.OH$, but contains also a variable quantity of active amyl alcohol.

It may be obtained by fractional distillation of the fusel oil from beet-root and potatoes, as well as of that from the *marc* of grapes, whiskey, etc. These products are only the residues of the distillation of alcohol from various sources. The inactive amyl alcohol or isobutylcarbinol may be separated by the following process, indicated by Pasteur.

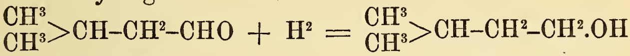
By treatment with sulphuric acid the crude amyl alcohol is converted into amylsulphuric acid. The liquid is diluted with water, neutralized with barium carbonate, and filtered. Two barium amylsulphates are thus obtained, of which the one is less soluble than the other, and crystallizes first when the solution is evaporated, while the other remains in the mother liquid. The former is derived from the inactive alcohol, the latter from the active alcohol; these alcohols are obtained by decomposing the corresponding barium salts with sulphuric acid, filtering, and distilling with water the free amylsulphuric acids.



$$SO^2<{}^{OC^5H^{11}}_{OH} + H^2O = SO^2(OH)^2 + C^5H^{11}.OH$$

Amylsulphuric acids. Sulphuric acid. Amyl alcohols.

Isobutylcarbinol has been obtained by synthesis, and the process clearly proves its constitution (Balbiano). The constitution of butyl alcohol of fermentation has been established with certainty by Erlenmeyer. This alcohol may be converted successively into iodide and cyanide, and this, by decomposition with potassium hydrate, into inactive valeric acid. The barium salt of the latter acid when distilled with calcium formate yields the corresponding aldehyde, valeraldehyde (Piria), and this is converted into inactive amyl alcohol by the action of nascent hydrogen.



$$\begin{matrix}CH^3\\CH^3\end{matrix}>CH-CH^2-CHO + H^2 = \begin{matrix}CH^3\\CH^3\end{matrix}>CH-CH^2-CH^2.OH$$

Valeraldehyde. Isobutylcarbinol.

Properties.—Pure isobutylcarbinol is a colorless, somewhat oily liquid, soluble in fifty parts of water at 13°. Its density at 0° is 0.823, and it boils at 131.4°. When oxidized it yields inactive valeraldehyde and acid.

$$C^5H^{12}O + O = H^2O + C^5H^{10}O$$

Amyl alcohol. Valeric aldehyde (valeral).

$$C^5H^{12}O + O^2 = H^2O + C^5H^{10}O^2$$

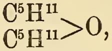
Valeric acid.

The crude alcohol of fermentation is an oily liquid, of a disagreeable odor. It boils at 129–132°. It turns the plane of polarized light to the left, but its rotatory power is variable, for it contains variable proportions of active amyl alcohol.

When distilled with zinc chloride, it yields ordinary amylene, which is a mixture of several isomeric amylenes, trimethylethylene being the most abundant.

$$\underset{\text{Amyl alcohol.}}{C^5H^{12}O} = \underset{\text{Amylenes.}}{C^5H^{10}} + H^2O$$

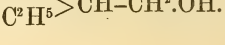
Many amyl derivatives have been studied. They resemble the ethyl compounds, but contain, of course, the group C^5H^{11} instead of C^2H^5.

Amyl oxide,  $\begin{matrix}C^5H^{11}\\C^5H^{11}\end{matrix}\!>\!O$, is formed, together with amylene, by the action of sulphuric acid on crude amyl alcohol (Williamson). It is a colorless liquid, of an aromatic odor, boiling at 176°.

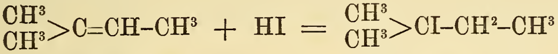
Amyl chloride, $C^5H^{11}Cl$, is a colorless liquid, boiling at 101.4°. *Amyl bromide*, $C^5H^{11}Br$, boils at 120.4°. *Amyl iodide*, $C^5H^{11}I$, is prepared by a process similar to that which yields ethyl iodide. It is a colorless liquid, boiling at 148°. It turns brown on exposure to the light.

Amyl nitrite, $C^5H^{11}NO^2$, is prepared by passing nitrous vapors, made by the action of nitric acid on starch, into amyl alcohol, and distilling the carefully washed product. It is a pale yellow liquid, boiling at 96°, and having a peculiar odor somewhat like that of apples. Its vapor when inhaled produces dilatation of the capillary system, and violent but transitory headache. Its inhalation has been recommended as a remedy for sea-sickness, in certain heart-affections, and as an antidote in cases of poisoning by chloroform vapor.

Active Amyl Alcohol is contained to the extent of about thirteen per cent. in crude amyl alcohol. One method of separation has already been indicated, but Le Bel has proposed a better method when it is desired to prepare only the active alcohol. If hydrochloric acid gas be passed through the crude alcohol, the inactive alcohol is first attacked and converted into chloride; the active alcohol then remains after the separation of the inactive chloride.

It boils at 127°. It rotates the plane of polarized light to the left $[\alpha]_D = -4.4°$. Its chloride boils at 97–99°; its iodide at 144–145°. Oxidation converts it into active valeric acid; hence its constitution is probably  $\begin{matrix}CH^3\\C^2H^5\end{matrix}\!>\!CH\text{–}CH^2.OH$.

Tertiary Amyl Alcohol, or Hydrate of Amylene. This alcohol is prepared by treating with hydriodic acid trimethylethylene, described on page 574, which forms the greater part of crude amylene.



$$\begin{matrix}CH^3\\CH^3\end{matrix}{>}C{=}CH{-}CH^3 + HI = \begin{matrix}CH^3\\CH^3\end{matrix}{>}CI{-}CH^2{-}CH^3$$

Trimethylethylene. Trimethylethyl iodide.

The iodide so formed, when acted on by water and silver oxide, yields the corresponding hydrate, which is tertiary amyl alcohol or dimethylethylcarbinol.

It is a mobile, colorless liquid, having an odor somewhat like camphor. At —12° it forms a crystalline mass; it boils at 102.5°, and at 200° is decomposed into amylene and water. By reason of the latter reaction, Wurtz, who discovered the alcohol, named it hydrate of amylene.

Its chloride boils at 86°, its bromide at 108–109°, and its iodide at 127–128°.

Oxidation converts it into acetic acid and acetone.

HIGHER ALCOHOLS.

Of the rapidly increasing number of members of this series which are becoming well known, we can consider but a few.

Hexyl and Heptyl Alcohols.—Faget announced that the residues from the distillation of fusel-oil from fermented grape-juice contained a small quantity of *hexyl* ($C^6H^{14}O$) and *heptyl* ($C^7H^{16}O$) alcohols, but the existence of such alcohols in that product has not been corroborated.

Normal hexyl alcohol has been obtained from the volatile oil of the seeds of *Heracleum giganteum*, an oil which contains butyrate of hexyl, $C^6H^{13}.C^4H^7O^2$. The normal alcohol boils at 157–158°.

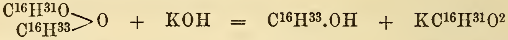
Normal heptyl alcohol, $C^7H^{16}O$, has been prepared by the action of nascent hydrogen on œnanthic aldehyde $C^7H^{14}O$. It boils at 175–177°, and has an aromatic odor.

Octyl Alcohols, $C^8H^{18}O$.—Normal octyl alcohol may be extracted from the seeds of *Heracleum spondylium* and *Heracleum giganteum*, in which octyl acetate, $C^8H^{17}.C^2H^3O^2$, exists. This ether is separated and decomposed by boiling potassium hydroxide. Its boiling-point is 199°.

Bouis discovered secondary octyl alcohol. By boiling one of the acids produced by the saponification of castor-oil, ricinolic acid, with potassium hydroxide, he succeeded in obtaining sebacic acid and a new secondary alcohol. This is octyl alcohol, $C^8H^{18}O$, a colorless liquid having a pleasant, aromatic odor, and boiling at 178°. The following equation explains its formation :

$$\underset{\text{Ricinolic acid.}}{C^{18}H^{34}O^3} + 2KOH = \underset{\text{Potassium sebacate.}}{K^2C^{10}H^{16}O^4} + \underset{\text{Octyl hydroxide.}}{C^8H^{18}O} + H^2$$

Cetyl Alcohol.—The solid portion of an oil which fills the cranial sinuses of the sperm-whale is called *spermaceti*. When properly purified it occurs in beautiful pearly plates, fusible at 49°. It is a compound ether of which the nature was recognized by Chevreul in 1823. By submitting it to the action of potassium hydroxide, that chemist decomposed it into palmitic acid and a new alcohol which he called *ethal*, to denote its relations with alcohol and ether. It is now called *cetyl alcohol*, or *cetyl hydroxide*.



$$\underset{\text{Cetyl palmitate.}}{\left.\begin{matrix}C^{16}H^{31}O\\C^{16}H^{33}\end{matrix}\right>O} + KOH = \underset{\text{Cetyl hydroxide.}}{C^{16}H^{33}.OH} + \underset{\text{Potassium palmitate.}}{KC^{16}H^{31}O^2}$$

It belongs to the same homologous series as the preceding alcohols.

Alcohols from Wax.—The most complex alcohols of the series under consideration were obtained from wax by Brodie. Ordinary beeswax is a mixture of a fatty acid, $C^{27}H^{54}O^2$, called *cerotic acid* (cerin), and a compound ether, the *palmitate of myricyl* (myricin). The two bodies are separated by alcohol, which readily dissolves the first, but in which the second is but slightly soluble. By boiling the palmitate of myricyl with potassium hydroxide, it breaks up into palmitic acid and *hydroxide of myricyl*, or *myricyl alcohol*, $C^{30}H^{62}O$.

Chinese wax is a compound ether; it is cerotate of ceryl, and may be decomposed by caustic potash into cerotic acid and *ceryl hydroxide*, or *ceryl alcohol*, $C^{27}H^{56}O$. The hydroxides of cetyl and ceryl are solid bodies.

ALLYL ALCOHOL.

$$C^3H^5.OH = CH^2{=}CH{-}CH^2.OH$$

All the alcohols thus far considered belong to the series $C^nH^{2n+2}O$. There are other monohydric alcohols which belong to different series, that is, in which there are different relations between the number of hydrogen atoms and the number of carbon atoms. Among these other alcohols, the most important is *allyl alcohol*, or *hydroxide of allyl*, so named because it is closely related to the essential oil of garlic, which is allyl sulphide. Another natural oil, that of mustard, is sulphocyanate of allyl.

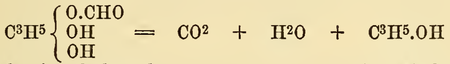
$$\underset{\text{Allyl hydroxide.}}{C^3H^5.OH}\qquad\qquad \underset{\text{Allyl sulphide.}}{(C^3H^5)^2S}\qquad\qquad \underset{\text{Allyl sulphocyanate.}}{C^3H^5.CNS}$$

Hofmann and Cahours prepared allyl hydroxide and a great number of its derivatives artificially by the aid of *allyl iodide*, C^3HI^5, which is formed when glycerol is acted upon by iodide of phosphorus, P^2I^4 (Berthelot and de Luca). This iodide, whose relations to allyl alcohol are the same as those of ethyl iodide to ordinary alcohol, is a colorless liquid, having a slightly pungent, garlicky odor, and boiling at 101°.

When heated with mercury and concentrated hydrochloric acid, it yields pure propylene gas (Berthelot).

$$\underset{\text{Allyl iodide.}}{2C^3H^5I} + 2HCl + 4Hg = \underset{\text{Propylene.}}{2C^3H^6} + Hg^2I^2 + Hg^2Cl^2$$

Tollens and Henninger discovered a very simple process for the preparation of allyl alcohol. It consists in heating formic acid, or oxalic acid, from which the former acid is produced, with glycerol to 220°. The allyl alcohol which distils is washed with a concentrated solution of potassium carbonate, and rectified over lime. In this reaction, a monoformine of glycerol is first produced, and this decomposes at 220° into carbon dioxide, water, and allyl alcohol.



$$C^3H^5\left\{\begin{array}{l}O.CHO\\ OH\\ OH\end{array}\right. = CO^2 + H^2O + C^3H^5.OH$$

Monoformine of glycerol. Allyl alcohol.

It will be seen that the reaction is really a reduction.

Allyl alcohol is a colorless liquid, boiling at 97°, and having a pungent, alcoholic odor. It dissolves in all proportions of water. Density at 0°, 0.858. Allyl alcohol is an unsaturated compound; it can fix directly two atoms of hydrogen, so forming normal propyl alcohol. It combines directly with bromine, forming dibromopropylalcohol. $CH^2Br{-}CHBr{-}CH^2OH$.

Acrolein, or *acraldehyde*, $CH^2 = CH{-}CHO$, a volatile liquid that is formed in the distillation of fatty bodies, is the aldehyde of allyl alcohol. *Acrylic acid* is the corresponding acid.

COMPOUND AMMONIAS, OR AMINES.

Wurtz gave these names to the basic combinations resulting from the substitution of alcoholic radicals, such as methyl, ethyl, etc., for the hydrogen of ammonia. This substitution may be more or less complete; 1, 2, or 3 atoms of hydrogen may be replaced by as many alkyl groups. Hence there are various classes of amines; they are designated by the names primary, secondary, and tertiary.

	PRIMARY AMINES.	SECONDARY AMINES.	TERTIARY AMINES.
$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$ Ammonia.	$\left.\begin{matrix}\mathrm{CH^3}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$ Methylamine.	$\left.\begin{matrix}\mathrm{CH^3}\\\mathrm{CH^3}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$ Dimethylamine.	$\left.\begin{matrix}\mathrm{CH^3}\\\mathrm{CH^3}\\\mathrm{CH^3}\end{matrix}\right\}\mathrm{N}$ Trimethylamine.
	$\left.\begin{matrix}\mathrm{C^2H^5}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$ Ethylamine.	$\left.\begin{matrix}\mathrm{C^2H^5}\\\mathrm{C^2H^5}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$ Diethylamine.	$\left.\begin{matrix}\mathrm{C^2H^5}\\\mathrm{C^2H^5}\\\mathrm{C^2H^5}\end{matrix}\right\}\mathrm{N}$ Triethylamine.

Lastly, bases are known which are the most energetic of all, and may be considered as derived from the hypothetical hydroxide of ammonium by the substitution of alcoholic radicals for 4 atoms of hydrogen.

$$\underset{\text{Ammonium hydroxide.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N.OH}} \qquad \underset{\text{Hydroxide of tetrethylammonium.}}{\left.\begin{matrix}\mathrm{C^2H^5}\\\mathrm{C^2H^5}\\\mathrm{C^2H^5}\\\mathrm{C^2H^5}\end{matrix}\right\}\mathrm{N.OH}}$$

The latter ammoniated bases, as well as the secondary and tertiary amines, were discovered by Hofmann.

The compound ammonias, or amines, are formed in the following reactions:

1. By the decomposition of an isocyanic or isocyanuric ether by potassium hydroxide. In this case primary amines are obtained (A. Wurtz).

$$\underset{\text{Ethyl isocyanate.}}{\mathrm{CO=N{-}C^2H^5}} + \mathrm{2KOH} = \underset{\text{Ethylamine.}}{\mathrm{NH^2(C^2H^5)}} + \mathrm{K^2CO^3}$$

2. By the action of alkyl bromides or iodides on ammonia (A. W. Hofmann).

$$\underset{\text{Ethyl iodide.}}{\mathrm{C^2H^5I}} + \mathrm{NH^3} = \underset{\text{Ethylamine hydriodide.}}{\mathrm{NH^2(C^2H^5)HI}}$$

$$\mathrm{2C^2H^5I} + \mathrm{NH^3} = \underset{\text{Diethylamine hydriodide.}}{\mathrm{NH(C^2H^5)^2HI}} + \mathrm{HI}$$

$$\mathrm{3C^2H^5I} + \mathrm{NH^3} = \underset{\text{Triethylamine hydriodide.}}{\mathrm{NH(C^2H^5)^3HI}} + \mathrm{2HI}$$

3. By decomposing carbylamines by dilute acids (Gautier).

4. By the reduction of nitromethane and its homologues by nascent hydrogen (V. Meyer, see p. 494).

5. By the action of nascent hydrogen on the alkyl cyanides, also called nitriles (Mendius).

$$CH^3.CN \quad + \quad H^4 \quad = \quad CH^3\text{–}CH^2\text{–}NH^2$$

Methyl cyanide, or acetonitrile. Ethylamine.

6. By reducing oximes (p. 554) or hydrazones (p. 554) in alcoholic solution by means of nascent hydrogen (E. Fischer).

General Properties.—The amines are energetic bases, presenting great analogies with ammonia, having a similar odor, a like solubility in water, and the same pronounced alkaline reaction. The more simple are combustible gases or volatile liquids. The basic energy increases with progressive substitutions: thus triethylamine is a stronger base than either ethylamine or ammonia, both of which it displaces from their combinations. The hydroxides of the quaternary bases, or compound ammoniums, are almost as caustic as potassium hydroxide. All the compound ammonias form with platinic chloride crystallizable double salts comparable to ammonium chloroplatinate. They can replace ammonia in ammonia alum.

When the hydrochlorides of the amines are subjected to destructive distillation, they decompose into an alkyl chloride and a lower amine, a reaction which allows the molecules to be simplified by a sort of inverse substitution.

$$N(CH^3)^4Cl \quad = \quad N(CH^3)^3 \quad + \quad CH^3Cl$$

Tetramethylammonium chloride. Trimethylamine.

$$N(CH^3)^3.HCl \quad = \quad NH(CH^3)^2 \quad + \quad CH^3Cl$$

Trimethylamine hydrochloride. Dimethylamine.

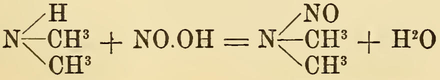
$$NH(CH^3)^2.HCl \quad = \quad NH^2(CH^3) \quad + \quad CH^3Cl$$

Dimethylamine hydrochloride. Methylamine.

Action of Nitrous Acid.—This acid converts primary amines into alcohols, water being formed and nitrogen disengaged.

$$NH^2(C^2H^5) + HO.NO = C^2H^5.OH + H^2O + N^2$$

With the same acid the secondary amines undergo a remarkable reaction, giving rise to *nitroso*-bases, or *nitroso*-amines, formed by the substitution of the group *nitrosyl*, NO, for the single atom of hydrogen in the ammonia residue NH (imidogen).



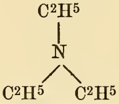
$$N\begin{cases}H\\CH^3\\CH^3\end{cases} + NO.OH = N\begin{cases}NO\\CH^3\\CH^3\end{cases} + H^2O$$

Dimethylamine. Nitrosodimethylamine.

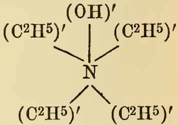
The nitrosamines are oleaginous liquids, insoluble in water; they can be distilled without decomposition, and, generally, are unalterable by either acids or alkalies. On the addition of phenol and sulphuric acid they produce intense colors. When their alcoholic solutions are treated with zinc and acetic acid, the nascent hydrogen evolved converts them into disubstituted hydrazines (see below).

In the amines, nitrogen acts as a triatomic element or trivalent; but it may assume two other atomicities. In sal-ammoniac, it is pentatomic, and it may play precisely the same part in the amines.

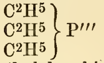

Ammonia.


Triethylamine.

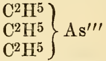

Ammonium chloride.


Tetrethylammonium hydroxide.

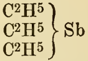
Related to the amines are various organic combinations which have the same constitution, but in which the nitrogen is replaced by an analogous element, such as phosphorus, arsenic, or antimony. A great number of these bodies have been discovered, of which the more important are


$\left.\begin{array}{r}C^2H^5\\C^2H^5\\C^2H^5\end{array}\right\}P'''$

Triethylphosphine.


$\left.\begin{array}{r}C^2H^5\\C^2H^5\\C^2H^5\end{array}\right\}As'''$

Triethylarsine.


$\left.\begin{array}{r}C^2H^5\\C^2H^5\\C^2H^5\end{array}\right\}Sb$

Triethylstibine.

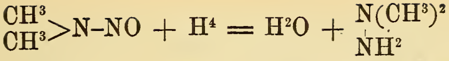
Hydrazines.—The nitrogenized bases that have just been considered belong either to the type NX^3 or to the type NX^5. A new class of compounds has recently been discovered, belonging to the type N^2X^4.

It is evident that the group NH^2 (amidogen) cannot exist in the free state. Hydrazine, discovered and described by Curtius, consists of two such groups, $NH^2–NH^2$. It is diamide (page 160).

Derivatives of hydrazine, in which one or two atoms of hydrogen are replaced by organic radicals, had previously been obtained by Fischer, who described *ethylhydrazine*, $NH^2–NH(C^2H^5)$, and *diethylhydrazine*

$$N(C^2H^5)^2–NH^2$$

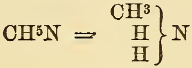
Dimethyl- and diethylhydrazine are formed by the action of nascent hydrogen on the corresponding nitroso compounds (page 531).



$$\begin{matrix}CH^3\\CH^3\end{matrix}\!>\!N\text{–}NO + H^4 = H^2O + \begin{matrix}N(CH^3)^2\\|\\NH^2\end{matrix}$$

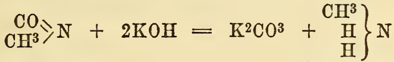
These hydrazines are closely related to the amines by their chemical and physical properties. They are very volatile liquids, having an ammoniacal odor, and soluble in water, alcohol, and ether.

METHYLAMINE.



$$CH^5N = \left.\begin{matrix}CH^3\\H\\H\end{matrix}\right\}N$$

This body may be prepared by boiling together potassium hydrate and methyl cyanate or cyanurate, and passing the vapors which are disengaged into dilute hydrochloric acid; methylamine hydrochloride is thus formed.



$$\begin{matrix}CO\\CH^3\end{matrix}\!>\!N + 2KOH = K^2CO^3 + \left.\begin{matrix}CH^3\\H\\H\end{matrix}\right\}N$$

Methyl cyanate. Methylamine.

The solution is evaporated to dryness, and the residue fused and allowed to cool; it is then mixed with double its weight of powdered quick-lime, and the mixture gently heated. The methylamine disengaged may be collected over mercury.

It is a colorless gas, which condenses to a light liquid at a temperature a few degrees below 0°. It is inflammable, and burns with a pale flame. Its odor is strongly ammoniacal and, at the same time, recalls that of the sea. It is the most soluble of all gases. 1 volume of water at 12.5° absorbs 1153 volumes of methylamine. The aqueous solution possesses the odor of the gas, a caustic taste, and a strong, alkaline reaction. Like ammonia, it precipitates the oxides from solutions of the metallic salts.

If a solution of methylamine be added to a solution of cupric sulphate, a light-blue precipitate is first formed, but disappears if an excess of methylamine be added, yielding a beautiful blue solution.

Methylamine Hydrochloride, $CH^5N.HCl$, differs from ammonium chloride by its solubility in boiling alcohol, from which it is deposited on cooling in large, colorless, deliquescent plates. With platinic chloride it forms a yellow precipitate, soluble in boiling water, from which it crystallizes in golden-yellow scales. It is a *chloroplatinate*, $(CH^5N.HCl)^2.PtCl^4$.

DIMETHYLAMINE, TRIMETHYLAMINE, TETRAMETHYLAMMONIUM HYDRATE.

These compounds were discovered by Hofmann.

Dimethylamine, $(CH^3)^2NH$, is a combustible gas which liquefies at 8°.

Trimethylamine, $(CH^3)^3N$, exists ready formed in the *Chenopodium vulvaria*, in the flowers of *Cratægus oxyacantha*, in herring-brine, in cod-liver oil, and in coal-gas tar. Vincent extracts large quatities of it from the residues of the distillation of fermented beet-juice.

At ordinary temperatures it is a gas; it liquefies at 9°. It is very soluble in water and in alcohol. It has a strong, ammoniacal odor, and an intense, alkaline reaction. It unites directly with methyl iodide, forming the iodide of tetramethylammonium.

$$(CH^3)^3N + CH^3I = (CH^3)^4NI$$

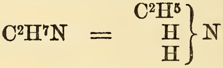
This iodide possesses all the appearances of a salt. It is soluble in water, and the solution treated with silver oxide yields silver iodide and tetramethylammonium hydroxide.

$$2(CH^3)^4NI + Ag^2O + H^2O = 2AgI + 2(CH^3)^4N.OH$$

The latter body is very soluble in water, and the solution is caustic. When submitted to dry distillation, it decomposes into trimethylamine and methyl alcohol.

$$(CH^3)^4N.OH = CH^3.OH + (CH^3)^3N$$

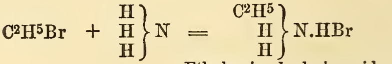
ETHYLAMINE.



$$C^2H^7N = \left.\begin{matrix} C^2H^5 \\ H \\ H \end{matrix}\right\} N$$

Ethylamine is prepared by a process analogous to that which yields methylamine; cyanate or cyanurate of ethyl is decomposed with boiling potassium hydroxide, and the vapors are condensed in very dilute hydrochloric acid. The dry ethylamine hydrochloride is then treated with quick-lime (A. Wurtz).

Another process has been indicated by Hofmann. It consists in causing ammonia to react upon the bromide or iodide of ethyl.



$$C^2H^5Br + \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N = \underbrace{\left.\begin{matrix} C^2H^5 \\ H \\ H \end{matrix}\right\} N.HBr}_{\text{Ethylamine hydrobromide.}}$$

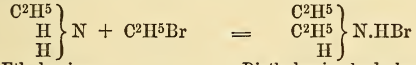
Ethylamine is a light, mobile, colorless liquid; it boils at 18.7°. Its odor is strong and exactly resembles that of ammonia.

Ethylamine is inflammable. It mixes with water, alcohol, and ether in all proportions. Its aqueous solution is caustic, and precipitates most of the metallic salts like solution of ammonia, and, like the latter, redissolves cupric hydrate, forming a blue liquid.

Ethylamine Hydrochloride, $C^2H^7N.HCl$.—This salt crystallizes in large, deliquescent plates, soluble in absolute alcohol. Its aqueous solution yields with platinic chloride a precipitate composed of yellow scales, soluble in boiling water, and constituting a chloro-platinate, $(C^2H^7N.HCl)^2.PtCl^4$.

DIETHYLAMINE, TRIETHYLAMINE, TETRETHYLAMMONIUM HYDROXIDE.

Diethylamine, $\left.\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right\}N$, was obtained by Hofmann by heating ethylamine with ethylbromide, and decomposing the diethylamine hydrobromide formed by an alkali.



$$\underset{\text{Ethylamine.}}{\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N} + C^2H^5Br = \underset{\text{Diethylamine hydrobromide.}}{\left.\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right\}N.HBr}$$

The free base is a liquid having an ammoniacal odor and boiling at 57.5°

Triethylamine may be formed by the action of ethyl bromide on diethylamine; triethylamine hydrobromide is formed, $\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}N.HBr$, from which alkalies cause the disengagement of triethylamine, a colorless liquid, boiling at 91°; its odor is ammoniacal and its reaction strongly alkaline.

Tetrethylammonium Hydroxide.—When a mixture of ethyl iodide and triethylamine is heated on a water-bath, the two bodies combine, forming the compound which Hofmann has named *tetrethylammonium iodide*.

$$\underset{\text{Ethyl iodide.}}{C^2H^5I} + \underset{\text{Triethylamine.}}{(C^2H^5)^3N} = \underset{\text{Tetrethylammonium iodide.}}{(C^2H^5)^4N.I}$$

When this is treated with silver oxide and water, it yields silver iodide and tetrethylammonium hydroxide, $(C^2H^5)^4N.OH$, a powerful base, which is crystallizable and soluble in water. Its alkalinity is comparable to that of potassium hydroxide.

ETHYLPHOSPHINES.

Primary, secondary, and tertiary ethylphosphines are known, as well as the compounds of tetrethylphosphonium.

$$\left.\begin{matrix} C^2H^5 \\ H \\ H \end{matrix}\right\} P''' \qquad \left.\begin{matrix} C^2H^5 \\ C^2H^5 \\ H \end{matrix}\right\} P''' \qquad \left.\begin{matrix} C^2H^5 \\ C^2H^5 \\ C^2H^5 \end{matrix}\right\} P''' \qquad \left.\begin{matrix} C^2H^5 \\ C^2H^5 \\ C^2H^5 \\ C^2H^5 \end{matrix}\right\} \overset{v}{P}-$$

Ethylphosphine. (Primary.) Diethylphosphine. (Secondary.) Triethylphosphine. (Tertiary.) Tetrethylphosphonium.

The first two were discovered by Hofmann. The third by Hofmann and Cahours, who obtained it by the action of phosphorus trichloride on zinc ethyl.

$$2PCl^3 + \underset{\text{Zinc ethyl.}}{3[Zn(C^2H^5)^2]} = \underset{\text{Triethylphosphine.}}{2[P(C^2H^5)^3]} + 3ZnCl^2$$

The operation must be conducted out of contact with the air, and the zinc ethyl must be diluted with anhydrous ether.

Monethylphosphine and diethylphosphine are produced when ethyl iodide is made to react upon phosphonium iodide, PH^4I, hydriodide of hydrogen phosphide (page 177), in presence of an excess of zinc oxide.

$$2C^2H^5I + 2PH^4I + ZnO = 2[(C^2H^5)H^2P.HI] + ZnI^2 + H^2O$$
$$2C^2H^5I + PH^4I + ZnO = (C^2H^5)^2HP.HI + ZnI^2 + H^2O$$

As both reactions are accomplished simultaneously, both phosphines are obtained at the same time. They are separated by the action of water upon the two hydriodides which are formed. That of monethylphosphine is decomposed by water, while that of diethylphosphine is only decomposed by the alkalies. It is sufficient then to add water to the product of the reaction in order to set free the monethylphosphine; when the latter has been completely expelled by heat, potassium hydrate added to the residue will cause the disengagement of the diethylphosphine. These operations should be conducted in a current of hydrogen.

Monethylphosphine, $(C^2H^5)H^2P$.—This is a colorless liquid, lighter than water, in which it is insoluble, and boiling at 25°. It has a most disagreeable odor. It takes fire on contact with chlorine or nitric acid. Its hydriodide crystallizes in beautiful, white, quadrangular tables.

Diethylphosphine, $(C^2H^5)^2HP$.—A colorless liquid, lighter than water, and boiling at 85°. It is very avid of oxygen, and sometimes takes fire spontaneously on contact with the air.

Triethylphosphine, $(C^2H^5)^3P$.—This is a colorless liquid, boiling at 127.5°. Density at 15°, 0.812. It combines directly with oxygen, forming *triethylphosphine oxide*, $(C^2H^5)^3PO$. The latter is a crystalline solid, very soluble in water and in alcohol. It distils at 240°.

When treated with ethyl iodide, triethylphosphine yields tetrethylphosphonium iodide, $(C^2H^5)^4PI$, a compound which may be obtained in beautiful crystals. When this iodide is acted upon by moist silver oxide, it furnishes the corresponding hydrate, which is an energetic base.

$$\underset{\text{Tetrethylphosphonium iodide.}}{2[(C^2H^5)^4PI]} + Ag^2O + H^2O = 2AgI + \underset{\text{Tetrethylphosphonium hydrate.}}{2[(C^2H^5)^4P.OH]}$$

PRODUCTS OF OXIDATION OF ETHYLPHOSPHINES.

When the ethylphosphines are treated with fuming nitric acid under suitable conditions, they act in a characteristic manner. Monethylphosphine is transformed into a dibasic acid, *monethylphosphinic;* diethylphosphine yields a monobasic acid, *diethylphosphinic.* Triethylphosphine yields an indifferent oxide, which has already been mentioned. Now, if it be remembered that under the same circumstances hydrogen phosphide furnishes phosphoric acid, it will be seen that the preceding oxidation compounds may be regarded as phosphoric acid, in which 1, 2, or 3 groups OH are replaced by as many ethyl groups.

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

Hydrogen phosphide.

$$PO\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$$

Phosphoric acid.

$$P\left\{\begin{matrix}C^2H^5\\H\\H\end{matrix}\right.$$

Monethylphosphine.

$$PO\left\{\begin{matrix}C^2H^5\\OH\\OH\end{matrix}\right.$$

Monethylphosphinic acid.

$$P\left\{\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right.$$

Diethylphosphine.

$$PO\left\{\begin{matrix}C^2H^5\\C^2H^5\\OH\end{matrix}\right.$$

Diethylphosphinic acid.

$$P\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.$$

Triethylphosphine.

$$PO\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.$$

Triethylphosphine oxide.

The compounds of arsenic and ethyl are entirely analogous to the phosphines; they have already been alluded to. Besides these, there are ethylic combinations corresponding to cacodyl and its derivatives.

SILICON-ETHYL.

$Si(C^2H^5)^4$

This compound is obtained by treating silicon chloride with zinc ethyl.

$$SiCl^4 + 2Zn(C^2H^5)^2 = 2ZnCl^2 + Si(C^2H^5)^4$$

Silicon-tetrethyl is a colorless, mobile liquid, not decomposed by water, combustible, burning with a brilliant white flame and production of white fumes of silicic acid. It is indifferent to the action of reagents, and acts in all points like a hydrocarbon, $C(C^2H^5)^4 = C^9H^{20}$, in which one atom of carbon is replaced by an atom of silicon. Its analogue, silicon-methyl, a liquid boiling at 30°, corresponds to tetramethylmethane, C^5H^{12}, a hydrocarbon boiling at 10°.

$Si(C^2H^5)^4$	$Si(CH^3)^4$	$C(CH^3)^4$
Silicon-ethyl.	Silicon-methyl.	Tetramethylmethane.

The following facts, discovered by Friedel, show the analogy between these compounds of silicon and the corresponding hydrocarbons:

When silicon-ethyl is submitted to the action of chlorine, an atom of hydrogen is exchanged for an atom of chlorine, and the chloride $Si(C^2H^4Cl)(C^2H^5)^3$ is formed. The latter is a liquid boiling at 185°, and can have its chlorine atom replaced by other atoms or groups, like the alcoholic chlorides. When distilled with potassium acetate, it yields the corresponding acetate, $(C^2H^5)^3Si{-}C^2H^4.O.C^2H^3O$, which may be saponified by potassium hydroxide, like an alcoholic acetate, the oxyacetyl group, OC^2H^3O, being replaced by a hydroxyl group. The alcohol so formed, $(C^2H^5)^3.Si{-}C^2H^4.OH$, has been named by Friedel siliconony1 hydroxide, on account of its analogy with nonyl hydroxide.

$SiC^8H^{19}.OH$	$C^9H^{19}.OH$
Siliconony1 hydroxide.	Nonyl hydroxide.

It is a colorless liquid, insoluble in water, and boiling at 190°.

ORGANO-METALLIC COMPOUNDS.

ZINC-ETHYL.

$Zn''(C^2H^5)^2$

One of the more important of the compounds formed by the union of the metals with alcoholic radicals is zinc-ethyl, discovered by Frankland.

It is prepared by heating ethyl iodide with zinc-turnings and a small quantity of sodium on a water-bath. Zinc iodide and zinc-ethyl are formed. When the reaction is terminated, the product is distilled and that portion collected which passes above 115°. All these operations are conducted in an atmosphere of carbon dioxide.

Zinc-ethyl is a colorless, mobile, and highly-refractive liquid. It has a peculiar, penetrating, and very disagreeable odor. It boils at 118°. It takes fire spontaneously on contact with the air, burning with a green flame, and producing white fumes of zinc oxide.

If water be added to a small quantity of zinc-ethyl contained in a tube, a brisk effervescence at once takes place, and a white deposit is formed. The gas is ethane, and the deposit is zinc hydrate.

$$Zn(C^2H^5)^2 + 2H^2O = Zn(OH)^2 + 2C^2H^6$$

Zinc-ethyl will enter into double decompositions, and is much used in the synthesis of organic substances.

By the action of phosphorus trichloride on this body, Hofmann and Cahours obtained triethylphosphine and zinc chloride.

There is a *zinc-methyl*, $Zn(CH^3)^2$, corresponding to zinc-ethyl.

MERCUR-METHYL AND MERCUR-ETHYL.

These compounds were obtained by Frankland and Duppa, by the action of methyl and ethyl iodides on sodium amalgam, in presence of a small quantity of acetic ether.

Mercur-ethyl is a colorless, inflammable liquid, insoluble in water. Density, 2.44. Boiling-point, 158–160°. It is one of the most dangerous poisons known. The inhalation of its vapor, even in small quantity, will produce fatal poisoning.

Chlorine, bromine, and iodine instantly decompose mercurethyl with formation of a compound of mercur-monethyl.

$$\underset{\text{Mercur-ethyl.}}{Hg\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} + I^2 = \underset{\text{Ethyl iodide.}}{C^2H^5I} + \underset{\text{Mercur-monethyl iodide.}}{Hg\left\{\begin{matrix}C^2H^5\\I\end{matrix}\right.}$$

STANNETHYLS.

The discovery of the numerous compounds of tin and ethyl is due to Löwig. Their history has been completed by Frankland, Cahours, and Riche.

As the nomenclature and constitution of the stannethyls have already been indicated (page 457), we need only consider a few of these interesting compounds.

Stannodiethyl, $Sn(C^2H^5)^2$.—The iodide of this compound is obtained when ethyl iodide is heated with tin-filings to about 180°. This iodide, $Sn(C^2H^5)^2I^2$, purified by crystallization in alcohol, furnishes free stannodiethyl when its solution is treated with zinc, which removes the iodine.

Stannodiethyl is an oily, yellow liquid, which does not volatilize without decomposition. When heated to 150° it begins to boil, but the greater part of it is decomposed into stannotetrethyl and tin.

$$2[Sn(C^2H^5)^2] = Sn(C^2H^5)^4 + Sn$$

The iodide of stannodiethyl crystallizes in pale yellow needles. In its solution, the alkalies precipitate the oxide $Sn(C^2H^5)^2O$, which forms an amorphous, white precipitate, insoluble in water and alcohol, but soluble in the alkalies and acids with which it forms salts.

Stannotriethyl or **Sesquistannethyl,** $Sn^2(C^2H^5)^6 = (C^2H^5)^3Sn\text{–}Sn(C^2H^5)^3$.—This is formed, together with the preceding compound, by the reaction of ethyl iodide on an alloy of tin and sodium. It is separated by fractional distillation; it boils between 265 and 270°. It plays the part of a radical and combines directly with oxygen. The oxide contains $Sn^2(C^2H^5)^6O = [Sn(C^2H^5)^3]^2O$. It combines with the elements of water, forming a hydrate, $Sn(C^2H^5)^3.OH$, crystallizable in prisms. These crystals are fusible at 44°. The oxide distils at 272°. It reacts with the acids to form crystallizable salts.

$$\underset{\text{Stannotriethyl oxide.}}{[Sn(C^2H^5)^3]^2O} + 2HNO^3 = \underset{\text{Stannotriethyl nitrate.}}{2[Sn(C^2H^5)^3.NO^3]} + H^2O$$

The iodide, $Sn(C^2H^5)^3I$, is a liquid having a mustard-like odor, and distilling without decomposition towards 235–238°. Density at 15°, 1.833.

Stannotetrethyl, $Sn(C^2H^5)^4$.—Colorless liquid, almost odorless, and boiling at 181°. Density, 1.187. It is formed by the action of zinc ethyl on stannodiethyl iodide.

$$\underset{\text{Stannnodiethyl iodide.}}{Sn(C^2H^5)^2I^2} + \underset{\text{Zinc-ethyl.}}{Zn(C^2H^5)^2} = \underset{\text{Stannotetrethyl.}}{Sn(C^2H^5)^4} + ZnI^2$$

It is a saturated compound, and does not enter into combination, but by the action of energetic reagents it yields compounds of stannodiethyl or stannotriethyl. Thus, with iodine, the following reaction takes place:

$$Sn(C^2H^5)^4 + I^2 = Sn(C^2H^5)^3I + C^2H^5I$$

VOLATILE FATTY ACIDS DERIVED FROM THE ALCOHOLS.

Modes of Formation and Constitution.—These acids result from the oxidation of the alcohols of which the principal compounds have been described. They are formed in a great number of reactions, and many of them exist already formed in nature, either in the free state or in combination in neutral fatty compounds, that is, the oils and fats.

Their composition is expressed by the general formula $C^nH^{2n}O^2$; they contain one more atom of oxygen and two atoms of hydrogen less than their corresponding alcohols.

Their principal modes of formation are as follows:

1. By oxidation of an alcohol:

$$\underset{\text{Methyl alcohol.}}{CH^4O} + O^2 = \underset{\text{Formic acid.}}{CH^2O^2} + H^2O$$

2. By oxidation of an aldehyde:

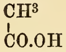
$$\underset{\text{Aldehyde.}}{C^2H^4O} + O = \underset{\text{Acetic acid.}}{C^2H^4O^2}$$

3. By the decomposition of an organic cyanide with boiling potassium hydroxide:

$$\underset{\text{Methyl cyanide.}}{\begin{matrix}CH^3\\|\\CN\end{matrix}} + KOH + H^2O = \underset{\text{Potassium acetate.}}{\begin{matrix}CH^3\\|\\CO.OK\end{matrix}} + NH^3$$

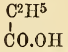
The acetic acid is formed in this last reaction, by the union of the carbon of the cyanogen group with the oxygen of both the potassium hydroxide and the water, the hydrogen of these two bodies combining with the nitrogen of the cyanogen to form ammonia. It may then be admitted that acetic acid contains a radical carbonyl, CO, united on the one hand with a methyl group (that of the methyl cyanide), and on the other with a hydroxyl group, OH.

The other acids of the series possess an analogous constitution.



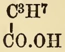
$$\begin{array}{l} CH^3 \\ | \\ CO.OH \end{array}$$

Acetic acid.



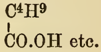
$$\begin{array}{l} C^2H^5 \\ | \\ CO.OH \end{array}$$

Propionic acid.



$$\begin{array}{l} C^3H^7 \\ | \\ CO.OH \end{array}$$

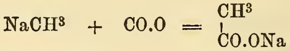
Butyric acid.



$$\begin{array}{l} C^4H^9 \\ | \\ CO.OH \text{ etc.} \end{array}$$

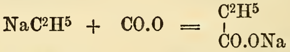
Valeric acid.

4. A method of synthesis, discovered by Wanklyn, furnishes a direct support to this theory of the constitution of the fatty acids. That chemist realized the synthesis of acetic and propionic acids by passing a current of carbonic acid gas over sodium-methyl and sodium-ethyl, organo-metallic compounds which result from the action of sodium upon zinc-methyl and zinc-ethyl.



$$NaCH^3 + CO.O = \begin{array}{l} CH^3 \\ | \\ CO.ONa \end{array}$$

Sodium-methyl. Sodium acetate.

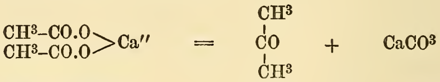


$$NaC^2H^5 + CO.O = \begin{array}{l} C^2H^5 \\ | \\ CO.ONa \end{array}$$

Sodium-ethyl. Sodium propionate.

General Properties.—1. The volatile fatty acids of the series $C^nH^{2n}O^2$ are monobasic; each contains one atom of hydrogen which may be replaced by an equivalent quantity of a metal.

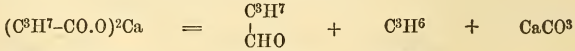
2. When submitted to dry distillation, many of their salts yield a ketone and a carbonate.



$$\begin{array}{l} CH^3\text{–}CO.O \\ CH^3\text{–}CO.O \end{array}\!\!>Ca'' = \begin{array}{l} CH^3 \\ | \\ CO \\ | \\ CH^3 \end{array} + CaCO^3$$

Calcium acetate. Acetone. Calcium carbonate.

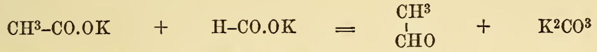
3. The same reaction may produce an aldehyde and a hydrocarbon of the series C^nH^{2n} (Chancel).



$$(C^3H^7\text{–}CO.O)^2Ca = \begin{array}{l} C^3H^7 \\ | \\ CHO \end{array} + C^3H^6 + CaCO^3$$

Calcium butyrate. Butaldehyde. Propylene.

4. When a mixture of a salt of a fatty acid and a formate is subjected to dry distillation, the principal product of the reaction is an aldehyde (Piria).



$$CH^3\text{-}CO.OK + H\text{-}CO.OK = \begin{array}{c}CH^3\\|\\CHO\end{array} + K^2CO^3$$

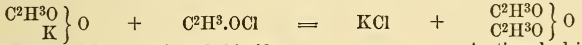
Potassium acetate. Potassium formate. Aldehyde.

5. The fatty acids are converted into chlorides by the action of phosphorus pentachloride, or oxychloride (Gerhardt).

$$C^2H^3O.OK + PCl^5 = C^2H^3O.Cl + POCl^3 + KCl$$

Potassium acetate. Acetyl chloride. Phosphorus oxychloride.

6. By the action of these chlorides upon the salts of the fatty acids, the anhydrides of the acids are formed (Gerhardt).



$$\left.\begin{array}{r}C^2H^3O\\K\end{array}\right\}O + C^2H^3.OCl = KCl + \left.\begin{array}{r}C^2H^3O\\C^2H^3O\end{array}\right\}O$$

Potassium acetate. Acetyl chloride. Acetic anhydride.

7. When subjected to the action of phosphoric anhydride, the ammonium salts of these acids lose $2H^2O$ and are converted into nitriles or cyanogen ethers (Dumas, Malaguti and Le Blanc, Frankland and Kolbe).

$$\begin{array}{l}CH^3\\|\\CO.O(NH^4)\end{array} = 2H^2O + \begin{array}{l}CH^3\\|\\CN\end{array}$$

Ammonium acetate. Acetonitrile. (Methyl cyanide.)

FORMIC ACID.

CH^2O^2

This acid, which was discovered by S. Fischer in 1760, in red ants, is formed in a great number of reactions, particularly in the oxidation of methyl alcohol, in the decomposition of hydrocyanic acid by acids or alkalies, in the distillation of oxalic acid, and in the oxidation of many organic matters, such as starch, sugar, etc. Berthelot achieved its direct synthesis by heating carbon monoxide for a long time to 100° in sealed flasks containing a concentrated solution of potassium hydrate.

$$CO + KOH = HCO.OK$$

Potassium formate.

Preparation.—Formic acid is best prepared by heating oxalic acid with glycerol; the latter is found unchanged after the reaction, but the oxalic acid is decomposed according to the equation $C^2O^4H^2 = H.COOH + CO^2$.

Equal weights of the two substances are heated to about 110° in a retort connected with a condenser; carbon dioxide is disengaged and dilute formic acid distils over. When the action has ceased, a fresh quantity of oxalic acid is added and the heating continued; the same decomposition takes place, but a more concentrated formic acid (56 per cent.) collects in the receiver. As the glycerol does not suffer a permanent change, the operation may be made continuous by adding fresh quantities of oxalic acid to the retort.

Anhydrous formic acid is prepared by decomposing the dry lead salt in a current of hydrogen sulphide.

$$(HCOO)^2Pb + H^2S = 2HCOOH + PbS$$

Properties.—Formic acid is a colorless liquid, having a pungent odor and a very acid taste. It boils at 101°, and solidifies to a crystalline mass at 8.5°. It mixes with water in all proportions.

If an excess of sulphuric acid be added to a small quantity of formic acid contained in a test-tube, and a gentle heat be applied, a regular disengagement of gas will take place; it may be ignited at the mouth of the tube, and will burn with a blue flame. It is carbon monoxide, formed according to the equation $CH^2O^2 = CO + H^2O$.

If formic acid be added to solution of silver nitrate, and the liquid heated, it soon becomes clouded; silver is precipitated, and carbon dioxide disengaged. The formic acid becomes oxidized in reducing the silver nitrate.

$$CH^2O^2 + O = CO^2 + H^2O$$

Chlorine determines an analogous decomposition.

$$CH^2O^2 + Cl^2 = CO^2 + 2HCl$$

Formates.—Formic acid is an energetic acid, perfectly neutralizing the bases. It is monobasic; one of its hydrogen atoms can be replaced by an equivalent quantity of metal. The formates are soluble; the most characteristic are *cupric formate*, $Cu(CHO^2)^2 + 4H^2O$, which crystallizes in magnificent, oblique rhombic prisms, and lead formate, $Pb(CHO^2)^2$, which forms long, colorless needles, slightly soluble in cold water.

Ammonium formate, which is obtained by saturating formic acid with ammonia, crystallizes in prisms which are very soluble in water. When quickly heated to about 200°, it breaks up into hydrocyanic acid (formonitrile) and water (Pelouze).

$$(NH^4)CHO^2 = 2H^2O + CNH$$

FORMALDEHYDE.

$CH^2O = H\text{-}CHO$

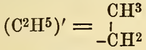
Hofmann obtained this body by the slow combustion of methyl alcohol, brought about by a spiral of platinum wire.

$$CH^4O + O = H^2O + CH^2O$$

It is also formed in the distillation of barium and calcium formates. Formaldehyde is known only as a vapor at high temperatures, and in aqueous solution. The latter has a pungent odor and powerful antiseptic properties; "formalin" is a 40 per cent. solution of it used as an antiputrescent and caustic. On evaporation of its aqueous solution, formaldehyde becomes polymerized, an amorphous solid called paraformaldehyde being produced. Dilute solutions of alkaline hydroxides convert the aldehyde into *formose*, a mixture of polymers containing *acrose*, $(CH^2O)^6$, related to the sugars.

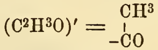
ACETIC COMBINATIONS.

It may be assumed that these compounds contain the monatomic radical acetyl $(C^2H^3O)' = (CH^3\text{-}CO)'$, which may be regarded as oxidized ethyl.



$$(C^2H^5)' = \begin{array}{c} CH^3 \\ | \\ -CH^2 \end{array}$$

Ethyl.



$$(C^2H^3O)' = \begin{array}{c} CH^3 \\ | \\ -CO \end{array}$$

Acetyl.

Diacetyl contains twice this radical, aldehyde is the hydride, and acetic acid the hydroxide. Besides these, there are known the oxide and chloride of acetyl, methyl acetyl (acetone), acetyl ammonia or acetamide, etc.

The following formulæ indicate the relations of these bodies:

$C^2H^3O.C^2H^3O$

Diacetyl.

$C^2H^3O.H$

Acetyl hydride (aldehyde).

$C^2H^3O.Cl$

Acetyl chloride.

$C^2H^3O.CH^3$

Acetyl methylide (acetone).

$C^2H^3O.OH$

Acetyl hydrate (acetic acid).

$(C^2H^3O)^2O$

Acetyl oxide (acetic anhydride).

$$\left.\begin{array}{r} C^2H^3O \\ H \\ H \end{array}\right\} N$$

Acetamide.

ACETIC ACID.

$C^2H^4O^2$

Acetic acid is the acid of vinegar. It is the product of the oxidation of alcohol. It is formed in a number of other reactions, among which we may mention the oxidation of aldehyde, the decomposition of methyl cyanide by potassium hydrate, the action of carbon dioxide on sodium-methyl, and the dry distillation of a great number of organic substances, such as wood, starch, gum, sugar, etc.

Preparation.—The large quantities of acetic acid employed in the arts are obtained by the destructive distillation of wood.

The operation is conducted in large iron cylinders, heated directly by a fire (Fig. 123). The products of the distillation consist of liquids and gases. The liquids are condensed in a large worm, *tt*, cooled by a continual circulation of cold water through surrounding pipes *mm;* the gases are conducted back to the fire-grate by the pipe *h*. The condensed product consists of an aqueous portion and of tar. The greater part of the latter is separated by a new distillation; the first portions which pass contain wood-spirit, after which acetic acid distils. The acid liquid is neutralized by lime, and the calcium acetate formed is converted into sodium acetate by adding a solution of sodium sulphate. The liquid, separated by filtration from the calcium sulphate, yields on evaporation sodium acetate, still colored brown by tarry matters. The latter are destroyed by *frying* the salt, that is, by heating it for some time to 250°, a temperature which carbonizes the tar but does not affect the sodium acetate. The mass is then exhausted with water, the solution filtered, concentrated, and crystallized. Crystals of pure sodium acetate are thus obtained, a salt which was formerly called *pyrolignite of soda*. Acetic acid is pre-

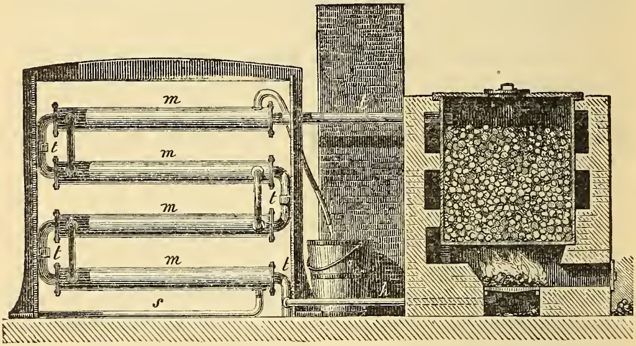


FIG. 127.

pared by drying this salt and distilling it with $\frac{3}{5}$ its weight of concentrated sulphuric acid.

Or the dry salt may be decomposed by an exact quantity of sulphuric acid. The acetic acid which separates from the sodium sulphate may then be decanted, and cooled in a freezing mixture. The portion remaining liquid is separated and the solid mass constitutes pure acetic acid.

Vinegar.—Vinegar is the product of the acid fermentation of wine and other alcoholic liquids. The following process is largely employed for the conversion of wine into vinegar. It is the Orleans process. A small quantity of warm vinegar is first introduced into large vats, which have already been used for the operation and are impregnated with the peculiar ferment formed; quantities of wine are then added at intervals of several days, the vats being maintained at a temperature between 24 and 27°. In a fortnight, the acetification is complete, and a portion of the vinegar is withdrawn and replaced by a new quantity of wine which also becomes converted into vinegar. The process is thus continuous. Under these circumstances, the alcohol is converted into acetic acid by the influence of a peculiar ferment that is called *mother of vinegar.* It is a vegetable product, a mycoderm (*Mycoderma aceti*), which appears on the surface of the liquid, where it absorbs oxygen from the air and subsequently cedes it to the alcohol (Pasteur). Its action may be compared to that of platinum black.

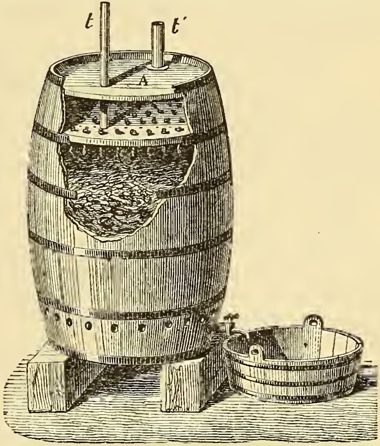


Fig. 128.

By another process, a mixture of weak alcohol, water, and albuminoid matter (the juice of potatoes, beets, etc.), containing the elements necessary for the production of the ferment, is allowed to trickle over beech-wood shavings. The latter, which have been previously steeped in strong vinegar, are contained in a large cask, A (Fig. 124), where they rest upon a double bottom perforated with holes. Tubes, *tt*, pass through the upper portion, maintaining a current of air which enters at the lower portion of the cask. Under these conditions, the liquid, which spreads over the shavings and exposes a considerable surface to the air, becomes oxidized with such energy that the temperature soon rises to 30°; a second passage of the liquid through the casks completes the acetification.

Properties of Acetic Acid.—Acetic acid is solid below 17°, and crystallizes in large plates. It boils at 118°. Its density at 0° is 1.0801. Its odor is pungent and acid. It is very corrosive. It mixes with water and alcohol in all proportions, and when it is added to water there is a contraction in volume. The maximum contraction, and consequently the maximum density of aqueous acetic acid, corresponds to a mixture containing $C^2H^4O^2 + H^2O$.

Vapor of acetic acid passed through an incandescent porcelain tube yields gases and deposits carbon, at the same time forming small quantities of acetone, benzene, phenol, and naphthalene (Berthelot).

Phosphorus pentachloride converts acetic acid into acetyl chloride, with formation of hydrochloric acid and phosphorus oxychloride.

$$\underset{\text{Acetic acid.}}{C^2H^3O.OH} + PCl^5 = \underset{\text{Acetyl chloride.}}{C^2H^3O.Cl} + HCl + POCl^3$$

If a mixture of small quantities of potassium acetate and arsenious oxide be heated in a test-tube, dense white vapors having an intense and disagreeable odor of garlic will be disengaged.

This experiment permits the detection of minute traces of acetic acid; if the latter exist in the free state in the liquid, its potassium compound must first be formed. The white vapor disengaged is due to a body formerly known as *fuming liquor of Cadet* (see page 496).

ACETATES.

The more important neutral acetates have the composition $R'(C^2H^3O^2)$ or $R''(C^2H^3O^2)^2$, according as the metal which replaces the basic hydrogen of the acetic acid is univalent or bivalent. There are many basic acetates.

Potassium Acetate, $KC^2H^3O^2$.—This is prepared by saturating acetic acid with potassium carbonate and evaporating to dryness. It is thus obtained in crystalline, very deliquescent laminæ. It melts at 292°, and is very soluble in water.

Sodium Acetate, $NaC^2H^3O^2 + 3H^2O$.—This salt is obtained on a large scale in the arts in the manufacture of acetic acid. It was formerly called *pyrolignite of soda.* It crystallizes in large, oblique rhombic prisms, which are very soluble in water, and effloresce in dry air.

Acetates of Lead.—Neutral lead acetate, $Pb(C^2H^3O^2)^2 + 3H^2O$, known also as *sugar of lead*, is made by neutralizing acetic acid with litharge. It crystallizes in transparent, efflorescent, oblique rhombic prisms, having a sweet and astringent taste. It dissolves in half its weight of cold water, and in 8 parts of alcohol. It melts in its water of crystallization at 75.5°.

The neutral solution of lead acetate dissolves oxide of lead, forming different basic salts, according to the proportion of oxide dissolved. The more important of these are a *dibasic acetate*, $Pb(C^2H^3O^2)^2 + PbO + 4H^2O$, and a tribasic acetate, $Pb(C^2H^3O^2)^2 + 2PbO + nH^2O$. These two salts are generally formed simultaneously when a solution of lead acetate is boiled with litharge. The solution thus obtained is used in medicine as *Goulard's solution.* If a few drops of it be added to ordinary river or well water, a cloud is produced, owing to the formation of lead sulphate and carbonate.

If carbonic acid gas be passed into a solution of the subacetate of lead, a deposit of lead carbonate is formed. In this reaction, which serves for the preparation of white lead by the Clichy method, the excess of lead is removed from the subacetate by the carbonic acid, neutral acetate being formed and remaining in solution.

Acetates of Copper.—The *neutral acetate* $Cu(C^2H^3O^2)^2 + H^2O$, is prepared by double decomposition by mixing hot solutions of sodium acetate and cupric sulphate. The cupric acetate is deposited on cooling in beautiful, oblique rhombic prisms of a deep bluish-green color. They dissolve in 5 times their weight of boiling water. The dilute aqueous solution is decomposed by boiling, a tribasic acetate being formed, while acetic acid is set free.

When cupric acetate is heated, it first loses its water of crystallization, and decomposes when the temperature reaches 240 or 250°, disengaging acetic acid, acetone, and carbon dioxide

The residue is finely-divided copper. The product of the distillation is a blue liquid, which, when rectified, yields colorless acetic acid mixed with a small quantity of acetone. It was formerly called *radical vinegar.*

The name *verdigris* is applied to a basic acetate of copper consisting mostly of a dibasic acetate, $Cu(C^2H^3O^2)^2 + CuO + 6H^2O$. Verdigris is prepared by exposing to the air copper sheets piled up in layers with the pulp of grapes. In a few weeks the metal becomes covered with bluish crusts of verdigris, which are scraped off and delivered to commerce in the form of light-blue balls. The alcohol, formed by the fermentation of the sugar contained in the grape-pulp, becomes oxidized by the air and is converted into acetic acid, and under the influence of the latter, the copper itself absorbs oxygen. Water and copper basic acetate are thus formed.

Ferric Acetate, $Fe(C^2H^3O^2)^3$.—The aqueous solution of this salt possesses a blood-red color. Boiling decomposes it, precipitating ferric hydroxide and liberating acetic acid. The salt is largely used as a mordant in dyeing.

Silver Acetate, $AgC^2H^3O^2$.—This salt, which is but slightly soluble in water, is precipitated when concentrated solutions of sodium acetate and silver nitrate are mixed. It is deposited from boiling water in brilliant, pearly, flexible plates, which darken on exposure to light.

Ammonium Acetate, $(NH^4)C^2H^3O^2$.—When acetic acid is saturated by a current of ammonia gas, this salt is obtained as a deliquescent, crystalline mass. It is very soluble in water and in alcohol. When heated, it first loses ammonia, then acetic acid, and acetamide finally distils.

$$\underset{\text{Ammonium acetate.}}{NH^4.C^2H^3O^2} = H^2O + \underset{\text{Acetamide.}}{C^2H^3O.NH^2}$$

When distilled with phosphoric anhydride, ammonium acetate yields methyl cyanide, or acetonitrile.

$$NH^4.C^2H^3O^2 = C^2H^3N + 2H^2O$$

Ethyl Acetate, $C^2H^5.C^2H^3O^2$, ordinarily known as acetic ether, is prepared by distilling a mixture of alcohol, sulphuric acid, and potassium or sodium acetate: ethyl acetate passes over, together with a certain quantity of alcohol which escapes the reaction. It is purified by agitation with a solution of calcium chloride, and the ether which floats is decanted, dried over calcium chloride, and rectified on the water bath.

It is a colorless liquid having a very agreeable, ethereal odor. It boils at 77°. Density at 0°, 0.9105. It is but slightly soluble in water, but dissolves in all proportions in alcohol and ether. Like all compound ethers, it is readily decomposed by potassium hydroxide.

$$C^2H^5.C^2H^3O^2 + KOH = KC^2H^3O^2 + C^2H^5.OH$$

Ammonia converts it into acetamide and alcohol.

$$C^2H^3O.OC^2H^5 + NH^3 = C^2H^5.OH + C^2H^3O.NH^2$$

It undergoes a remarkable reaction with sodium, which dissolves in it, forming sodium ethylate and the compound $C^6H^9NaO^3$.

$$2[C^2H^3O.OC^2H^5] + Na^2 = NaO.C^2H^5 + C^6H^9NaO^3 + H^2$$

The body $C^6H^9NaO^3$ is the sodium compound of *acetoacetic ether*, $C^6H^{10}O^3 = C^2H^2(C^2H^3O)O{-}OC^2H^5$, which is derived from acetic ether, $C^2H^3O{-}OC^2H^5$, by the substitution of an acetyl group, C^2H^3O, for one atom of hydrogen in the radical acetyl. Free acetoacetic ether may be obtained by the action of dilute hydrochloric acid upon the sodium compound $C^6H^9NaO^3$. It is a colorless liquid having an agreeable odor, and boiling at 182°. Density at 15°, 1.03. Sodium acetoacetic ether is extensively used in organic synthesis: it reacts readily with many halogen compounds, such as ethyl iodide, thus:

$$\underbrace{CH^3{-}CO{-}CHNa{-}COO.C^2H^5}_{\text{Sodium acetoacetic ether.}} + C^2H^5I =$$

$$\underbrace{CH^3{-}CO{-}CH(C^2H^5){-}COO.C^2H^5}_{\text{Ethyl acetoacetic ether.}} + NaI$$

The hydrogen of the CH group in the latter compound can be successively replaced by sodium and an alkyl group, thus:

$$\underbrace{CH^3{-}CO{-}CNa(C^2H^5){-}COO.C^2H^5}_{\text{Sodium ethyl acetoacetic ether.}} \text{ and } \underbrace{CH^3{-}CO{-}C(C^2H^5)^2{-}COO.C^2H^5}_{\text{Diethyl acetoacetic ether.}}$$

SUBSTITUTION PRODUCTS OF ACETIC ACID.

Three chlorinated acids are derived from acetic acid:

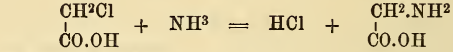
Monochloracetic acid	$C^2H^3ClO^2$
Dichloracetic acid	$C^2H^2Cl^2O^2$
Trichloracetic acid	$C^2HCl^3O^2$

Monochloracetic acid is formed when a current of chlorine is passed into acetic acid heated to 100°, and containing a small quantity of iodine.

Monochloracetic acid is solid, and crystallizes in deliquescent, rhomboidal tables or in prisms. It boils between 185 and 187.8°. It is very corrosive. It is converted into glycollic acid when heated with an excess of potassium hydrate.

$$\underset{\text{Potassium monochloracetate.}}{KC^2H^2ClO^2} + KOH = \underset{\text{Potassium glycollate.}}{KC^2H^2(OH)O^2} + KCl$$

Ammonia converts it into amidoacetic acid, $C^2H^2(NH^2)O.OH$.



$$\underset{\text{Monochloracetic acid.}}{\begin{matrix}CH^2Cl\\ | \\ CO.OH\end{matrix}} + NH^3 = HCl + \underset{\text{Glycocoll.}}{\begin{matrix}CH^2.NH^2\\ | \\ CO.OH\end{matrix}}$$

Monochloracetic acid. Glycocoll.

Trichloracetic acid, $C^2HCl^3O^2$, a very important compound in the history of the science, was discovered by Dumas in 1840. It was then one of the most remarkable examples of a body formed by substitution, and a comparison of its properties with those of acetic acid led Dumas to announce the first idea of chemical types.

It is obtained by exposing acetic acid to the action of a large excess of chlorine in direct sunlight; more conveniently by oxidizing chloral with concentrated nitric acid (page 556).

It forms transparent and deliquescent crystals, fusible at 52.3°, and boiling between 195 and 200°.

Its aqueous solution regenerates acetic acid by the action of sodium amalgam, an interesting reaction, since it furnished one of the first examples of *inverse substitution* (Melsens), as the replacement of chlorine by hydrogen is called.

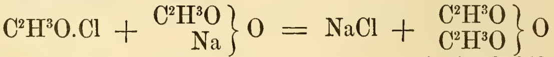
When boiled with potassium hydrate, trichloracetic acid furnishes potassium carbonate and chloroform.

$$C^2HCl^3O^2 = CHCl^3 + CO^2$$

ACETIC ANHYDRIDE.

$(C^2H^3O)^2O$

This important body, discovered by Gerhardt in 1852, is prepared by the action of one part of phosphorus oxychloride on three parts of dry sodium acetate. In this operation, acetyl chloride is first formed, and this reacts upon an excess of sodium acetate, producing sodium chloride and acetyl acetate, or acetic anhydride.



$$\underset{\text{Acetyl chloride.}}{C^2H^3O.Cl} + \underset{\text{Sodium acetate.}}{\left.\begin{matrix}C^2H^3O\\ Na\end{matrix}\right\}O} = NaCl + \underset{\text{Acetic anhydride.}}{\left.\begin{matrix}C^2H^3O\\ C^2H^3O\end{matrix}\right\}O}$$

Acetyl chloride. Sodium acetate. Acetic anhydride.

Acetic anhydride is a colorless, mobile liquid, having a strong odor of acetic acid. It boils at 138°. When thrown into water, it sinks to the bottom, and, absorbing one molecule of water, is converted into acetic acid, which dissolves. It acts upon many other substances containing the hydroxyl group, forming acetyl derivatives. For example:

$$2C^2H^5OH + (C^2H^3O)^2O = H^2O + 2C^2H^5.C^2H^3O^2$$

ALDEHYDE, OR HYDRIDE OF ACETYL.

$$C^2H^4O = CH^3\text{–}CHO$$

This body was discovered by Döbereiner in 1821; its composition and principal properties were studied by Liebig.

Preparation.—Aldehyde is prepared by oxidizing alcohol by heating it with manganese dioxide and dilute sulphuric acid, or better, with potassium dichromate and sulphuric acid. The vapors disengaged are condensed in a well-cooled receiver. The distilled liquid is rectified over calcium chloride, only the more volatile portion being collected. This is mixed with twice its volume of ether, and the ethereal solution saturated with ammonia gas. Crystals are deposited which constitute a combination of aldehyde with ammonia, and the aldehyde is obtained from them by adding a quantity of sulphuric acid exactly sufficient to form ammonium sulphate with the ammonia; a gentle heat is applied, and the aldehyde vapor is passed through a tube filled with calcium chloride, and finally condensed in a well-cooled receiver (Liebig).

Properties.—Aldehyde is a colorless, very mobile liquid, having a penetrating and somewhat suffocating odor. It boils at 21°. It mixes in all proportions with water, alcohol, and ether.

It combines with ammonia, forming aldehyde-ammonia (Liebig).

$$C^2H^4O.NH^3 = C^2H^2O.NH^4$$

It unites with the alkaline acid-sulphites, forming crystallizable combinations.

It is readily oxidized, being transformed into acetic acid.

$$C^2H^4O + O = C^2H^4O^2$$

If some aldehyde and a few drops of ammonia be added to a solution of silver nitrate, and a gentle heat be applied, the liquid soon becomes clouded, and the sides of the vessel containing it are covered with a brilliant deposit of metallic silver.

By the action of sodium amalgam and water, aldehyde fixes two atoms of hydrogen, and is converted into alcohol (A. Wurtz). $C^2H^4O + H^2 = C^2H^6O$.

When hydrochloric gas is passed into a mixture of aldehyde and absolute alcohol, monochlorether is formed.

$$C^2H^4O + C^2H^5.OH + HCl = H^2O + \begin{matrix} C^2H^4Cl \\ C^2H^5 \end{matrix}\!\!>O$$

Monochlorether.

Chlorine converts aldehyde into acetyl chloride and then into butyl chloral.

$$C^2H^3O.H \quad + \quad Cl^2 \quad = \quad C^2H^3O.Cl \quad + \quad HCl$$

Acetyl chloride.

Phosphorus pentachloride converts aldehyde into *ethylidene chloride*, $C^2H^4Cl^2$, thus:

$$\begin{matrix} CH^3 \\ | \\ CHO \end{matrix} \quad + \quad PCl^5 \quad = \quad \begin{matrix} CH^3 \\ | \\ CHCl^2 \end{matrix} \quad + \quad POCl^3$$

Aldehyde. Ethylidene chloride.

By the action of hydrochloric acid diluted with twice its volume of water, aldehyde doubles its molecule and is converted into a thick, colorless, neutral body, boiling at 95° in a vacuum; it is soluble in water and reduces ammoniacal silver nitrate. This body is *aldol*, $C^4H^8O^2$ (A. Wurtz).

When heated with ordinary hydrochloric acid, aldehyde gives crotonic aldehyde (Kekulé).

$$2C^2H^4O \quad = \quad H^2O \quad + \quad C^4H^6O$$

Aldehyde. Crotonic aldehyde.

The same transformation takes place when aldehyde is heated to 100° with a small quantity of zinc chloride and a trace of water.

An important derivative of aldehyde, known as *acetaldoxime*, results from the action of hydroxylamine upon aldehyde.

$$CH^3CHO \quad + \quad H^2NOH \quad = \quad CH^3CHNOH \quad + \quad H^2O$$

Hydroxylamine. Acetaldoxime.

This body represents a numerous class, the *oximes*, which are formed by the reaction of hydroxylamine with bodies containing the carbonyl group.

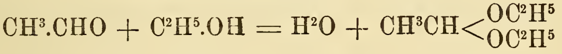
Phenylhydrazine, $H^2N\text{–}NH.C^6H^5$ (page 676), is another important reagent for compounds containing the carbonyl group. It forms with them condensation products known as *phenylhydrazones*, water being eliminated. With aldehyde the reaction is expressed as follows:

$$CH^3.CHO + H^2N.NH.C^6H^5 = CH^3.CH{=}N\text{–}NH.C^6H^5 + H^2O$$

Like all of its analogues, aldehyde can unite with hydrocyanic acid, forming the compound $CH^3\text{–}CH(OH)(CN)$, a liquid soluble in water and alcohol, boiling at 183°, and converted by acids and alkalies into lactic acid, with disengagement of ammonia (see page 598).

If sulphur dioxide be added to a dilute magenta solution until the latter is decolorized, the addition of a trace of aldehyde will immediately restore the pink color. Nearly all the aldehydes respond to this test.

When aldehyde is heated to 100° with alcohol, *acetal* is formed; this is also found in small quantities among the products of the oxidation of alcohol.



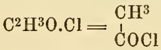
$$CH^3.CHO + C^2H^5.OH = H^2O + CH^3CH{<}\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}$$

Aldehyde. Alcohol. Acetal.

Polymerides of Aldehyde.—Aldehyde has a great tendency to become converted into polymeric modifications. Among these are *paraldehyde*, which is liquid, and *metaldehyde*, which is solid (Liebig).

Paraldehyde, $C^6H^{12}O^3$, is formed by the action of a trace of sulphuric acid or of zinc chloride on aldehyde. It is a colorless liquid, having a density of 0.998 at 15°, and boiling at 124°. At a low temperature it solidifies to a leaf-like, crystalline mass, fusible at 10.5°. It dissolves in eight times its volume of water. When distilled with a small quantity of sulphuric acid, it is again converted into aldehyde.

ACETYL CHLORIDE.



$$C^2H^3O.Cl = \begin{matrix}CH^3\\|\\COCl\end{matrix}$$

This body was obtained by Gerhardt in 1852, by treating sodium acetate with pentachloride, or oxychloride of phosphorus.

$$NaC^2H^3O^2 + PCl^5 = C^2H^3OCl + NaCl + POCl^3$$

Sodium acetate. Acetyl chloride. Phosphorus oxychloride.

It is also formed by the action of chlorine on aldehyde.

It is a colorless, mobile liquid, having a pungent odor. It boils at 55°.

If it be poured into water, it sinks to the bottom, but rapidly decomposes into hydrochloric and acetic acids.

$$C^2H^3O.Cl + H^2O = HCl + C^2H^3O.OH$$

It undergoes a similar decomposition with alcohol, forming ethyl acetate and hydrochloric acid.

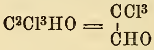
$$C^2H^3O.Cl + C^2H^5.OH = HCl + C^2H^5.C^2H^3O^2$$

With ammonia, it forms acetamide and ammonium chloride.

$$C^2H^3O.Cl + 2NH^3 = NH^4Cl + C^2H^3O.NH^2$$

It reacts with acetates, forming acetic anhydride.

CHLORAL, OR TRICHLORALDEHYDE.



$$C^2Cl^3HO = \begin{matrix} CCl^3 \\ | \\ CHO \end{matrix}$$

This important body was discovered by Liebig and Dumas. It is formed by the prolonged action of chlorine on alcohol. It is a colorless, mobile liquid, having a peculiar, penetrating odor. It boils at 97.7°.

Gerhardt regarded it as aldehyde in which the three atoms of hydrogen of the radical are replaced by three atoms of chlorine.

$C^2H^3O.H$	$C^2Cl^3O.H$
Aldehyde. (Acetyl hydride.)	Chloral. (Trichloracetyl hydride.)

Its reactions resemble those of aldehyde. It forms crystallizable compounds with the disulphites. Its ammoniacal solution reduces silver nitrate. These facts indicate that chloral contains the group CHO, characteristic of the aldehydes.

It regenerates aldehyde by the action of nascent hydrogen (Personne).

The caustic alkalies decompose it into chloroform and a formate (Dumas).

$$\underset{\text{Chloral.}}{C^2HCl^3O} + KOH = \underset{\text{Potassium formate.}}{KCHO^2} + CHCl^3$$

Nitric acid converts it into trichloracetic acid, in the same manner that aldehyde is converted into acetic acid.

$$C^2HCl^3O + O = C^2HCl^3O^2$$

Chloral forms a crystallizable compound with water, $C^2HCl^3O + H^2O = \begin{matrix} CCl^3 \\ | \\ CH(OH)^2 \end{matrix}$, called chloral hydrate. The latter melts at 57°, and boils at 98° (Personne), being at the same time decomposed into anhydrous chloral and water. It is very soluble in water.

In contact with concentrated sulphuric acid, chloral is rapidly converted into a white, solid substance which is insoluble in water; it has the same composition as ordinary chloral, and is called insoluble chloral.

Chloral also combines with alcohol, forming *alcoholate of chloral* (Personne).

Chloral hydrate has for some time been successfully employed in medicine as a soporific and anodyne (Liebreich).

DIACETYL.

$(CH^3.CO)^2$

Two acetyl radicals which cannot exist alone unite together forming the interesting compound diacetyl. This has been obtained in various ways by reactions too intricate to describe here. It is a yellow liquid having a characteristic odor. It boils at 87°, and mixes readily with water and alcohol. Like other ketones, it will combine with hydroxylamine, and since it contains two carbonyl groups it is capable of forming a monoxime and a dioxime. The latter is highly characteristic, being a white crystalline body, insoluble in water. Its melting-point is 234°. Diacetyl also combines with phenylhydrazine and hydrocyanic acid.

ACETONE.

C^3H^6O

Acetone is the methylide of acetyl, $C^2H^3O.CH^3$, and since acetyl itself is carbonyl (carbon monoxide) methylide, $CH^3\text{–}CO$, acetone can be regarded as carbonyl dimethylide, $CH^3\text{–}CO\text{–}CH^3$.

$$\underset{\text{Carbonyl chloride.}}{CO'' \left\{ \begin{matrix} Cl \\ Cl \end{matrix} \right.} \qquad \underset{\text{Carbonyl dimethylide (acetone).}}{CO'' \left\{ \begin{matrix} CH^3 \\ CH^3 \end{matrix} \right.}$$

Indeed, the synthesis of acetone has been made both by treating acetyl chloride with zinc methyl (Pebal and Freund), and by treating sodium methyl with carbonyl chloride.

$$\underset{\text{Zinc methyl.}}{Zn(CH^3)^2} + \underset{\text{Acetyl chloride.}}{2(C^2H^3O.Cl)} = \underset{\text{Acetone.}}{2(C^2H^3O.CH^3)} + ZnCl^2$$

$$\underset{\text{Sodium methyl.}}{2(CH^3.Na)} + \underset{\text{Carbonyl chloride.}}{CO \left\{ \begin{matrix} Cl \\ Cl \end{matrix} \right.} = 2NaCl + \underset{\text{Acetone.}}{CO \left\{ \begin{matrix} CH^3 \\ CH^3 \end{matrix} \right.}$$

Preparation.—Acetone is prepared by distilling dry calcium acetate in a clay retort. The vapors given off are condensed in a well-cooled receiver, and the liquid obtained is distilled on a water-bath with an excess of calcium chloride.

$$Ca(C^2H^3O^2)^2 = C^3H^6O + CaCO^3$$

Properties.—Acetone is a colorless liquid, having a slightly empyreumatic, ethereal odor. It boils at 56°. It dissolves in all proportions in water, alcohol, ether, and wood-spirit.

Like aldehyde, it forms crystallizable combinations with the alkaline acid-sulphites.

Acetone and its homologues are not susceptible of direct oxidation. If it be heated with a mixture of sulphuric acid and potassium dichromate, it breaks up into acetic acid and formic acid, a portion of the latter being oxidized to carbon dioxide.

$$CH^3.CO.CH^3 + O^3 = CH^3\text{–}CO.OH + HCO.OH$$

Nascent hydrogen, produced by sodium amalgam and water, converts it into secondary propyl alcohol (page 521).

Besides isopropyl alcohol, the action of nascent hydrogen on acetone gives rise to a product of condensation of H^2 with two molecules of acetone, which is named *pinacone*.

$$2C^3H^6O + H^2 = C^6H^{14}O^2$$

Pinacone.

It is a tertiary glycol (see page 578). It constitutes a colorless, crystallizable mass, fusible at 42°, and boiling at 172°.

When acetone is added in small portions to phosphorus pentachloride, a very energetic reaction takes place and two chlorides are formed. One of them, $C^3H^6Cl^2$ (methylchloracetol), boils at 70°. The other, C^3H^5Cl (monochloropropylene), boils at 23° (Friedel).

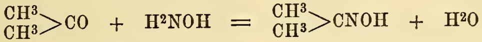
$$C^3H^6O + PCl^5 = C^3H^6Cl^2 + POCl^3$$
$$C^3H^6Cl^2 = C^3H^5Cl + HCl$$

Like aldehyde, acetone will unite with hydrocyanic acid, forming a cyanide (or cyanhydrin), which is decomposed by both acids and alkalies, with disengagement of ammonia and formation of an acid; the group CN is then converted in carboxyl CO.OH.

$$\begin{matrix}CH^3\\CH^3\end{matrix}\!>CO + HCN = \begin{matrix}CH^3\\CH^3\end{matrix}\!>C<\!\begin{matrix}OH\\CN\end{matrix}$$

Acetone. Acetone cyanhydrin.

Acetone unites with hydroxylamine, forming a highly characteristic, colorless crystalline compound, acetoxime, which melts at 59°.



$$\begin{matrix}CH^3\\CH^3\end{matrix}\!>CO + H^2NOH = \begin{matrix}CH^3\\CH^3\end{matrix}\!>CNOH + H^2O$$

With phenylhydrazine it condenses to acetone phenylhydrazone, $(CH^3)^2{=}N{-}NH.C^6H^5$, a reaction which is likewise characteristic of bodies containing the carbonyl group.

ACETAMIDE.

$C^2H^3O.NH^2$

This amide may be obtained by heating ethyl acetate to 100° in sealed tubes with aqueous ammonia. Alcohol and acetamide are formed according to the equation

$$C^2H^5.C^2H^3O^2 + NH^3 = C^2H^3O.NH^2 + C^2H^5.OH$$

When the resulting liquid is evaporated in a vacuum, the acetamide remains. It may be purified by distillation, collecting that which passes above 200°.

Acetamide is also formed by the action of ammonia on acetyl chloride; one of the readiest methods of preparing it consists in simply distilling ammonium acetate.

It is a solid, crystallizable body, soluble in water in all proportions. Its odor resembles that of mice. Boiling potassium hydrate reacts with it, forming potassium acetate and ammonia. Phosphoric anhydride removes from it the elements of water, converting it into acetonitrile or methyl cyanide.

$$C^2H^3O.NH^2 = C^2H^3N + H^2O$$

ACIDS OF THE SERIES $C^nH^{2n}O^2$

Formic and acetic acids, of which the principal derivatives have just been described, are the first terms of a very extensive homologous series. It is the series of volatile fatty acids, so named because it includes a great number of compounds which were at first obtained from the natural fatty bodies, and which are the fatty acids proper. Among the bodies congeneric with acetic acid, those of which the molecules are less complicated are liquid at ordinary temperatures; the others are solid. The following table gives the nomenclature, composition, and principal physical properties of these acids:

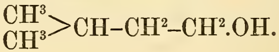
NAMES OF ACIDS.	CRUDE FORMULÆ.	RATIONAL FORMULÆ.	MELTING-POINTS.	BOILING-POINTS.
Formic acid	CH^2O^2	$H{-}CO.OH$	8°	101°
Acetic acid	$C^2H^4O^2$	$CH^3{-}CO.OH$	17°	118°
Propionic acid . . .	$C^3H^6O^2$	$C^2H^5{-}CO.OH$	—36.5°	140.7°
Butyric acid	$C^4H^8O^2$	$C^3H^7{-}CO.OH$	0°	163°
Valeric acid (isovaleric)	$C^5H^{10}O^2$	$C^4H^9{-}CO.OH$	—51°	175°
Caproic acid (isocaproic)	$C^6H^{12}O^2$	$C^5H^{11}{-}CO.OH$	8°	205°
Œnanthylic acid . . .	$C^7H^{14}O^2$	$C^6H^{13}{-}CO.OH$	—10.5°	212°
Caprylic acid	$C^8H^{16}O^2$	$C^7H^{15}{-}CO.OH$	16.5°	236°
Pelargonic acid . . .	$C^9H^{18}O^2$	$C^8H^{17}{-}CO.OH$	12.5°	260°
Capric acid	$C^{10}H^{20}O^2$	$C^9H^{19}{-}CO.OH$	31.4°	
Lauric acid	$C^{12}H^{24}O^2$	$C^{11}H^{23}{-}CO.OH$	43.6°	
Myristic acid	$C^{14}H^{28}O^2$	$C^{13}H^{27}{-}CO.OH$	53.8°	
Palmitic acid	$C^{16}H^{32}O^2$	$C^{15}H^{31}{-}CO.OH$	62°	
Margaric acid	$C^{17}H^{34}O^2$	$C^{16}H^{33}{-}CO.OH$	60°	
Stearic acid	$C^{18}H^{36}O^2$	$C^{17}H^{35}{-}CO.OH$	69.2°	
Arachnic acid	$C^{20}H^{40}O^2$	$C^{19}H^{39}{-}CO.OH$	75°	
Benic acid	$C^{22}H^{44}O^2$	$C^{21}H^{43}{-}CO.OH$	96°	
Cerotic acid	$C^{27}H^{54}O^2$	$C^{26}H^{53}{-}CO.OH$	78°	
Melissic acid	$C^{30}H^{60}O^2$	$C^{29}H^{59}{-}CO.OH$	88°	

We have already noticed the existence of numerous isomeric alcohols, and in their study the principles of isomerism have been explained. Such isomerides exist also in the series of acids, and are caused by the different atomic structure of the radicals, C^nH^{2n+1}, which figure in the preceding formulæ. We will consider two examples. 1. When normal butyl alcohol, $CH^3{-}CH^2{-}CH^2{-}CH^2.OH$, is oxidized, normal butyric acid, or the butyric acid of fermentation, is obtained, $CH^3{-}CH^2{-}CH^2{-}CO.OH$. The acid obtained by oxidation of the butyl alcohol of fermentation is different from this, and the difference is caused by the difference in structure of the radicals $(C^3H^7)'$.

Isobutyric acid, derived from the alcohol of fermentation, whose constitution is $\begin{matrix}CH^3\\CH^3\end{matrix}{>}CH{-}CH^2.OH$, contains $\begin{matrix}CH^3\\CH^3\end{matrix}{>}CH{-}CO.OH$.

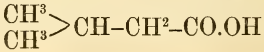
The acid is derived from the alcohol by the substitution of O for H^2 in the group $(CH^2.OH)'$.

2. As we have already seen, the constitution of amyl alcohol of fermentation is expressed by the formula



$$\begin{matrix}CH^3\\CH^3\end{matrix}{>}CH{-}CH^2{-}CH^2.OH.$$

The valeric acid produced by its oxidation is then



$$\begin{matrix}CH^3\\CH^3\end{matrix}{>}CH{-}CH^2{-}CO.OH$$

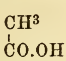
Normal valeric acid results from the oxidation of normal amyl alcohol, and contains

$$CH^3\text{–}CH^2\text{–}CH^2\text{–}CH^2\text{–}CO.OH$$

Methylethylacetic acid, $\begin{matrix} CH^3 \\ C^2H^5 \end{matrix}\!\!>\!CH\text{–}CO.OH$, or optically active valeric acid, is derived from active amyl alcohol.

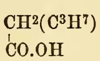
The trimethylacetic acid, which was discovered by Butlerow, contains $(CH^3)^3C\text{–}CO.OH$; it is derived from the alcohol $(CH^3)^3C\text{–}CH^2.OH$, which is not known.

If we compare the three isomeric acids, $C^5H^{10}O^2$, with acetic acid itself, we will find that their isomeric relations can be expressed in a very simple manner, by saying that normal valeric acid is propylacetic acid, the acid derived from the alcohol of fermentation is isopropylacetic acid, and that the last two are methylethylacetic and trimethylacetic acids.



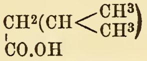
$$\begin{array}{l} CH^3 \\ | \\ CO.OH \end{array}$$

Acetic acid.



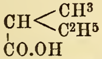
$$\begin{array}{l} CH^2(C^3H^7) \\ | \\ CO.OH \end{array}$$

Propylacetic acid.



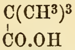
$$\begin{array}{l} CH^2\left(CH\!<\!\begin{matrix} CH^3 \\ CH^3 \end{matrix}\right) \\ | \\ CO.OH \end{array}$$

Isopropylacetic acid.



$$\begin{array}{l} CH\!<\!\begin{matrix} CH^3 \\ C^2H^5 \end{matrix} \\ | \\ CO.OH \end{array}$$

Methylethylacetic acid.



$$\begin{array}{l} C(CH^3)^3 \\ | \\ CO.OH \end{array}$$

Trimethylacetic acid.

The foregoing facts are sufficient to elucidate the isomerism of acids of the series $C^nH^{2n}O^2$.

PROPIONIC ACID.

$$C^3H^6O^2 = CH^3\text{–}CH^2\text{–}CO.OH$$

This acid is formed by the action of potassium hydrate on ethyl cyanide. It is also a product of fermentation; thus, it has been obtained by allowing a solution of sugar, mixed with chalk and cheese, to ferment during a year. It is also formed in small quantity in the distillation of wood.

Wanklyn made its synthesis by passing carbon dioxide over sodium ethyl.

$$CO.O \quad + \quad C^2H^5Na \quad = \quad \underset{\text{Sodium propionate.}}{C^2H^5\text{–}CO.ONa}$$

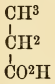
It is most conveniently prepared by oxidizing normal propyl alcohol by means of chromic acid (Pierre and Puchot).

$$CH^3\text{–}CH^2\text{–}CH^2.OH + O^2 = CH^3CH^2COOH + H^2O$$

ll

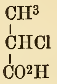
Properties.—It is a colorless, mobile liquid, having an odor like that of acetic acid. It solidifies at —36.5°, and boils at 140.7°. Density at 21°, 0.996. It is miscible with water in all proportions. Calcium chloride separates it from its aqueous solution.

There are a great number of substitution products directly related to propionic acid. Among these are the chlorine, bromine, and iodine derivatives, and the amides. Two of these derivatives are known of each particular species, presenting curious isomeric relations. The following examples will serve as illustrations:



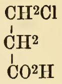
$$\begin{array}{l} CH^3 \\ | \\ CH^2 \\ | \\ CO^2H \end{array}$$

Propionic acid.



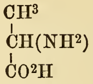
$$\begin{array}{l} CH^3 \\ | \\ CHCl \\ | \\ CO^2H \end{array}$$

α-Chloropropionic acid.



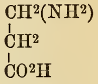
$$\begin{array}{l} CH^2Cl \\ | \\ CH^2 \\ | \\ CO^2H \end{array}$$

β-Chloropropionic acid.



$$\begin{array}{l} CH^3 \\ | \\ CH(NH^2) \\ | \\ CO^2H \end{array}$$

α-Amidopropionic acid.



$$\begin{array}{l} CH^2(NH^2) \\ | \\ CH^2 \\ | \\ CO^2H \end{array}$$

β-Amidopropionic acid.

Only the iodo-derivatives will be described here, and farther on we will mention the amides.

a-iodopropionic acid, $C^3H^5IO^2$, is prepared by the action of concentrated hydriodic acid or phosphorus iodide on lactic acid.

$$\underset{\text{Lactic acid.}}{C^3H^6O^3} + HI = C^3H^5IO^2 + H^2O$$

It is a thick, oily body, almost insoluble in water.

β-iodopropionic acid is formed by the action of concentrated hydriodic acid or phosphorus iodide and water on glyceric acid.

$$\underset{\text{Glyceric acid.}}{C^3H^6O^4} + 3HI = C^3H^5IO^2 + 2H^2O + I^2$$

It is also formed by the direct combination of hydriodic acid and acrylic acid, $C^3H^4O^2$.

$$C^3H^4O^2 + HI = C^3H^5IO^2$$

It is a solid, occurring in crystalline laminæ, fusible at 82°. It is very soluble in boiling water. When heated to 180° with hydriodic acid, it is converted into propionic acid.

$$C^3H^5IO^2 + HI = I^2 + C^3H^6O^2$$

BUTYRIC ACIDS.

$C^4H^8O^2$

Normal Butyric Acid, $CH^3\text{–}CH^2\text{–}CH^2\text{–}CO.OH$, was discovered by Chevreul in butter, where it exists in combination with glycerol in butyrin. Pelouze and Gélis have shown that it is formed in abundance when a solution of sugar, glucose, or even starch is abandoned for several weeks with the addition of chalk and old cheese. In about ten days a mass of calcium lactate is formed, but this soon disappears, gases being at the same time disengaged. The mass again becomes liquid, and the solution contains calcium butyrate. This is converted into sodium butyrate, which is finally decomposed by sulphuric acid; the butyric acid separates in the form of an oily liquid, which is decanted and distilled.

Properties.—Butyric acid is a colorless liquid, having a pungent and disagreeable odor which recalls that of rancid butter. It is quite soluble in water. Density at 14°, 0.958. Boiling-point, 163°.

It perfectly neutralizes the bases, forming butyrates. These salts, which are mostly soluble in water, have a fatty aspect. Calcium butyrate, $Ca(C^4H^7O^2)^2$, is more soluble in cold water than in hot water, so that its cold saturated solution becomes a solid mass when heated to 70°.

Butyrone, or Dipropyl Ketone.—When calcium butyrate is subjected to dry distillation, it yields, as principal product, butyrone, one of the homologues of acetone (Chancel).

$$\underset{\text{Calcium butyrate.}}{Ca(C^4H^7O^2)^2} = \underset{\text{Butyrone.}}{(C^3H^7)^2CO} + CaCO^3$$

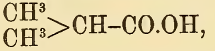
Butyrone is a colorless liquid, lighter than water, and having a peculiar, ethereal odor. It boils at 144°.

Butaldehyde, C^4H^8O, is the principal product of the distillation of a mixture of butyrate and formate of calcium.

$$Ca(C^4H^7O^2)^2 + Ca(CHO^2)^2 = 2CaCO^3 + 2C^4H^8O$$

This important reaction, discovered by Piria, permits of the conversion of butyric acid into its aldehyde; it can also be applied to the transformation of other acids into aldehydes.

Butaldehyde, which was discovered by Chancel, is a liquid, boiling at 74°. Like aldehyde, it forms a crystallizable compound with ammonia, unites with the alkaline acid-sulphites, and reacts with hydroxylamine and phenylhydrazine, as do the other aldehydes and the ketones.

Isobutyric Acid, 
$\begin{matrix}CH^3\\CH^3\end{matrix}\!>CH{-}CO.OH$, isomeric with butyric acid, was discovered by Markownikow.

It is formed by the oxidation of butyl alcohol of fermentation, and exists naturally in the fruit of the *Ceratonia siliqua* (carob locust, St. John's bread). It is also obtained by decomposing isopropyl cyanide with potassium hydroxide.

$$(C^3H^7)^iCN + 2H^2O = NH^3 + (C^3H^7)^i\text{–}CO^2H$$

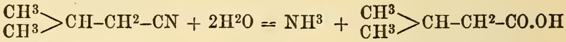
It is a liquid having a disagreeable odor, like that of the acid of fermentation. Density at 20°, 0.9503. It boils at 154°.

Its calcium salt differs from that of the normal acid in being more soluble in hot than in cold water.

VALERIC ACIDS.

$C^5H^{10}O^2$

Isovaleric Acid, $\begin{matrix}CH^3\\CH^3\end{matrix}\!\!>CH\text{–}CH^2\text{–}CO.OH$, was discovered by Chevreul, who obtained it from dolphin oil. It may be prepared by distillation of valerian root with water; hence its name. It occurs also in angelica root and in *Viburnum opulus.* The same acid is formed when amyl alcohol is oxidized by a mixture of potassium dichromate and sulphuric acid. It is also formed when potassium hydrate is boiled with isobutyl cyanide, a reaction similar to that which has been indicated for the formation of isobutyric acid.



$$\begin{matrix}CH^3\\CH^3\end{matrix}\!\!>CH\text{–}CH^2\text{–}CN + 2H^2O = NH^3 + \begin{matrix}CH^3\\CH^3\end{matrix}\!\!>CH\text{–}CH^2\text{–}CO.OH$$

Isobutyl cyanide. Isovaleric acid.

Valeric acid is a colorless liquid, having a pungent, disagreeable odor. Density at 0°, 0.947. It boils at 175°. It dissolves in 30 parts of water, from which it is precipitated by the addition of neutral salts. Its ammonium salt is used in medicine.

Normal Valeric Acid, which has already been mentioned (page 561), is a colorless liquid, smelling like butyric acid. It boils at 184–185°, and its density at 0° is 0.9577.

Methylethylacetic Acid, $\begin{matrix}CH^3\\C^2H^5\end{matrix}\!\!>CH\text{–}CO.OH$, or optically active valeric acid, has been obtained by the oxidation of active amyl alcohol. It boils at 173°.

Trimethylacetic Acid is formed when potassium hydrate is boiled with the cyanide derived from trimethylcarbinol.

$$(CH^3)^3C\text{–}CN + 2H^2O = (CH^3)^3C\text{–}CO.OH + NH^3$$

It is a crystalline mass, fusible at 35°, and boiling at 163.8°. It dissolves in 40 parts of water at 20°.

CAPROIC ACIDS.

$C^6H^{12}O^2$

There are at present known seven isomeric acids having the composition $C^6H^{12}O^2$. One of them was discovered in butter by Chevreul. Normal caproic acid is formed by the oxidation of normal hexyl alcohol, and in the decomposition of normal amyl cyanide by boiling potassium hydrate. It is an oily liquid, having but a faint odor; its density at 0° is 0.945, and it boils at 205°. *Leucine*, $C^6H^{13}NO^2$, an important nitrogenized body which exists in the animal economy, is an amide, $C^6H^{11}(NH^2)O^2$, of normal caproic acid.

The caproic acid mentioned on page 560 is an isomeride of the preceding acid. It is obtained by decomposing, by potassium hydrate, amyl cyanide derived from the alcohol of fermentation.

HIGHER FATTY ACIDS.

Our limited space will not permit of a description of all of the acids of this series; we can only briefly consider the last members.

Palmitic Acid, $C^{16}H^{32}O^2$.—This exists in palm-oil in combination with glycerol. It is prepared on a large scale by distilling palm-oil by means of superheated steam, which decomposes the oil into fatty acid and glycerol. The fatty acids solidify on cooling. The mass is expressed to remove the liquid oleic acid with which it is impregnated, and so obtained in dry, white cakes, which are used for the manufacture of candles. The pure acid melts at 62°.

Margaric Acid, $C^{17}H^{34}O^2$.—This acid was supposed by Chevreul to exist in most solid fats, but Heintz has shown that the so-called margaric acid derived from fats consists of a mixture of palmitic and stearic acids. Normal margaric acid was prepared synthetically by Krafft by decomposing cetyl cyanide by potassium hydroxide.

$$C^{16}H^{31}.CN + 2H^2O = C^{16}H^{31}.COOH + NH^3$$

It is said to exist in *adipocere*, a waxy substance formed by the prolonged action of air and moisture on certain animal substances.

Margaric acid crystallizes in white scales fusible at 60°, and soluble in alcohol and ether.

Stearic Acid, $C^{18}H^{36}O^{2}$, was obtained from tallow by Chevreul. It is a solid, melting at 69.2°. After cooling, the fused acid becomes a laminated, white mass. It is insoluble in water, but dissolves in alcohol and ether. The alcoholic solution deposits it in small pearly scales, which are not greasy to the touch. Stearic acid is used for the manufacture of stearin candles.

The alkaline stearates are soluble in water. If a large excess of water be added to the solution of a neutral stearate, a crystalline precipitate is formed which, according to Chevreul, is an acid stearate. On this reaction he has founded a method for the preparation of stearic acid.

The stearates of calcium, barium, and lead are insoluble in water, and can be obtained by double decomposition.

Cerotic and Melissic Acids.—These acids have been obtained from wax by Brodie (page 528).

OLEIC ACID AND ITS HOMOLOGUES.

Oleic acid, which has just been mentioned and which Chevreul obtained from olein, is the principal constituent of a great number of oils and fats; it does not belong to the series of volatile fatty acids. Its formula, $C^{18}H^{34}O^{2}$, shows that it differs from stearic acid by containing two atoms of hydrogen less than the latter acid. It belongs to the series $C^{n}H^{2n-2}O^{2}$.

Acrylic Acid, $CH^{2}{=}CH{-}CO.OH$.—This is the first term of the series $C^{n}H^{2n-2}O^{2}$. It receives its name from the fact that it results from the oxidation of *acrolein*, or *acraldehyde*, $C^{3}H^{4}O$, which is formed in the destructive distillation of neutral fatty substances and glycerol and its compounds; it is a product of the dehydration of glycerol.

$$\underset{\text{Glycerol.}}{C^{3}H^{8}O^{3}} = \underset{\text{Acrolein.}}{C^{3}H^{4}O} + 2H^{2}O$$

Acrolein reduces silver oxide, like the other aldehydes, being converted into acrylic acid. This acid is liquid, and boils at 140°. Like other unsaturated acids, it combines directly with nascent hydrogen, bromine, and the halogen acids. Fusion with potassium hydrate decomposes it into formic and acetic acids. A similar decomposition occurs with the other unsaturated acids. By fusion with alkaline hydroxides all are decomposed, yielding salts of two acids, but the split does not always take place at the double bond.

Crotonic Aldehyde and Acid.—These two bodies are homologues of acrylic aldehyde and acid.

C^3H^4O acraldehyde.	$C^3H^4O^2$ acrylic acid.
C^4H^6O crotonaldehyde	$C^4H^6O^2$ crotonic acid.

Crotonaldehyde is one of the numerous transformation products of ordinary aldehyde. When the latter body is subjected to the action of certain salts, it loses the elements of water and is converted into crotonaldehyde.

$$2C^2H^4O = C^4H^6O + H^2O$$

This aldehyde is a liquid having a very irritating odor and an acrid taste. It boils at 103°.

When submitted to the action of oxidizing agents, such as silver oxide in presence of water, it is converted into *crotonic acid.*

$$C^4H^6O + O = C^4H^6O^2$$

This acid crystallizes in large plates, fusible at 72°. It boils at 182°. Nascent hydrogen, produced by the action of sulphuric acid and zinc, converts it into normal butyric acid, $CH^3–CH^2–CH^2–CO.OH$. It combines directly with bromine, producing heat, and is changed into dibromobutyric acid, $CH^3–CHBr–CHBr–CO.OH$. Fusion with potassium hydrate decomposes it into two molecules of acetic acid.

There is an *isocrotonic acid*, $CH^2{=}CH–CH^2–CO.OH$, a liquid boiling at 172°. When heated to 170–180° in sealed tubes, it is converted into crotonic acid.

Oleic Acid, $C^{18}H^{34}O^2$.—This acid, of which the preparation has been indicated (page 565), is an oily liquid, which solidifies to a crystalline mass at 4°. Its concentrated alcoholic solution deposits it, when cooled, in small needles fusible at 14°. Under a pressure of 10 m.m. it distils without decomposition at 223°. When pure it is odorless, and does not redden litmus paper. On exposure to the air it absorbs oxygen, and becomes rancid and acid. Fusion with potassium hydrate converts it into acetic and palmitic acids.

When boiled with nitric acid, it is oxidized, losing carbon dioxide, and there are formed volatile fatty acids from acetic to capric acid, and homologues of oxalic acid, including suberic ($C^8H^{14}O^4$) and succinic ($C^4H^6O^4$) acids; nitrogen peroxide converts oleic acid into an isomeride, *elaidic acid*, a solid body, crystallizing in brilliant plates, fusible at 44–45° (Boudet).

POLYATOMIC COMPOUNDS.

After the description of the comparatively simple compounds which are naturally grouped with the monohydric alcohols, we proceed to the more complex compounds constituting the polyhydric alcohols and their derivatives. The latter alcohols are neutral hydroxides, capable of reacting with the acids to form neutral combinations analogous to the compound ethers. Those better known are related to the saturated hydrocarbons, from which they are derived by the substitution of several hydroxyl groups for as many atoms of hydrogen.

C^2H^6	C^3H^8	C^4H^{10}	C^6H^{14}
Ethane.	Propane.	Butane.	Hexane.
$C^2H^4(OH)^2$	$C^3H^5(OH)^3$	$C^4H^6(OH)^4$	$C^6H^8(OH)^6$
Dihydroxyethane (glycol).	Trihydroxypropane (glycerol).	Erythritol.	Mannitol.

By oxidation of these polyhydric alcohols, acids are produced which bear the same relation to the former that acetic acid bears to ordinary alcohol.

It will be noticed that the radicals of these alcohols are unsaturated hydrocarbons, that is, they contain less hydrogen than the saturated hydrocarbons, C^nH^{2n+2}. Of these radicals, only those can exist in a free state which contain an even number of atoms of hydrogen. We will briefly consider the more important of them.

ETHYLENE.

$$C^2H^4 = CH^2{=}CH^2$$

This gas, formerly known as olefiant gas or heavy carburetted hydrogen, is formed in a great number of reactions. It is produced, together with other hydrocarbons, when substances rich in carbon and hydrogen, such as fats and resins, are decomposed by dry distillation, that is, by the destructive action of heat.

Preparation.—A mixture of 25 grammes of alcohol with 150 grammes of sulphuric acid is heated in a 2-litre flask provided with a delivery-tube and a funnel-tube. When the evolution of gas begins, a mixture of 1 part alcohol and 2 parts sulphuric acid is allowed to drop in slowly through the funnel-tube, and the gas is washed first through sulphuric acid and afterwards through potassium hydroxide solution. It may be collected over water.

Towards the close of the operation the liquid blackens, and much sulphurous and carbonic acid gases are disengaged. These are absorbed by the caustic potash in the wash-bottle.

The following equation expresses the reaction by which ethylene is formed:

$$C^2H^6O = C^2H^4 + H^2O$$

Composition and Properties.—Ethylene is a colorless gas, having a feeble, ethereal odor. Its density is 0.9784 compared to air, or 14 compared to hydrogen. It is liquefied by a pressure of 60 atmospheres at 13° (its critical temperature), and the evaporation of the liquid under reduced pressures affords a valuable means of attaining low temperatures. Its composition may be deduced from the following experiment:

2 volumes of ethylene (2 cubic centimetres, for example) and 6 volumes of oxygen are introduced into an eudiometer over mercury. After the passage of the spark, the 8 volumes will be found to be reduced to 4 volumes, all of which will be entirely absorbed if a solution of potassium hydrate be passed into the tube. The 4 volumes are therefore carbon dioxide.

4 volumes of carbon dioxide represent $2CO^2$.

2 volumes of ethylene therefore contain C^2.

4 volumes of carbon dioxide contain but 4 of the 6 volumes of oxygen employed; the other two have therefore been used in the formation of water and have burned 4 volumes of hydrogen.

2 volumes of ethylene then contain 4 volumes of hydrogen.

Eudiometric analysis therefore indicates the composition of ethylene to be $C^2H^4 = 2$ volumes.

This gas is inflammable and burns in the air with a brilliant flame. When mixed with three volumes of oxygen and ignited, it produces a violent explosion.

It is slowly absorbed by concentrated sulphuric acid, ethylsulphuric acid being formed. When ethylene is heated with hydriodic acid, the two bodies combine directly to form ethyl iodide.

If one volume of ethylene and two volumes of chlorine be rapidly mixed in a tall jar, and a lighted match be applied, the mixture takes fire and burns with a red flame extending to the bottom of the jar, which becomes covered with a black deposit of carbon.

$$C^2H^4 + 2Cl^2 = 4HCl + C^2$$

If equal volumes of ethylene and chlorine be mixed and exposed to diffused light on the pneumatic trough, the water will soon rise in the jar, and the two gases will disappear. At the same time, oily drops will appear on the sides of the jar and upon the surface of the liquid. The body so formed is a liquid insoluble in water, and results from the direct combination of ethylene and chlorine. It was formerly called *Dutch liquid*, or *Dutch oil* (hence the old name olefiant gas); it is now called *ethylene chloride.* Its composition is expressed by the formula $C^2H^4Cl^2$. It boils at 82.5°.

If a small quantity of bromine be poured into a large flask filled with ethylene, and manipulated so that the bromine may form a thin layer on the sides of the flask, an elevation of temperature will be observed, and the liquid will rapidly become colorless. The bromine has combined with the ethylene to form a colorless liquid, *ethylene bromide*, boiling at 131°.

Ethylene iodide, $C^2H^4I^2$, may be obtained by introducing iodine into large jars filled with ethylene, and exposing to diffused light during several days. The iodine gradually disappears and a white solid is formed which may be purified by crystallization in alcohol; it is ethylene iodide.

Chloro-Derivatives of Ethylene and Ethylene Chloride.—If ethylene chloride be heated with an alcoholic solution of caustic potash, a brisk reaction soon takes place. A gas is disengaged and may be collected over water; on contact with a lighted taper, it burns with a flame tinged with green. This gas is *chlorethylene.* It is formed according to the following equation:

$$C^2H^4Cl^2 + KOH = H^2O + KCl + C^2H^3Cl$$

Like ethylene itself, chlorethylene will combine directly with two atoms of chlorine, forming chlorethylene chloride, $C^2H^3Cl.Cl^2$, which may also be obtained by the action of chlorine on ethylene chloride.

Chlorethylene chloride is decomposed by alcoholic potash, like ethylene chloride. Water, potassium chloride, and *dichlorethylene* are formed.

$$\underset{\text{Chlorethylene chloride.}}{C^2H^3Cl^3} + KOH = H^2O + KCl + \underset{\text{Dichlorethylene.}}{C^2H^2Cl^2}$$

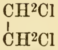
In its turn, dichlorethylene can fix two atoms of chlorine, forming dichlorethylene chloride.

These reactions have permitted the preparation of two classes of chloro-compounds,—one derived from ethylene chloride, the other from ethylene itself.

		DENSITIES.	BOILING-POINTS.
$C^2H^4Cl^3$	ethylene chloride.	1.256 at 12°	82.5°
$C^2H^3Cl^3$	chlorethylene chloride.	1.422 at 17°	115°
$C^2H^2Cl^4$	dichlorethylene chloride.	1.576 at 19°	137°
C^2HCl^5	trichlorethylene chloride.		158°
C^2Cl^6	carbon sesquichloride.		182°
C^2H^4	ethylene.		
C^2H^3Cl	chlorethylene.		—18 to —15°
$C^2H^2Cl^2$	dichlorethylene.	1.250 at 14°	55°
C^2HCl^3	trichlorethylene.		87 to 88°
C^2Cl^4	tetrachlorethylene.	2.619 at 20°	121°

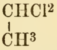
Regnault, who carefully studied these bodies, has shown that the terms of the first series are isomeric with the chloro-derivatives of ethyl chloride, with the exception of the last two, which are the same in both series.

That we may more thoroughly understand this isomerism, we will consider ethylene chloride, $C^2H^4Cl^2$, and its isomeride dichlorethane, called also ethylidene chloride. In the first, two atoms of chlorine are united, each to a different atom of carbon; in the second, both are united to the same carbon atom.



$$\begin{array}{c} CH^2Cl \\ | \\ CH^2Cl \end{array}$$

Ethylene chloride.



$$\begin{array}{c} CHCl^2 \\ | \\ CH^3 \end{array}$$

Ethylidene chloride.

Tetrachlorethylene was discovered by Faraday in 1821. It is formed by the action of alcoholic potassium hydrate on trichlorethylene chloride.

$$C^2HCl^5 = C^2Cl^4 + HCl$$

It is also formed by the action of a red heat on carbon sesquichloride.

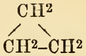
$$C^2Cl^6 = C^2Cl^4 + Cl^2$$

It is a very mobile liquid, which does not solidify at —18°. It absorbs chlorine under the influence of direct sunlight, being transformed into carbon sesquichloride, C^2Cl^6.

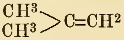
HOMOLOGOUS SERIES, C^nH^{2n}

Ethylene is the first member of a long series of homologues, of which we will summarily describe a few of the others. Since ethylene is $(CH^2)^2$, the constitution of the higher members of the series, properly speaking, should be represented by the formula $(CH^2)^n$.

Such bodies have been prepared, but they cannot be regarded as the true homologues of ethylene. Their molecules do not contain any doubly-linked carbon atoms, and consequently they do not readily combine with the halogens. The superior homologue of ethylene is propylene, $CH^3{-}CH{=}CH^2$, and isomeric with this is trimethylene, which is represented by the formula

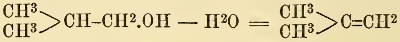


Above the fourth member of this series, butylene, the number of isomerides increases rapidly. Thus, the butylene derived by dehydration from butyl alcohol of fermentation is



$$\begin{matrix}CH^3\\CH^3\end{matrix}\!>C{=}CH^2$$

It is formed according to the following reaction:



$$\begin{matrix}CH^3\\CH^3\end{matrix}\!>CH{-}CH^2.OH - H^2O = \begin{matrix}CH^3\\CH^3\end{matrix}\!>C{=}CH^2$$

Independently of this butylene, there are two others, the formation and principal properties of which will be indicated farther on.

Their constitutions are expressed by the formulæ

$$CH^3{-}CH{=}CH{-}CH^3$$
$$CH^3{-}CH^2{-}CH{=}CH^2$$

The isomeric relations of these three butylenes may be represented in a very simple manner if we consider them to be derived from ethylene, $H^2C{=}CH^2$, the hydrogen of which is partly replaced by methyl or ethyl. The following compounds are thus obtained:

Dimethylethylene α	$(CH^3)^2C{=}CH^2$, boils at —6°.
Dimethylethylene β (normal)	$(CH^3)HC{=}CH(CH^3)$, boils at +3°.
Ethylethylene	$(C^2H^5)HC{=}CH^2$, boils at —5°.

The fifth member of the series, *amylene* or *pentene*, C^5H^{10}, presents still more numerous isomerides, but they can all be explained by the principles already exposed: they may be regarded as derivatives of ethylene by the substitution of a propylic or isopropylic group for one atom of hydrogen, or by the substitution of an ethyl group and a methyl group for two atoms of hydrogen, or lastly, by the substitution of three methyl groups for three atoms of hydrogen.

PROPYLENES.

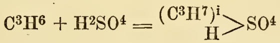
C^3H^6

Ordinary Propylene, $CH^3{-}CH{=}CH^2$.—To prepare this gas in a pure state Berthelot and de Luca heat allyl iodide with mercury and concentrated hydrochloric acid.

$$2C^3H^5I + 4Hg + 2HCl = Hg^2Cl^2 + Hg^2I^2 + 2C^3H^6$$

It may also be made by allowing propyl alcohol to fall drop by drop on highly heated zinc chloride (Le Bel).

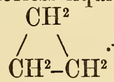
Propylene is a colorless gas, having a feeble, alliaceous odor. It is rapidly absorbed by sulphuric acid, with formation of isopropylsulphuric acid (Berthelot).



$$C^3H^6 + H^2SO^4 = \begin{matrix}(C^3H^7)^i\\H\end{matrix}{>}SO^4$$

It unites directly with hydriodic acid, forming an iodide which is isomeric with propyl iodide. $C^3H^6 + HI = (C^3H^7)^iI$

Propylene unites directly with chlorine and bromine, forming propylene chloride, $C^3H^6Cl^2$, and propylene bromide, $C^3H^6Br^2$. The latter is a colorless liquid, boiling at 145°.

Trimethylene,  .—This remarkable body was first described by Freund, who prepared it by heating with sodium the bromide, $CH^2Br{-}CH^2{-}CH^2Br$. It is a gas which is absorbed by bromine more slowly than ordinary propylene, the normal bromide, boiling at 164–165°, being regenerated. It combines with hydriodic acid forming the iodide of normal propyl, $CH^3{-}CH^2{-}CH^2I$. Normal propylene bromide is obtained by heating allyl bromide, C^3H^5Br, with hydrobromic acid.

$$\underset{\text{Allyl bromide.}}{CH^2{=}CH{-}CH^2Br} + HBr = \underset{\text{Normal propylene bromide.}}{CH^2Br{-}CH^2{-}CH^2Br}$$

It is a colorless liquid, boiling at 165°.

BUTYLENES, C^4H^8.

1. **Dimethylethylene** *α*, $(CH^3)^2C{=}CH^2$. — This body is formed when isobutyl alcohol is dehydrated by zinc chloride, or by the action of alcoholic potassium hydrate on butyl iodide, C^4H^9I. It boils at —6°. It unites directly with hydriodic acid, forming tertiary butyl iodide, $(CH^3)^2CI{-}CH^3$, and combines

with bromine, forming the bromide $(CH^3)^2CBr-CH^2Br$, which boils at 149°.

2. **Dimethylethylene** β (normal or symmetric), $(CH^3)HC=CH(CH^3)$.—Is formed by the action of alcoholic potash on secondary butyl iodide, $CH^3-CH^2-CHI-CH^3$. Boils at +3° and solidifies to a crystalline mass at 0°. Unites with HI, regenerating secondary butyl iodide, and with bromine, forming the bromide $(CH^3)HBrC-CHBr(CH^3)$, which boils at 159°.

Le Bel and Greene have obtained normal dimethylethylene by dropping ordinary isobutyl alcohol on highly heated zinc chloride; the disengaged gases are passed through bromine, and the bromides of β dimethylethylene and ethylethylene—both gases are produced in the decomposition—separated by fractional distillation.

De Luynes obtained secondary butyl iodide by reducing erythritol with a large excess of hydriodic acid (page 634).

3. **Ethylethylene (ethyl-vinyl)**, $(C^2H^5)HC=CH^2$.—Is obtained by the action of sodium on a mixture of ethyl iodide and bromethylene.

$$C^2H^5I + BrHC=CH^2 + Na^2 = NaI + NaBr + (C^2H^5)HC=CH^2$$

Boiling-point, —5°. It unites with HI, forming secondary butyl iodide, and with bromine, forming the bromide $CH^3-CH^2-CHBr-CH^2Br$, boiling at 166°.

AMYLENES, OR PENTENES, C^5H^{10}.

Several isomeric hydrocarbons are known of the composition C^5H^{10}. They exist in unequal proportions in the product of the reaction of zinc chloride on amyl alcohol, a product generally designated as amylene. It is prepared by heating amyl alcohol with zinc chloride, and passing the vapors given off into a well-cooled receiver. The product is rectified, that portion being retained which passes below 40°. It is a mixture of isomeric amylenes, whose boiling-points vary from 22 to 40°, and which result from the dehydration of amyl alcohol.

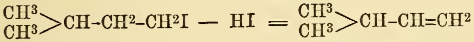
Trimethylethylene or ordinary Amylene may be obtained in a pure state by dehydrating tertiary amyl alcohol (the hydrate of amylene of Wurtz), which may be accomplished by simply heating it.

$$\underset{\text{Tertiary amyl alcohol.}}{(CH^3)^2{=}C(OH)-CH^2-CH^3} - H^2O = \underset{\text{Trimethylethylene.}}{(CH^3)^2C=CH(CH^3)}$$

It boils at 36°, and unites directly with hydriodic acid, forming tertiary amyl iodide, $(CH^3)^2CI-CH^2-CH^3$, boiling at 129°.

When bromine is poured into cooled amylene, the addition of each drop produces a hissing noise, indicating a violent reaction, and the product is a liquid amylene bromide, boiling between 170 and 180°. If the operation be performed upon crude amylene, a mixture of several bromides will result. Trimethylethylene yields a bromide containing $(CH^3)^2{=}CBr{-}CHBr{-}CH^3$.

Isopropylethylene is formed by the action of alcoholic potassium hydrate on amyl iodide (Flavitzky).



$$\begin{matrix}CH^3\\CH^3\end{matrix}{>}CH{-}CH^2{-}CH^2I - HI = \begin{matrix}CH^3\\CH^3\end{matrix}{>}CH{-}CH{=}CH^2$$

Amyl iodide. Isopropylethylene.

This body also exists in small quantity in the mixture of hydrocarbons formed by the action of zinc chloride on amyl alcohol. Boiling-point, 25°. It unites with hydriodic acid, forming a secondary iodide, $(CH^3)^2{=}CH{-}CHI{-}CH^3$, which boils at 137–139°. It combines with bromine, forming the bromide $(CH^3)^2{=}CH{-}CHBr{-}CH^2Br$, which boils between 180 and 190°.

Propylethylene or Ethylallyl may be obtained by heating with sodium a mixture of allyl iodide and ethyl iodide.

$$CH^3{-}CH^2I + CH^2{=}CH{-}CH^2I + Na^2 = 2NaI + CH^3{-}CH^2{-}CH^2{-}CH{=}CH^2$$

Ethyl iodide. Allyl iodide. Ethylallyl.

It is also formed by the action of zinc ethyl on ethyl iodide. It boils at 37°, and combines with hydriodic acid, forming the iodide $C^3H^7{-}CHI{-}CH^3$, boiling at 144°. It combines energetically with bromine, forming a bromide $C^3H^7{-}CHBr{-}CH^2Br$, boiling at 175°.

Polymerides of Amylene.—By the action of zinc chloride on amyl alcohol, there are formed, independently of amylene, other hydrocarbons, among which are the polymeric modifications known as diamylene, $C^{10}H^{20}$; triamylene, $C^{15}H^{30}$; tetramylene, $C^{20}H^{40}$ (Balard, Bauer). These bodies are formed by the union of two, three, or four molecules of amylene.

HYDROCARBONS OF THE SERIES C^nH^{2n-2}.

Among the more simple hydrocarbons is one which was discovered by E. Davy, and which Berthelot has succeeded in preparing by various processes. It is acetylene, and is the first member of a series which includes, among others, the following hydrocarbons:

Acetylene	C^2H^2	(E. Davy, Berthelot).
Allylene	C^3H^4	(Sawitsch).
Crotonylene	C^4H^6	(E. Caventou).
Valerylene	C^5H^8	(Reboul).

Acetylene, C^2H^2 or $CH{\equiv}CH$.—This hydrocarbon is a product of the incomplete combustion of many organic substances, and is the only compound of hydrogen and carbon that has been obtained by direct union of these elements.

According to Berthelot, it is formed when the electric arc is passed between carbon electrodes in an atmosphere of hydrogen.

It may be obtained by heating ethylene bromide with an alcoholic solution of potassium hydroxide, thus:

$$C^2H^4Br^2 + 2KOH = 2KBr + C^2H^2 + 2H^2O$$

The most convenient mode of preparing acetylene is by the action of water upon calcium carbide, which is readily produced in the electrical furnace (Moissan) (page 327).

$$C^2Ca + 2H^2O = C^2H^2 + Ca(OH)^2$$

The reaction takes place at ordinary temperatures.

Acetylene is a colorless gas, having a peculiar odor, suggesting that of garlic. At ordinary temperatures it dissolves in about its own volume of water. Its critical temperature is 37°. At 19.5° it is liquefied by a pressure of 39.8 atmospheres; the resulting liquid boils at —83°, and in evaporating absorbs enough heat to freeze a portion to a snow-like mass.

Acetylene burns with a highly luminous and smoky flame. With 2.5 times its volume of oxygen, acetylene constitutes one of the most explosive gaseous mixtures. It combines directly with bromine, with which it yields a dibromide, $C^2H^2Br^2$, and a tetrabromide, $C^2H^2Br^4$.

When conducted into an ammoniacal solution of cuprous chloride, it produces a brownish red precipitate of cuprous acetylide. This reaction affords a delicate test for acetylene, and an excellent means of removing it from gaseous mixtures. An analogous silver compound is similarly obtained. Both acetylides are highly explosive in the dry state; with hydrochloric acid they yield acetylene and the metallic chlorides.

$$C^2H^2Cu^2O + 2HCl = Cu^2Cl^2 + C^2H^2 + H^2O$$

On account of its superior illuminating power, acetylene is now manufactured as a substitute for the ordinary gas from bituminous coal.

Allylene, C^3H^4, the second member of the acetylene series, exists in two isomeric forms, *methylacetylene*, $CH^3{-}C{\equiv}CH$, a gas which resembles acetylene in its general properties and forms a precipitate when passed into solution of silver nitrate, and *symmetrical allylene*, $CH^2{=}C{=}CH^2$, which forms no precipitate with silver nitrate.

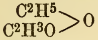
The number of isomers increases rapidly in this series as the molecules contain a greater number of carbon atoms.

DIHYDRIC ALCOHOLS, OR GLYCOLS.

The name glycols was given by Wurtz to the hydroxides of the series of hydrocarbons, C^nH^{2n}. If ordinary alcohol be ethyl hydroxide, ordinary glycol is ethylene hydroxide.

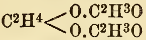
$C^2H^5.OH$	$C^2H^4(OH)^2$
Ethyl hydroxide.	Ethylene hydroxide.

While alcohol reacts with a single molecule of a monobasic acid to form a neutral ether, glycol can react with either one or two molecules of a monobasic acid, thus forming two ethers. In other words, while the monohydric alcohols contain but one atom of hydrogen which is replaceable by a single radical of a monobasic acid, glycol contains in the two groups OH two such atoms of hydrogen, capable of being replaced by two radicals of a monobasic acid, or one radical of a dibasic acid.



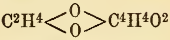
$\begin{matrix}C^2H^5\\C^2H^3O\end{matrix}\!>\!O$

Ethyl acetate.



$C^2H^4\!<\!\begin{matrix}O.C^2H^3O\\O.C^2H^3O\end{matrix}$

Ethylene diacetate.



$C^2H^4\!<\!\begin{matrix}O\\O\end{matrix}\!>\!C^4H^4O^2$

Ethylene succinate.

The glycols yield diatomic acids by oxidation.

There are isomeric glycols, or *isoglycols*, corresponding to the isoalcohols which have already been defined (page 521).

A number of glycols of the series $C^nH^{2n+2}O^2$ are now known.

		DENSITY AT 0°.	BOILING-POINTS.
Ethylene glycol, or glycol . . .	$C^2H^6O^2$	1.125	197.5°
Propylene glycol, or propylglycol .	$C^3H^8O^2$	1.051	188–189°
Butylene glycol, or butylglycol .	$C^4H^{10}O^2$	1.048	183–184°
Amylene glycol, or amylglycol . .	$C^5H^{12}O^2$	0.987	177°

It is to be remarked that all of the members of the above series are not, strictly speaking, homologous.

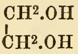
The isomerism of the glycols, like that of the alcohols, is due to the constitutions of their molecules, which can contain, like the molecules of the alcohols, the following groups:

The primary group $-CH^2.OH$
The secondary group $=CH.OH$
The tertiary group $\equiv C.OH$

Thus, ethylene glycol is primary, since it contains two groups, $CH^2.OH$.

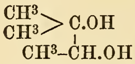
The amylene glycol derived from trimethylethylene is at the same time secondary and tertiary.

Pinacone, which has already been mentioned (page 558), is a tertiary glycol; it contains two groups $\equiv(C.OH)$.

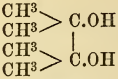


$$\begin{matrix}CH^2.OH\\|\\CH^2.OH\end{matrix}$$

Glycol.

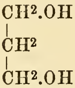


Amylene glycol.
(Secondary and tertiary.)



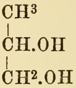
Pinacone.
(Tertiary.)

Among the *mixed* glycols, that is, those containing at the same time two different alcoholic groups, is ordinary propylene glycol, which is primary and secondary.



$$\begin{matrix}CH^2.OH\\|\\CH^2\\|\\CH^2.OH\end{matrix}$$

Normal propylene glycol.
(Primary.)



$$\begin{matrix}CH^3\\|\\CH.OH\\|\\CH^2.OH\end{matrix}$$

Ordinary propylene glycol.
(Primary and secondary.)

GLYCOL, OR ETHYLENE ALCOHOL.

$$C^2H^6O^2 = C^2H^4(OH)^2$$

Wurtz first obtained glycol by causing either iodide or bromide of ethylene to react with silver acetate

$$C^2H^4I^2 + \underset{\text{Silver acetate.}}{\begin{matrix}Ag.C^2H^3O^2\\Ag.C^2H^3O^2\end{matrix}} = \underset{\text{Ethylene diacetate.}}{(C^2H^4)''\left\{\begin{matrix}C^2H^3O^2\\C^2H^3O^2\end{matrix}\right.} + 2AgI$$

and saponifying the resulting ethylene diacetate by potassium hydroxide.

$$\underset{\text{Ethylene diacetate.}}{\left.\begin{matrix}C^2H^3O.O\\C^2H^3O.O\end{matrix}\right\}(C^2H^4)''} + 2KOH = \underset{\text{Potassium acetate.}}{2(C^2H^3O.OK)} + \underset{\text{Glycol.}}{(C^2H^4)''\left\{\begin{matrix}OH\\OH\end{matrix}\right.}$$

It is best prepared by Hüfner and Zöller's process, which consists in heating ethylene bromide with an aqueous solution of potassium carbonate, thus:

$$C^2H^4Br^2 + K^2CO^3 + H^2O = C^2H^4(OH)^2 + 2KBr + CO^2$$

188 grammes of ethylene bromide, 138 grammes of potassium carbonate, and 1 litre of water are introduced into a large flask connected with a reversed condenser, and the mix-

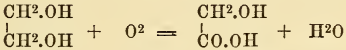
ture is boiled until all of the ethylene bromide has disappeared. The aqueous liquid is then concentrated on a water-bath, and alcohol is added to precipitate the potassium bromide; the alcoholic liquid is then distilled. Alcohol and water first pass, and when the temperature rises above 150°, the liquid which condenses is nearly pure glycol.

Properties.—Glycol is a somewhat syrupy, colorless, and odorless liquid, having a sweet taste. It mixes with water and alcohol in all proportions, but is scarcely soluble in ether. It boils at 197.5°, and distils without alteration.

Its analogy to alcohol, from which it differs by containing one more atom of oxygen, is demonstrated by the following experiments:

1. If platinum black be moistened with glycol and then rapidly plunged into a jar of oxygen, a brilliant incandescence is manifested immediately, due to the energetic absorption of oxygen.

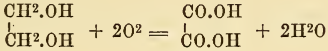
With dilute glycol, the oxidation is slower, and glycollic acid is formed.



$$\begin{array}{l}\mathrm{CH^2.OH}\\ |\\ \mathrm{CH^2.OH}\end{array} + \mathrm{O^2} = \begin{array}{l}\mathrm{CH^2.OH}\\ |\\ \mathrm{CO.OH}\end{array} + \mathrm{H^2O}$$

Glycol. Glycollic acid.

2. If glycol be heated with ordinary nitric acid, torrents of red vapor are disengaged, and the liquid deposits crystals of oxalic acid on cooling.



$$\begin{array}{l}\mathrm{CH^2.OH}\\ |\\ \mathrm{CH^2.OH}\end{array} + \mathrm{2O^2} = \begin{array}{l}\mathrm{CO.OH}\\ |\\ \mathrm{CO.OH}\end{array} + \mathrm{2H^2O}$$

Glycol. Oxalic acid.

3. When glycol is heated with potassium hydrate to 250°, pure hydrogen is disengaged and potassium oxalate is formed.

$$\mathrm{C^2H^6O^2 + 2KOH = C^2O^4K^2 + 4H^2}$$

Glycol. Potassium oxalate.

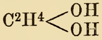
These experiments establish between glycol and glycollic and oxalic acids, relations analogous to those which exist between alcohol and acetic acid.

Ethylene Chlorhydrate, or Glycol Chlorhydrin.—When hydrochloric acid gas is passed into glycol, a neutral compound is formed which constitutes the *monochlorhydrin of glycol*, or *ethylene chlorhydrate.*

$$\mathrm{C^2H^4}<\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} + \mathrm{HCl} = \mathrm{C^2H^4}<\begin{matrix}\mathrm{OH}\\ \mathrm{Cl}\end{matrix} + \mathrm{H^2O}$$

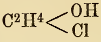
Glycol. Ethylene chlorhydrate.

This compound is intermediate between glycol and ethylene chloride, which is the dichlorhydrin of glycol.



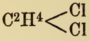
$C^2H^4<\begin{matrix}OH\\OH\end{matrix}$

Glycol.



$C^2H^4<\begin{matrix}OH\\Cl\end{matrix}$

Monochlorhydrin of glycol.



$C^2H^4<\begin{matrix}Cl\\Cl\end{matrix}$

Dichlorhydrin of glycol (ethylene chloride).

Glycol chlorhydrin is also formed by the direct union of ethylene gas and hypochlorous acid (Carius).

$$C^2H^4 + HClO = C^2H^5ClO$$

It is a colorless liquid, having a density of 1.24 at 8°. It boils at 130–131°.

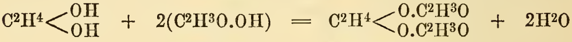
Ethylene bromhydrate, or *glycol bromhydrin*, is formed under circumstances analogous to those which furnish the chlorhydrate. It is a thick, colorless liquid, boiling at 147°.

Ethylene Nitrates.—By the reaction of ethylene bromhydrate on silver nitrate, at ordinary temperatures or by the aid of gentle heat, ethylene mononitrate, $C^2H^4<\begin{matrix}O.NO^2\\OH\end{matrix}$, is obtained as a colorless or slightly yellow liquid, which is soluble in water. Density at 11°, 1.31.

Ethylene dinitrate, $C^2H^4<\begin{matrix}O.NO^2\\O.NO^2\end{matrix}$, is formed by the action of ethylene bromide on an alcoholic solution of silver nitrate. It is a mobile, colorless liquid, insoluble in water. Density at 8°, 1.4837. It explodes by percussion (Henry).

Ethylene Acetates.—When glycol is heated with acetic acid, it is converted into acetic ethers.

$$C^2H^4<\begin{matrix}OH\\OH\end{matrix} + \underset{\text{Acetic acid.}}{C^2H^3O.OH} = \underset{\text{Ethylene monacetate.}}{C^2H^4<\begin{matrix}O.C^2H^3O\\OH\end{matrix}} + H^2O$$



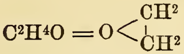
$$C^2H^4<\begin{matrix}OH\\OH\end{matrix} + \underset{\text{Acetic acid.}}{2(C^2H^3O.OH)} = \underset{\text{Ethylene diacetate.}}{C^2H^4<\begin{matrix}O.C^2H^3O\\O.C^2H^3O\end{matrix}} + 2H^2O$$

Ethylene monacetate, or monacetic glycol, is a liquid miscible with water and alcohol, and boiling at 182°.

Ethylene diacetate, or diacetic glycol, can be prepared by the reaction of ethylene iodide on silver acetate. It is a colorless liquid, soluble in 7 parts of water; it boils at 186°.

It is thus seen that two neutral ethereal compounds can be formed by the action of one and the same monobasic acid on glycol, while the monohydric alcohols would furnish but a single compound ether under the same circumstances.

ETHYLENE OXIDE.



$$C_2H_4O = O\begin{cases} CH_2 \\ | \\ CH_2 \end{cases}$$

If an excess of potassium hydroxide be added to glycol chlorhydrin contained in a test-tube, and a gentle heat be applied, a brisk effervescence will take place, due to a disengagement of vapor which may be ignited at the mouth of the tube.

At a low temperature, this vapor condenses to a colorless liquid, which is ethylene oxide.

$$\underset{\text{Glycol chlorhydrin.}}{C^2H^5ClO} = \underset{\text{Ethylene oxide.}}{C^2H^4O} + HCl$$

Ethylene oxide has the composition of glycol, less the elements of one molecule of water.

$$C^2H^4O = C^2H^6O^2 - H^2O$$

However, it cannot be obtained by direct dehydration of glycol, for when that body is distilled with zinc chloride, among other products, aldehyde, which is isomeric with ethylene oxide, is obtained.

Greene has obtained ethylene oxide by double decomposition, by heating ethylene bromide with anhydrous sodium oxide.

$$C^2H^4Br^2 + Na^2O = C^2H^4O + 2NaBr$$

Properties.—Ethylene oxide boils at 13.5°. It dissolves in all proportions in water, alcohol, and ether. Under the influence of sodium amalgam and water, it fixes hydrogen directly, being transformed into alcohol.

$$C^2H^4O + H^2 = C^2H^6O$$

It combines directly with water at 100°, regenerating glycol.

$$C^2H^4O + H^2O = C^2H^6O^2$$

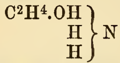
It possesses basic properties.

If equal volumes of hydrochloric gas and vapor of ethylene oxide be mixed over the mercury-trough (the mercury should be slightly warmed) the two gases will disappear; they combine to form a liquid which is glycol chlorhydrin.

$$C^2H^4O + HCl = C^2H^5ClO$$

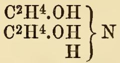
If liquid ethylene oxide be added to a cooled solution of magnesium chloride, an abundant precipitate of magnesium hydroxide will be formed in the course of a day, and the liquid will contain glycol chlorhydrin. Oxide of ethylene precipitates magnesia as would a powerful base (A. Wurtz).

Bases Derived from Ethylene Oxide.—Oxide of ethylene combines with ammonia, yielding a series of bases, the *hydroxethylenamines*, which are formed by the direct union of one, two, or three molecules of ethylene oxide with one molecule of ammonia.



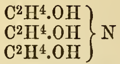
$$\left.\begin{matrix} C^2H^4.OH \\ H \\ H \end{matrix}\right\} N$$

Hydroxethylenamine.



$$\left.\begin{matrix} C^2H^4.OH \\ C^2H^4.OH \\ H \end{matrix}\right\} N$$

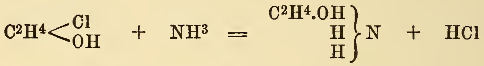
Dihydroxethylenamine.



$$\left.\begin{matrix} C^2H^4.OH \\ C^2H^4.OH \\ C^2H^4.OH \end{matrix}\right\} N$$

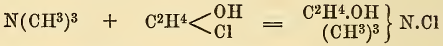
Trihydroxethylenamine.

These bases are also formed by the action of ammonia on ethylene chlorhydrin.



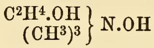
$$C^2H^4{<}\begin{matrix} Cl \\ OH \end{matrix} \quad + \quad NH^3 \quad = \quad \left.\begin{matrix} C^2H^4.OH \\ H \\ H \end{matrix}\right\} N \quad + \quad HCl$$

When ethylene chlorhydrin is treated with trimethylamine, the bodies combine, forming a chloride.



$$N(CH^3)^3 \quad + \quad C^2H^4{<}\begin{matrix} OH \\ Cl \end{matrix} \quad = \quad \left.\begin{matrix} C^2H^4.OH \\ (CH^3)^3 \end{matrix}\right\} N.Cl$$

When this chloride is treated with water and silver oxide, it is converted into a hydroxide.



$$\left.\begin{matrix} C^2H^4.OH \\ (CH^3)^3 \end{matrix}\right\} N.OH$$

Choline, or bilineurine.—This hydroxide is an energetic natural base which exists in the bile, and is also a product of the position of a complex substance, *lecithine*, which exists in the brain, in the nerves, and in the yolk of eggs.

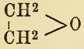
Sulphonal.—Analogous to the glycols are the diatomic hydrosulphides, of which the type is methylene mercaptan, $CH^2(SH)^2$. The oxidation of these hydrosulphides yields *disulphones*, which may also be obtained by condensation from the alkyl hydrosulphides. Thus, when a mixture of ethylmercaptan with acetone is cautiously oxidized by means of potassium permanganate, condensation takes place and diethylsulphon-dimethylmethane is formed.

$$\underset{\text{Ethyl hydrosulphide.}}{2(C^2H^5.SH)} + (CH^3)^2CO + O^4 = \underset{\text{Sulphonal.}}{(CH^3)^2C(SO^2.C^2H^5)^2} + H^2O$$

The latter is used under the name sulphonal as one of the most favored hypnotics. It is a colorless solid, crystallizing in prisms melting at 125°, and it boils at 300°. It is only slightly soluble in cold water.

ACETAL.

We may conceive of the existence of a glycol isomeric with that which has been described, and bearing the same relations to the latter that aldehyde has to ethylene oxide.

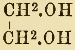


$$\begin{matrix}CH^2\\|\\CH^2\end{matrix}>O$$

Ethylene oxide.

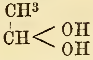
$$\begin{matrix}CH^3\\|\\CHO\end{matrix}$$

Aldehyde.



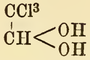
$$\begin{matrix}CH^2.OH\\|\\CH^2.OH\end{matrix}$$

Ethylene glycol.



$$\begin{matrix}CH^3\\|\\CH\end{matrix}<\begin{matrix}OH\\OH\end{matrix}$$

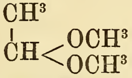
Ethylidene glycol.



$$\begin{matrix}CCl^3\\|\\CH\end{matrix}<\begin{matrix}OH\\OH\end{matrix}$$

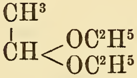
Chloral hydrate.

Just as glycol is formed by the hydration of ethylene oxide, ethylidene glycol should be formed by the hydration of aldehyde. Indeed, on contact with water aldehyde becomes heated, and doubtless is converted into the glycol in question, which is, however, too unstable to be isolated. In general, all compounds which contain two hydroxyl groups in combination with the same carbon atom are quite unstable, and readily decompose, giving up a molecule of water. It is so with chloral hydrate, which must be considered as a trichlor-derivative of ethylidene glycol. The latter is at once resolved into aldehyde and water, but its methyl and ethyl derivatives are stable, and have long been known under the names *dimethyl-acetal* and acetal.



$$\begin{matrix}CH^3\\|\\CH\end{matrix}<\begin{matrix}OCH^3\\OCH^3\end{matrix}$$

Dimethylacetal.

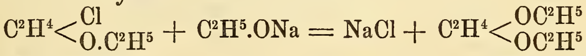


$$\begin{matrix}CH^3\\|\\CH\end{matrix}<\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}$$

Acetal.

Dimethylacetal is produced when a mixture of methyl and ethyl alcohols is oxidized by sulphuric acid and manganese dioxide. It boils at 64°, and much resembles acetal.

Acetal.—This compound was discovered by Liebig. It exists in the more volatile portions of the product of the distillation of crude alcohol. It is formed synthetically when alcohol is heated to 160° with aldehyde, and also by the action of sodium ethylate on monochlorether.



$$C^2H^4<\begin{matrix}Cl\\O.C^2H^5\end{matrix} + C^2H^5.ONa = NaCl + C^2H^4<\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}$$

Monochlorether. Acetal.

It is found among the products of the oxidation of alcohol.

Properties.—Acetal is a liquid, having a peculiar, agreeable odor, insoluble in water. Its density at 20° is 0.821. It boils at 104°.

ETHYLENE-DIAMINES.

These bases result from the substitution of one, two, or three ethylene groups, $(C^2H^4)''$, each for two atoms of hydrogen in two molecules of ammonia, and are formed by the action of alcoholic ammonia on ethylene bromide at ordinary temperatures.

$$C^2H^4Br^2 + 2NH^3 = \underset{\text{Ethylene-diamine hydrobromide.}}{C^2H^4(NH^2)^2.2HBr}$$

Ethylene-diamine, $\begin{array}{l} CH^2\text{–}NH^2 \\ | \\ CH^2\text{–}NH^2 \end{array} = N^2 \left\{ \begin{array}{l} (C^2H^4)'' \\ H^2 \\ H^2 \end{array} \right.$ is a liquid base, boiling at 116.5°, and melts at 8.5°. By the prolonged action of an excess of ethylene bromide, it is converted successively into *diethylene-diamine* and *triethylene-diamine*.

$$\underset{\text{Ethylene-diamine.}}{N^2 \left\{ \begin{array}{l} (C^2H^4)'' \\ H^2 \\ H^2 \end{array} \right.} \qquad \underset{\text{Diethylene-diamine.}}{N^2 \left\{ \begin{array}{l} (C^2H^4)'' \\ (C^2H^4)'' \\ H^2 \end{array} \right.} \qquad \underset{\text{Triethylene-diamine.}}{N^2 \left\{ \begin{array}{l} (C^2H^4)'' \\ (C^2H^4)'' \\ (C^2H^4)'' \end{array} \right.}$$

Diethylene-diamine, or *piperazine*, forms tetragonal crystals which melt at 104°. It boils without decomposition at 146°. The ethylene-diamines are *diacid*, that is, they combine with two molecules of a monobasic acid, such as hydrochloric or hydrobromic acid (Hofmann).

Tetramethylene diamine (*putrescine*), $NH^2\text{–}CH^2\text{–}CH^2\text{–}CH^2\text{–}CH^2\text{–}NH^2$, and **Pentamethylene diamine** (*cadaverine*), $NH^2\text{–}(CH^2)^5\text{–}NH^2$, are ptomaines formed during the putrefaction of animal matters. Ladenburg has synthesized them.

ISETHIONIC ACID.

$$C^2H^6SO^4 = C^2H^4 < \begin{array}{l} OH \\ SO^2.OH \end{array}$$

Oxide of ethylene unites directly with sodium acid-sulphite (bisulphite), forming sodium isethionate.

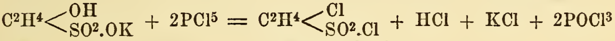
$$C^2H^4.O + \begin{array}{l} Na \\ H \end{array} > SO^3 = \underset{\text{Sodium isethionate.}}{C^2H^4 < \begin{array}{l} OH \\ SO^3Na \end{array}}$$

The same salt is formed when ethylene chlorhydrin is heated with neutral sodium sulphite.

$$C^2H^4 < \begin{array}{l} OH \\ Cl \end{array} + Na^2SO^3 = C^2H^4 < \begin{array}{l} OH \\ SO^3Na \end{array} + NaCl$$

Isethionic acid is prepared by the action of sulphuric anhydride upon alcohol or ether. The product is diluted with water, boiled for some time, and then neutralized with barium carbonate. The liquid is filtered and the filtrate decomposed exactly with sulphuric acid: isethionic acid remains in solution.

Isethionic acid is a sour liquid which solidifies to a crystalline mass on long standing over sulphuric acid. Its salts are very stable. It is isomeric with ethylsulphuric acid. Phosphorus pentachloride transforms it into a chloride.



$$C^2H^4 < \begin{matrix} OH \\ SO^2.OK \end{matrix} + 2PCl^5 = C^2H^4 < \begin{matrix} Cl \\ SO^2.Cl \end{matrix} + HCl + KCl + 2POCl^3$$

Potassium isethionate. Chlorethylsulphonic chloride.

The latter is a liquid, boiling at 120°; it is decomposed by water at 100°, into *chlorethylsulphonic* and hydrochloric acids.

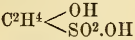
$$C^2H^4 < \begin{matrix} Cl \\ SO^2.Cl \end{matrix} + H^2O = C^2H^4 < \begin{matrix} Cl \\ SO^2.OH \end{matrix} + HCl$$

Chlorethylsulphonic acid.

TAURINE.

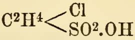
$C^2H^7NSO^3$

This important acid, whose existence in the bile was discovered by Gmelin in 1824, is related to isethionic acid; it is *amido-isethionic acid*, that is, it is derived from the latter acid by the substitution of a group NH^2 for a group OH. It may be obtained by synthesis by the action of ammonia on chlorethylsulphonic acid or on silver chlorethylsulphonate. The following formulæ indicate the relations between isethionic and chlorethylsulphonic acids and taurine:



$$C^2H^4 < \begin{matrix} OH \\ SO^2.OH \end{matrix}$$

Isethionic acid.



$$C^2H^4 < \begin{matrix} Cl \\ SO^2.OH \end{matrix}$$

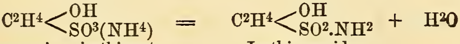
Chlorethylsulphonic acid.

$$C^2H^4 < \begin{matrix} NH^2 \\ SO^2.OH \end{matrix}$$

Taurine.

Taurine crystallizes in large, brilliant, oblique rhombic prisms, very soluble in boiling water and but slightly soluble in cold water. When the crystals are heated they melt, and decompose at an elevated temperature.

Strecker has obtained an isomeride of taurine by heating ammonium isethionate.



$$C^2H^4 < \begin{matrix} OH \\ SO^3(NH^4) \end{matrix} = C^2H^4 < \begin{matrix} OH \\ SO^2.NH^2 \end{matrix} + H^2O$$

Ammonium isethionate. Isethionamide.

PROPYLENE GLYCOLS.

$C^3H^6(OH)^2$

Normal propylene glycol (page 577) has been obtained from normal propylene bromide (page 573). This bromide is mixed with acetic acid and heated with silver acetate: propylene diacetate is formed, $C^3H^6(C^2H^3O^2)^2$, and separated by distillation, after which it is decomposed by a quantity of dry potassium hydroxide just sufficient to remove its acetic acid.

Normal propylene glycol is a colorless, syrupy liquid, boiling at 216°, and having a density of 1.0652 at 0°. It is miscible with water and alcohol in all proportions. When oxidized, it yields hydracrylic acid (Géromont, Reboul).

Ordinary propylene glycol is prepared from ordinary propylene bromide by the same process indicated above. It is a thick, colorless liquid, having a density of 1.051 at 0°. It boils at 188–189°. When diluted with water and mixed with platinum black, it absorbs oxygen, and is converted into lactic acid (A. Wurtz).

GLYCEROL (GLYCERIN).

$C^3H^8O^3 = C^3H^5(OH)^3$

Glycerol was discovered by Scheele in 1779, and studied by Chevreul, Pelouze, and especially by Berthelot, who demonstrated its character of a trihydric alcohol.

Pelouze and Gélis realized the first artificial formation of a fatty body by passing hydrochloric acid gas into a mixture of butyric acid and glycerol: butyrin was thus produced.

Preparation.—Glycerol is an accessory product in the manufacture of lead plaster. When the preparation of that substance is terminated, the water is decanted from the lead soap which separates, and hydrogen sulphide is passed through the liquid in order to precipitate as sulphide any traces of lead that may be dissolved. It is then filtered and evaporated on a water-bath. The glycerol remains as a colorless, syrupy liquid.

It is obtained in large quantities in the arts as an accessory product in the manufacture of stearin candles.

Properties.—Glycerol is a colorless liquid, having a syrupy consistence and a sweet taste. Its density at 15° is 1.28. It dissolves in all proportions in water and alcohol, but is almost insoluble in ether. When quickly heated, it distils between 275 and 280°; and it may be readily distilled in a vacuum.

Pure glycerol is crystallizable, and solidifies below 0°, but solid glycerol melts only at 17°.

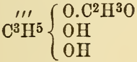
When subjected to the action of dilute nitric acid, glycerol is converted into a triatomic acid, which is called glyceric acid (Debus, Socoloff).

$$\underset{\text{Glycerol.}}{C^3H^8O^3} + O^2 = H^2O + \underset{\text{Glyceric acid.}}{C^3H^6O^4}$$

When heated with phosphorus iodide, P^2I^4, glycerol is converted into allyl iodide (Berthelot and de Luca) (page 529).

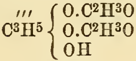
ETHERS OF GLYCEROL.

Glycerol, $C^3H^5(OH)^3$, which contains three groups OH, can form three classes of ethers by the substitution of one, two, or three monobasic acid radicals for as many atoms of hydrogen in these hydroxyl groups. If acetic acid be heated with glycerol, according to the proportions of the mixture, three different acetic ethers of glycerol may be obtained, ethers which Berthelot has designated as *acetins.*



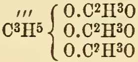
$$\overset{'''}{C^3H^5}\left\{\begin{array}{l}O.C^2H^3O\\OH\\OH\end{array}\right.$$

Monacetin.



$$\overset{'''}{C^3H^5}\left\{\begin{array}{l}O.C^2H^3O\\O.C^2H^3O\\OH\end{array}\right.$$

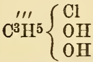
Diacetin.



$$\overset{'''}{C^3H^5}\left\{\begin{array}{l}O.C^2H^3O\\O.C^2H^3O\\O.C^2H^3O\end{array}\right.$$

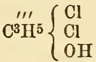
Triacetin.

In the same manner, by the action of the hydracids upon glycerol, neutral combinations are formed, analogous to the chlorides of the radicals C^nH^{2n+1}, as well as to the dichloride of ethylene and to ethylene chlorhydrate. These compounds are formed by the substitution of one, two, or three atoms of chlorine or bromine for as many hydroxyl groups in glycerol.



$$\overset{'''}{C^3H^5}\left\{\begin{array}{l}Cl\\OH\\OH\end{array}\right.$$

Monochlorhydrin.

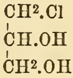


$$\overset{'''}{C^3H^5}\left\{\begin{array}{l}Cl\\Cl\\OH\end{array}\right.$$

Dichlorhydrin.

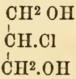
Chlorine Ethers of Glycerol, or Chlorhydrins.—There are two monochlorhydrins, two dichlorhydrins, and one trichlorhydrin.

Monochlorhydrins.—The two monochlorhydrins have been studied by Hanriot, and differ by the position of the chlorine atom.



$$\begin{array}{l}CH^2.Cl\\|\\CH.OH\\|\\CH^2.OH\end{array}$$

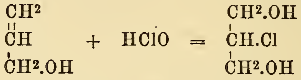
α monochlorhydrin.



$$\begin{array}{l}CH^2\,OH\\|\\CH.Cl\\|\\CH^2.OH\end{array}$$

β monochlorhydrin.

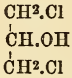
a monochlorhydrin, obtained by Berthelot by the action of hydrochloric acid on glycerol, is a thick, colorless liquid, soluble in water, alcohol, and ether, and boils at 213° (Hanriot). Density, 1.338. *β* monochlorhydrin has been obtained by the direct union of hypochlorous acid and allyl alcohol.



$$\begin{array}{l}CH^2\\ \|\\ CH\\ |\\ CH^2.OH\end{array} + HClO = \begin{array}{l}CH^2.OH\\ |\\ CH.Cl\\ |\\ CH^2.OH\end{array}$$

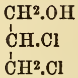
Its density at 13° is 1.328, and it boils at 230–235°.

Dichlorhydrins.—The isomerism of the dichlorhydrins is analogous to that of the monochlorhydrins.



$$\begin{array}{l}CH^2.Cl\\ |\\ CH.OH\\ |\\ CH^2.Cl\end{array}$$

α dichlorhydrin.

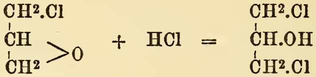


$$\begin{array}{l}CH^2.OH\\ |\\ CH.Cl\\ |\\ CH^2.Cl\end{array}$$

β dichlorhydrin.

Both are formed, the first in larger quantity, when glycerol is heated with a large excess of hydrochloric acid.

Pure *a* dichlorhydrin is prepared by treating epichlorhydrin (see farther on) with hydrochloric acid.

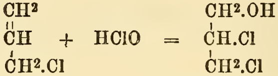


$$\begin{array}{l}CH^2.Cl\\ |\\ CH\\ |\\ CH^2\end{array}\!\!>O + HCl = \begin{array}{l}CH^2.Cl\\ |\\ CH.OH\\ |\\ CH^2.Cl\end{array}$$

Epichlorhydrin. **a dichlorhydrin.**

It is a liquid of an ethereal odor, slightly soluble in water. Its density at 0° is 1.3835, and it boils at 172–173°. When heated with a large excess of hydriodic acid, it is converted into isopropyl iodide.

β dichlorhydrin is formed by the action of chlorine on allyl alcohol, or that of hypochlorous acid on allyl chloride.



$$\begin{array}{l}CH^2\\ \|\\ CH\\ |\\ CH^2.Cl\end{array} + HClO = \begin{array}{l}CH^2.OH\\ |\\ CH.Cl\\ |\\ CH^2.Cl\end{array}$$

Allyl chloride. **β dichlorhydrin.**

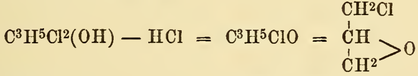
Its density at 0° is 1.371, and it boils at 182–183°. Concentrated caustic potash converts it, like its isomeride, into epichlorhydrin.

Trichlorhydrin.—When dichlorhydrin is heated with phosphorus pentachloride, the last hydroxyl group is replaced by chlorine; trichlorhydrin is thus obtained (Berthelot).

$$\underset{\text{Dichlorhydrin.}}{C^3H^5\left\{\begin{matrix}Cl\\Cl\\OH\end{matrix}\right.} + PCl^5 = \underset{\text{Trichlorhydrin.}}{C^3H^5\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.} + POCl^3 + HCl$$

It is a liquid, boiling at about 155°.

Epichlorhydrin.—When dichlorhydrin is treated with a concentrated solution of caustic potash, the elements of hydrochloric acid are removed, and a body is obtained which Berthelot has named *epichlorhydrin.*



$$C^3H^5Cl^2(OH) - HCl = C^3H^5ClO = \begin{matrix}CH^2Cl\\ | \\ CH\\ | \\ CH^2\end{matrix}\!\!>O$$

Dichlorhydrin. Epichlorhydrin.

Epichlorhydrin is a mobile liquid, heavier than water, and having an agreeable, ethereal odor. Its taste is at first sweet, afterwards sharp and burning. It boils at 118–119°. It is soluble in all proportions in alcohol and ether, but not in water.

It combines directly with hydrochloric acid, regenerating dichlorhydrin. When heated for a long time with water, it combines with one molecule of that liquid, forming monochlorhydrin.

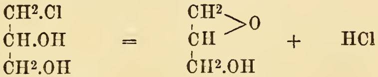
$$C^3H^5ClO + H^2O = C^3H^5Cl(OH)^2$$

Tribromhydrin, or Propenyl Tribromide, $C^3H^5Br^3 = CH^2Br\text{–}CHBr\text{–}CH^2Br$.—This is obtained by adding 1.5 parts of bromine to one part of cooled allyl iodide. Iodine separates, and the liquid is washed with potassium hydrate and distilled.

$$C^3H^5I + 3Br = C^3H^5Br^3 + I$$

Tribromhydrin crystallizes in brilliant colorless prisms, fusible at 16°. It boils at 219–220°.

Glycide.—When α monochlorhydrin is treated with baryta and anhydrous ether, it loses the elements of hydrochloric acid, and is converted into glycide (Hanriot).



$$\begin{matrix}CH^2.Cl\\ | \\ CH.OH\\ | \\ CH^2.OH\end{matrix} = \begin{matrix}CH^2\\ | \\ CH\\ | \\ CH^2.OH\end{matrix}\!\!>O \quad + \quad HCl$$

Monochlorhydrin. Glycide.

Glycide is a mobile liquid, boiling at 157°. Its density at 0° is 1.165. Water dissolves it, regenerating glycerol.

$$C^3H^5O.OH + H^2O = C^3H^5(OH)^3$$

Trinitroglycerol, or Propenyl Trinitrate.—When glycerol is poured drop by drop into a mixture of concentrated nitric and sulphuric acids, cooled in a vessel of cold water, oily drops of *trinitroglycerol*, $C^3H^5(O\text{–}NO^2)^3$, are precipitated. It is a colorless oil, insoluble in water, and explodes with great violence by percussion, by heat, or, when impure, even spontaneously.

On account of this property, nitroglycerin is employed as an explosive; but it is generally incorporated with inert matter, such as finely-divided silica. Such mixtures are called *dynamites.* The manufacture of nitroglycerin is usually conducted in wooden structures which are partly underground, and removed from exposure to influences which might cause the explosion of the product. The explosive force of the compound is more than six times as great as that of an equal quantity of gunpowder, and nitroglycerin produces effects equal to those of powder with an economy of about thirty per cent. Its explosion is too violent to permit its use in fire-arms, but it is well adapted to blasting operations. Curiously enough, while a drop of nitroglycerin placed on an anvil and struck with a hammer explodes with a loud report, the same drop would burn quietly if brought into a flame.

Other Glycerol Ethers.—Berthelot has obtained a number of glycerol ethers by directly heating glycerol with acids. When the reaction is terminated (it is often very slow), he saturates the excess of acid with calcium hydrate, and extracts the neutral fatty body, that is, the ether of glycerol, with ether. In this manner he has formed a certain number of natural fatty bodies by combining their acids with glycerol.

NATURAL FATTY BODIES.

The fats encountered in nature are *glycerides*, that is, ethers of glycerol. The memorable researches of Chevreul have shown that when these fats are methodically treated with different solvents, various immediate principles are separated, of which the most common are stearin, palmitin, and olein.

They are the *tristearic*, *tripalmitic*, and *trioleic* ethers of glycerol.

$$C^3H^5\begin{cases}O.C^{18}H^{35}O\\O.C^{18}H^{35}O\\O.C^{18}H^{35}O\end{cases}$$

Stearin.

$$C^3H^5\begin{cases}O.C^{16}H^{31}O\\O.C^{16}H^{31}O\\O.C^{16}H^{31}O\end{cases}$$

Palmitin.

$$C^3H^5\begin{cases}O.C^{18}H^{33}O\\O.C^{18}H^{33}O\\O.C^{18}H^{33}O\end{cases}$$

Olein.

When these glycerol ethers are subjected to the action of alkalies, lime, or oxide of lead, in presence of boiling water, they are decomposed, absorbing at the same time the elements of water: glycerol and the acid are set free, and the latter combines with the base forming a soap (see page 593). Thus, when stearin is boiled with milk of lime, calcium stearate and glycerol are formed. When olein is heated with water and litharge, it yields lead oleate and glycerol.

Most of the fats and oils occurring in nature consist of such glycerides mixed in various proportions, and may be resolved into the respective acids and glycerol.

Stearin and palmitin are solids, olein is liquid. In the *fats*, the solid principles predominate; the *oils* contain a larger proportion of olein.

Stearin is extracted from tallow. That substance is dissolved in boiling ether and made to crystallize. The crystals are pressed, and the operation is repeated with them many times until a substance is obtained which crystallizes in brilliant little scales, fusible at 66.5°. They are but slightly soluble in alcohol and in cold ether, but freely soluble in boiling ether.

Palmitin has been extracted, by the aid of boiling alcohol, from palm-oil which has previously been submitted to heavy pressure between sheets of porous paper. It melts at 60° (Heintz).

Olein is the predominating principle of olive-oil and almond-oil, from which it is difficult to obtain it in a pure state. Berthelot has prepared triolein artificially by heating glycerol to a temperature between 200 and 240° with an excess of oleic acid. The mass thus obtained is treated with lime and ether; the latter dissolves the triolein and leaves calcium oleate. The ethereal solution is decolorized with animal charcoal and mixed with eight times its volume of alcohol, which precipitates the triolein. When dried in a vacuum, triolein is an oil which solidifies at—6°. Its density is between 0.90 and 0.92. It is insoluble in water, and very slightly soluble in alcohol.

In contact with mercuric nitrate or with peroxide of nitrogen (red vapors), olein is converted into a crystalline, solid, fatty body, fusible at 36°, to which Boudet has given the name *elaidin*.

Fat Oils and Drying Oils.—The oils of olives, sweet almonds, rape-seed, beech-nuts, etc., acquire an acrid taste and a disagreeable odor when they are long exposed to the air, but they do not solidify. They are called *fat*, or *non-siccative* oils.

Olive-oil is the type of this class. It is extracted by pressure from crushed olives, and has a greenish-yellow color; its taste is sweet and agreeable; it is odorless. At a temperature a few degrees above 0°, it becomes a solid mass. When agitated with mercurous nitrate, it becomes solid, the olein which it contains being transformed into elaidin. It becomes rancid by exposure to the air.

When other oils, such as linseed, walnut, hemp-seed, poppy and castor oils are exposed to the air, they thicken and finally are converted into somewhat elastic, yellow, transparent masses, species of soft varnishes. They are, therefore, called *drying oils*, and are employed in the preparation of paints and varnishes.

The changes which oils undergo on contact with the air are caused by an absorption of oxygen, and are accompanied by a disengagement of more or less carbon dioxide. Every one is familiar with the uses of the natural fatty bodies in the arts and in domestic economy. Among the industrial applications, we can only mention the employment of tallow and palm-oil in the manufacture of candles, and of these as well as other oils and fats in soap-making.

Stearin Candles.—To convert tallow into stearin candles, it is saponified by lime, that is, it is first converted into a lime soap, which is then decomposed by sulphuric acid. The latter acid causes the fatty acids to separate, and they solidify on cooling. They are strongly compressed, first between warm, and finally between hot plates, so that the oleic acid is expressed, while the fatty acids proper remain. This process, which was invented by de Milly and Motard in 1829, consists, as may be seen, in entirely saponifying the tallow by lime. In 1854, de Milly modified it by considerably reducing the amount of lime, and consequently the proportion of sulphuric acid required. But it is then necessary to operate at higher temperatures by the aid of superheated steam. The operation is conducted in closed vessels, and with 2.5 parts of lime, 100 parts of tallow may be saponified at a temperature of 170 or 180°.

Palm-oil may be converted into candles by a still more simple process, which consists in subjecting it to the action of superheated steam at 300°. It is thus directly decomposed into fatty acids and glycerol, for the vapor of water, at the high temperature employed, acts precisely as would an alkali.

Soaps.—In the south of Europe, and principally at Marseilles, oils of inferior quality are used for the manufacture of soap, and the oils of sesame and earth-nut have been employed for this purpose for some years. These oils are saponified by boiling them in large boilers with a weak solution of caustic soda. The oil thus becomes pasty, the excess of oil making an emulsion with the solution of soap which is first formed. More concentrated soda lye containing common salt is then added, and the saponification is finished by boiling; the soap, which is insoluble in the concentrated lye, comes to the surface of the liquid, and the lye is then drawn off. When the soap is well made, the paste hardens on cooling; it has a bluish-gray color, due to a ferruginous soap mixed with sulphide of iron. The iron and sulphur are derived from the materials employed, crude caustic soda containing a small quantity of iron. If this paste be heated with about one-twelfth its weight of water, or a very weak solution of caustic soda, it melts, and if the mass be allowed to stand undisturbed, it will separate into two portions, the lower and strongly-colored layer containing the more dense ferruginous soap; the upper layer constitutes white soap. When the latter is completely clarified by the deposit of the ferruginous soap, it is drawn off into large moulds, where it solidifies. *White soap* is thus obtained. If, on the contrary, marbled soap be desired, the paste is frequently agitated during the cooling. The colored part, that is, the ferruginous soap, thus becomes diffused throughout the whole mass, forming bluish veins.

For some years, large quantities of soap have been prepared by combining with caustic soda the oleic acid obtained as an accessory product in the manufacture of stearin candles.

Soft soaps have potash for their base. They are manufactured from various oils, such as hemp, poppy, and linseed oils, which are saponified by caustic potash lye.

Saponification.—It will have been noticed that all of these industrial operations have for their object the decomposition of neutral fats into fatty acids, either free or combined with a base. This decomposition has received the name saponification. It may be effected by the action of water and heat alone, by the action of a base, or by the action of a powerful acid, such as sulphuric acid (sulphuric saponification). In the latter case, the acid acts upon the glycerol, forming a sulphoglyceric acid. Whatever process be employed to effect this decomposition, the presence of water is always necessary, for the elements of that liquid combine directly with the fatty body which is decomposed, as Chevreul has very well shown. In this respect, the decomposition of palmitin by superheated steam may serve as a type for all reactions of this class.

$$\underset{\text{Palmitin.}}{C^3H^5\left\{\begin{array}{l}O.C^{16}H^{31}O\\O.C^{16}H^{31}O\\O.C^{16}H^{31}O\end{array}\right.} + 3H^2O = \underset{\text{Glycerol.}}{C^3H^5\left\{\begin{array}{l}OH\\OH\\OH\end{array}\right.} + \underset{\text{Palmitic acid.}}{3C^{16}H^{31}O.OH}$$

POLYATOMIC AND POLYBASIC ACIDS.

These acids are related to the polyhydric alcohols, just as the acids containing two atoms of oxygen, and which we have already studied, are related to the monohydric alcohols.

The polyatomic acids are classed in several series, among which we must consider in a special manner those which include glycollic and oxalic acids. As we have already seen, these two acids are products of the direct oxidation of glycol.

Their homologues are related to the higher glycols.

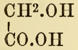
Glycols.	Acids, $C^nH^{2n}O^3$.	Acids, $C^nH^{2n-2}O^4$.
$\begin{array}{l}CH^2.OH\\\vert\\CH^2.OH\end{array}$ Glycol.	$\begin{array}{l}CH^2.OH\\\vert\\CO.OH\end{array}$ Glycollic acid.	$\begin{array}{l}CO.OH\\\vert\\CO.OH\end{array}$ Oxalic acid.
$\begin{array}{l}CH^2.OH\\\vert\\CH^2\\\vert\\CH^2.OH\end{array}$ Normal propylglycol.	$\begin{array}{l}CH^2.OH\\\vert\\CH^2\\\vert\\CO.OH\end{array}$ Hydracrylic acid.	$\begin{array}{l}CO.OH\\\vert\\CH^2\\\vert\\CO.OH\end{array}$ Malonic acid.
$\begin{array}{l}CH^3\\\vert\\CH.OH\\\vert\\CH^2.OH\end{array}$ Isopropylglycol.	$\begin{array}{l}CH^3\\\vert\\CH.OH\\\vert\\CO.OH\end{array}$ Lactic acid of fermentation.	
$\begin{array}{l}CH^2.OH\\\vert\\CH^2\\\vert\\CH^2\\\vert\\CH^2.OH\end{array}$ Normal butylglycol.		$\begin{array}{l}CO.OH\\\vert\\CH^2\\\vert\\CH^2\\\vert\\CO.OH\end{array}$ Succinic acid.

The first of the above series is that of glycol and the higher glycols. Among the latter, the true homologues of glycol would be those which differ from the latter by nCH^{2}, and of which the formulæ would consequently be analogous to that of normal propylglycol. Ordinary propylglycol, which yields lactic acid by oxidation, is an isomeride of normal propylglycol.

The second series is that of glycollic acid and its homologues. They are derived from the corresponding glycols by the substitution of O for H^{2} in one group, $CH^{2}.OH$ They consequently contain but one carboxyl group, CO.OH; they are monobasic, for the hydrogen atom of the last group can be replaced by a metal. It will also be noticed that they are at the same time acids and alcohols,—acids by virtue of the carboxyl, CO.OH, primary alcohols by virtue of the group $CH^{2}.OH$, or secondary alcohols by virtue of the group CH.OH.

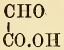
The third series is that of oxalic acid and its homologues. They are derived from the glycols by substitution of O^{2} for $2H^{2}$ in two groups, $CH^{2}.OH$. They consequently contain two carboxyl groups, CO.OH, and they are dibasic because the H of each of these groups may be replaced by an equivalent quantity of metal.

Between glycollic and oxalic acids there exists a remarkable acid, because it is at the same time a monobasic acid and an aldehyde: it is *glyoxylic acid*. It contains $C^{2}H^{2}O^{3}$, one more atom of oxygen than oxalic aldehyde, which is called *glyoxal*, $C^{2}H^{2}O^{2}$, and two atoms of hydrogen less than glycollic acid. These relations of composition will be clearly seen from the following formulæ:



$$\begin{array}{c} CH^{2}.OH \\ | \\ CO.OH \end{array}$$

Glycollic acid.

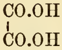


$$\begin{array}{c} CHO \\ | \\ CO.OH \end{array}$$

Glyoxylic acid.

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

Glyoxal.



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

Oxalic acid.

GLYCOLLIC ACID, GLYOXYLIC ACID, AND GLYOXAL.

Glycollic Acid, $CH^{2}(OH)\text{–}COOH$.—This acid is formed by the oxidation of glycol, but is best prepared by heating potassium monochloracetate with dilute potassium hydroxide.

$$\underset{\text{Potassium monochloracetate.}}{KC^{2}H^{2}ClO^{2}} + KOH = KCl + \underset{\text{Potassium glycollate.}}{KC^{2}H^{3}O^{3}}$$

The acid forms deliquescent crystals, very soluble in water, alcohol, and ether. It has a strong acid reaction. When heated, it loses the elements of water, and is converted into *glycollide*, or *glycollic anhydride*, $C^2H^2O^2$, or $C^4H^4O^4$.

Glyoxylic Acid, CHO–COOH.—When fuming nitric acid, water, and 80 per cent. alcohol are carefully superposed in layers in a tall jar, and left for some days at ordinary temperatures, mixture takes place by diffusion, and the products of this slow oxidation of the alcohol are glycollic acid, glyoxylic acid, and glyoxal. When the carefully evaporated liquid is neutralized with chalk, calcium salts of the two acids are formed and may be precipitated by the addition of alcohol, in which they are insoluble. From an aqueous solution of the two salts the glyoxylate deposits first on spontaneous evaporation. The free acids may be obtained by decomposing the calcium salts with oxalic acid. Glyoxylic acid is also formed by the careful oxidation of glycol.

Glyoxylic acid is a syrupy and very acid liquid. It has the properties of an acid and those of an aldehyde, as is indicated by its formula. Its solution reduces ammoniacal silver nitrate. When heated with sulphuric acid it disengages carbon monoxide.

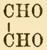
$$C^2H^2O^3 = 2CO + H^2O$$

Nascent hydrogen converts it into glycollic acid.

$$C^2H^2O^3 + H^2 = C^2H^4O^3$$

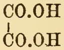
Glyoxal, CHO–CHO, may be obtained from the alcoholic liquid above mentioned, from which calcium glycollate and glyoxylate have been precipitated.

It is a deliquescent, amorphous solid, slightly colored, and very soluble in water and alcohol. Its aqueous solution energetically reduces ammonio-nitrate of silver. Like other aldehydes, glyoxal combines with sodium acid-sulphite, with phenylhydrazine, and with hydroxylamine. With the latter it forms the compound HO.N=CH–CH=N.OH, *glyoxime*, which is the type of a *dioxime*. Glyoxal is the aldehyde corresponding to oxalic acid.



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

Glyoxal.



$$\begin{matrix} CO.OH \\ | \\ CO.OH \end{matrix}$$

Oxalic acid.

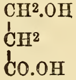
LACTIC AND PARALACTIC ACIDS.

[α-OXYPROPIONIC ACID.]

$$C^3H^6O^3 = CH^3\text{-}CH(OH)\text{-}CO.OH$$

Formation and Constitution.—Lactic acid was discovered by Scheele in sour milk. Berzelius discovered the existence in various liquids of the animal economy of an acid which was at first believed to be identical with that which results from the acid fermentation of milk. Later, an acid identical with the latter was found in various vegetable juices, and was recognized to be the product of a peculiar fermentation of glucose, called the lactic fermentation (see page 647). It was also discovered that the lactic acid of fermentation is not identical with that which exists in the animal liquids, especially that liquid which impregnates the muscular fibres. The latter acid is called *paralactic* or *dextrolactic acid.* It rotates the plane of polarized light to the right, and its salts differ in certain properties from those of ordinary lactic acid. Wislicenus, who has most carefully investigated this isomerism, believes it to be caused by a different arrangement of the atoms in space, and the results of many researches tend to confirm this view. Such cases of isomerism which cannot be represented by the ordinary structural formula are classed as *stereoisomerism,* and will be more fully explained farther on (see Tartaric Acid). An acid of the same chemical properties, but turning the plane of polarization to the left, has recently been discovered by Schardinger. It is distinguished as *levolactic acid.*

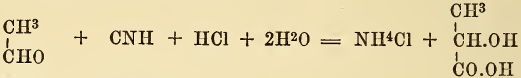
Independently of these stereoisomeric lactic acids, there is another isomer which was at first named ethylene-lactic acid, and which results from the oxidation of normal propylglycol; its constitution is expressed by the formula



$$\begin{array}{l} CH^2.OH \\ | \\ CH^2 \\ | \\ CO.OH \end{array}$$

It is *hydracrylic acid;* it is also formed when β-iodopropionic acid is treated with water and silver oxide. Its characteristic property is its easy decomposition into water and acrylic acid, hence the name hydracrylic (Wislicenus).

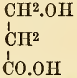
Its isomeride, lactic acid of fermentation, is formed by the oxidation of ordinary propylglycol (A. Wurtz). This fact determines its constitution, which can also be deduced from a very interesting mode of formation discovered by Strecker. When a mixture of aldehyde, hydrocyanic acid, and hydrochloric acid is allowed to stand for some time, ammonium chloride and lactic acid are formed.



$$\begin{array}{l}\mathrm{CH^3}\\ |\\ \mathrm{CHO}\end{array} + \mathrm{CNH} + \mathrm{HCl} + \mathrm{2H^2O} = \mathrm{NH^4Cl} + \begin{array}{l}\mathrm{CH^3}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CO.OH}\end{array}$$

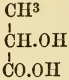
Aldehyde. Hydrocyanic acid. Lactic acid.

The isomerism of lactic and hydracrylic acids may be readily understood by the aid of the following formulæ:



$$\begin{array}{l}\mathrm{CH^2.OH}\\ |\\ \mathrm{CH^2}\\ |\\ \mathrm{CO.OH}\end{array}$$

Hydracrylic acid.



$$\begin{array}{l}\mathrm{CH^3}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CO.OH}\end{array}$$

Lactic acid.

Both acids are monobasic; each contains the group CO.OH, which is characteristic of organic acids. The third oxygen atom exists in alcoholic hydroxyl, either in the primary group $\mathrm{CH^2.OH}$, or in the secondary group CH.OH.

The preceding formulæ show that lactic acid has a mixed function; it is at the same time an alcohol and an acid. This is made evident in all of its compounds, and it will be sufficient to mention that one molecule of lactic acid in its function as an *acid*, can react with and etherify another molecule in its function of an *alcohol*, the hydroxyl of the group CO.OH forming a molecule of water with the hydrogen of the alcoholic hydroxyl in the second molecule of the acid. The dilactic acid, lactic anhydride, and lactide which are formed by the more or less complete dehydration of two molecules of lactic acid, are veritable *dilactic ethers.* This point has been developed by Grimaux.

Preparation of Lactic Acid.—A mixture of 3 kilogrammes of glucose dissolved in 13 litres of water, 4 kilogrammes of sour milk, 100 grammes of old cheese, and 1.5 kilogrammes of pulverized chalk, is exposed to a temperature of 30 or 35°. At the end of a week, the whole solidifies to a mass of calcium lactate. The salt is purified by crystallization, and is exactly decomposed by dilute sulphuric acid. The calcium sulphate is separated by filtration, and the acid liquid is boiled and saturated with hydrocarbonate of zinc;

It is then filtered and allowed to cool. The zinc lactate crystallizes, and its solution being decomposed by hydrogen sulphide, zinc sulphide and lactic acid are obtained. The filtered solution is evaporated on a water-bath.

For the preparation of lactic acid on a smaller scale, advantage is taken of the fact that some sugars (glucose, fructose) upon heating with alkalies yield considerable quantities of the acid.

Properties.—Lactic acid is generally obtained as a colorless, syrupy liquid, having a decided acid taste. In the pure state it forms hard crystals, which melt at 18°. When heated, it begins to lose water at 130°, and is converted, little by little, into a yellow, amorphous mass, insoluble in water, but soluble in alcohol and ether. This body is *dilactic acid*, $C^6H^{10}O^5$.

$$2C^3H^6O^3 = C^6H^{10}O^5 + H^2O$$

At 230°, it disengages a small quantity of carbon monoxide and carbon dioxide, and a product distils which often solidifies on cooling. It is *lactide*, or *dilactic anhydride*, and is derived directly from dilactic acid.

$$\underset{\text{Dilactic acid.}}{C^6H^{10}O^5} = \underset{\text{Lactide.}}{C^6H^8O^4} + H^2O$$

Lactide has been represented by the more simple formula $C^3H^4O^2$, but its vapor density as well as the depression it produces in the freezing points of its solvents show that the double formula represents the true constitution of this body.

Lactide occurs in colorless crystals, soluble in water and alcohol. It possesses the property of combining directly with the elements of water, lactic acid being re-formed; it also combines with ammonia, forming lactamide.

Paralactic Acid.—This is the lactic acid which may be extracted from meat. It is also called *sarcolactic* acid. It may be prepared from commercial extract of meat; this is dissolved in 4 parts of water, and the solution precipitated by 8 parts of 90 per cent. alcohol. The alcoholic solution is decanted, and the residue, which is insoluble in alcohol, is exhausted with 2 parts of lukewarm water, the solution again being precipitated by alcohol. The alcoholic solutions are united and distilled on a water-bath. The residue is rendered strongly acid by sulphuric acid, and agitated with ether which dissolves the paralactic acid set free. The ethereal solution is evaporated, and the acid is converted into the salt of zinc, which is subsequently decomposed by hydrogen sulphide, as has been indicated for the preparation of ordinary lactic acid. Paralactic acid is syrupy like its isomeride. It turns the plane of polarized light to the right (Wislicenus). When heated, it becomes dehydrated, yielding lactide.

Levolactic Acid.—An acid which rotates the plane of polarization to the left, but otherwise identical with paralactic acid, has been obtained by a peculiar fermentation of sugar (Schardinger).

Ordinary lactic acid can be resolved into the two active modifications.

Lactates and Paralactates.—Lactic acid is a monobasic acid; the neutral lactates contain $R'C^3H^5O^3$, or $M''(C^3H^5O^3)^2$. The most characteristic is *zinc lactate*, $Zn(C^3H^5O^3)^2 + 3H^2O$, which is but slightly soluble in cold water, and separates from its boiling solution in brilliant needles or laminæ.

Zinc paralactate crystallizes with two molecules of water, and is much more soluble than the ordinary lactate.

Calcium lactate, $Ca(C^3H^5O^3)^2 + 5H^2O$, crystallizes in rounded masses, formed of little needles grouped around a common centre. Like all the lactates, it is very soluble in water and alcohol.

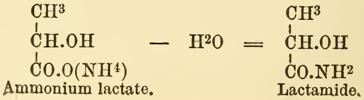
Ferrous lactate, $Fe(C^3H^5O^3)^2$, prepared by double decomposition of calcium lactate and ferrous sulphate, forms greenish, crystalline crusts, soluble in water. It is employed in medicine.

Lactamide, $C^3H^7NO^2$.—When an alcoholic solution of lactide is treated with ammonia and the liquid is evaporated, crystals are obtained which are soluble in water and alcohol. They constitute lactamide.

$$C^6H^8O^4 + 2NH^3 = 2C^3H^7NO^2$$

Potassium hydrate decomposes lactamide into lactic acid and ammonia.

Lactamide represents ammonium lactate less the elements of water.



$$\underset{\text{Ammonium lactate.}}{\begin{array}{l}CH^3\\ |\\ CH.OH\\ |\\ CO.O(NH^4)\end{array}} - H^2O = \underset{\text{Lactamide.}}{\begin{array}{l}CH^3\\ |\\ CH.OH\\ |\\ CO.NH^2\end{array}}$$

HYDRACRYLIC ACID.

(ETHYLENELACTIC, OR β-HYDROXYPROPIONIC ACID.)

$$C^3H^6O^3 = CH^2(OH)\text{-}CH^2\text{-}CO.OH$$

This acid is formed by the oxidation of normal propylglycol. It is also formed by the action of water and silver oxide on β–iodopropionic acid.

$$\underset{\beta\text{-Iodopropionic acid.}}{CH^2I\text{-}CH^2\text{-}CO^2H} + AgOH^* = \underset{\text{Hydracrylic acid.}}{CH^2.OH\text{-}CH^2\text{-}CO.OH} + AgI$$

The silver salt formed in the latter reaction is converted into the zinc salt, and the latter is decomposed by hydrogen sulphide.

Hydracrylic acid is syrupy. When heated, it breaks up into acrylic acid and water.

$$C^3H^6O^3 = C^3H^4O^2 + H^2O$$

When heated with hydriodic acid, it is again converted into β–iodopropionic acid. Its *sodium salt*, $NaC^3H^5O^3$, deposits from alcohol in crystals fusible at 142–143°. Between 180 and 200°, it loses water, and is partly converted into sodium acrylate.

Zinc hydracrylate, $Zn(C^3H^5O^3)^2 + 4H^2O$, is characteristic. It forms large, very brilliant crystals, soluble in about one part of water.

GLYCERIC (DIHYDROXYPROPIONIC) ACID.

$$C^3H^6O^4 = CH^2(OH)\text{-}CH(OH)\text{—}CO.OH$$

This acid is obtained by oxidizing glycerol with nitric acid. or by treating it with bromine and water. It is also formed by the spontaneous decomposition of nitroglycerin.

It is prepared by introducing into a tall jar one part of nitric acid of specific gravity 1.5, and 1 part of glycerol diluted with its own volume of water. Care is taken that the two liquids may not mix, and the whole is left to itself for five or six days. The two bodies gradually mingle and react upon each other. The liquid is evaporated on a water-bath, and the residue is boiled with well-washed hydrate of lead suspended in water, after which the solution of lead-salt is filtered hot. Crystals of lead

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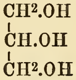
* Instead of $Ag^2O + H^2O$.

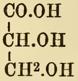
glycerate separate on cooling; they are purified, and their aqueous solution when decomposed by hydrogen sulphide, furnishes glyceric acid.

Properties.—Glyceric acid is a thick, light-yellow syrup, soluble in water and alcohol. Its reaction is acid; it is monobasic. Hydriodic acid, by the aid of heat, converts it into β–iodopropionic acid. Its relations with glycerol may be seen in the following formulæ:



$$\begin{array}{l} CH^2.OH \\ | \\ CH.OH \\ | \\ CH^2.OH \end{array}$$

Glycerol.



$$\begin{array}{l} CO.OH \\ | \\ CH.OH \\ | \\ CH^2.OH \end{array}$$

Glyceric acid.

Closely related to glycollic and lactic acids are two important nitrogenized bodies, glycocoll and alanine. They form part of a series which includes among other bodies leucine, a nitrogenized compound which plays a part in the animal economy.

When a current of nitrous anhydride is passed into solutions of glycocoll, alanine, and leucine, nitrogen is disengaged, and these bodies are converted into glycollic, lactic, and leucic acids. We then have the following series:

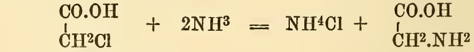
$C^2H^4O^3$ Glycollic acid.	$C^2H^5NO^2$ Glycocoll.
$C^3H^6O^3$ Lactic acid.	$C^3H^7NO^2$ Alanine.
$C^6H^{12}O^3$ Leucic acid.	$C^6H^{13}NO^2$ Leucine.

GLYCOCOLL, OR GLYCINE.

$$C^2H^5NO^2 = CH^2(NH^2)\text{–}CO.OH$$

This body is related to glycollic acid. It was discovered by Braconnot, who obtained it by boiling gelatin with dilute sulphuric acid for a long time, saturating the solution with barium carbonate and evaporating the filtered liquid. Hence the name sugar of gelatin or glycocoll.

Cahours obtained it by the action of ammonia on monochloracetic acid.

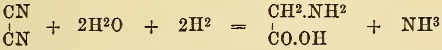


$$\begin{array}{l} CO.OH \\ | \\ CH^2Cl \end{array} + 2NH^3 = NH^4Cl + \begin{array}{l} CO.OH \\ | \\ CH^2.NH^2 \end{array}$$

Monochloracetic acid. Glycocoll.

It is therefore amidacetic acid.

It may also be formed by passing cyanogen gas into boiling hydriodic acid, which is reduced with separation of iodine, the hydrogen effecting the change.



$$\begin{array}{c}CN\\|\\CN\end{array} + 2H^2O + 2H^2 = \begin{array}{c}CH^2.NH^2\\|\\CO.OH\end{array} + NH^3$$

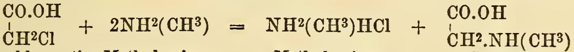
It is a solid body, crystallizing in oblique rhombic prisms, fusible at 235°. Its taste is sweet. It is soluble in 4 parts of water, slightly soluble in alcohol, insoluble in ether. Its solution has a feeble acid reaction. Indeed, glycocoll can react with the bases, forming compounds; when it is digested for several hours at a temperature between 80 and 104° with silver oxide, the latter is dissolved, and the compound $C^2H^4AgNO^2$ is formed. The cupric compound, $(C^2H^4NO^2)^2Cu + H^2O$, crystallizes in beautiful, dark-blue needles. On the other hand, glycocoll will combine with the acids; there is a nitrate of glycocoll crystallizable in large prisms containing $C^2H^5NO^2.HNO^3$.

With ferric chloride, glycocoll gives an intense red color decolorized by acids and reappearing on the addition of ammonia.

When nitrous anhydride is passed into a solution of glycocoll, the latter is converted into glycollic acid, nitrogen being at the same time disengaged.

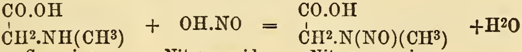
$$\underset{\text{Glycocoll.}}{2C^2H^5NO^2} + N^2O^3 = \underset{\text{Glycollic acid.}}{2C^2H^4O^3} + H^2O + 2N^2$$

Methylglycocoll or Sarcosine, $C^3H^7NO^2$.—This compound is obtained by the reaction of methylamine and monochloracetic acid, by an interchange analogous to that which yields glycocoll.



$$\underset{\text{Monochloracetic acid.}}{\begin{array}{c}CO.OH\\|\\CH^2Cl\end{array}} + \underset{\text{Methylamine.}}{2NH^2(CH^3)} = \underset{\text{Methylamine hydrochloride.}}{NH^2(CH^3)HCl} + \underset{\text{Sarcosine.}}{\begin{array}{c}CO.OH\\|\\CH^2.NH(CH^3)\end{array}}$$

It is also formed in the decomposition of creatine and caffeine by baryta water (Liebig). It crystallizes in rhomboidal prisms, very soluble in water, slightly soluble in alcohol. It melts and decomposes at 210°–220°, yielding dimethylamine and carbon dioxide. Like glycocoll, it forms compounds with acids. When distilled with soda-lime, it yields methylamine. It may be distinguished from glycocoll by the action of nitrous acid, which converts it and all compounds which contain the group NH into nitroso-derivatives.



$$\underset{\text{Sarcosine.}}{\begin{array}{c}CO.OH\\|\\CH^2.NH(CH^3)\end{array}} + \underset{\text{Nitrous acid.}}{OH.NO} = \underset{\text{Nitrososarcosine.}}{\begin{array}{c}CO.OH\\|\\CH^2.N(NO)(CH^3)\end{array}} + H^2O$$

ALANINE.

$$C^3H^7NO^2 = CH^3\text{–}CH(NH^2)\text{–}CO.OH$$

Strecker made the synthesis of alanine by passing hydrochloric acid gas into a mixture of aldehyde-ammonia and hydrocyanic acid.

$$C^2H^4O + CNH + H^2O = C^3H^7NO^2$$

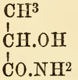
The brown liquid resulting from this reaction is evaporated. Alanine crystallizes in hard needles, grouped in stars or tufts. It is soluble in water, only slightly soluble in alcohol, insoluble in ether. The aqueous solution is neutral, and is converted by nitrous anhydride into lactic acid, with evolution of nitrogen.

$$\underset{\text{Alanine.}}{2C^3H^7NO^2} + N^2O^3 = \underset{\text{Lactic acid.}}{2C^3H^6O^3} + H^2O + 2N^2$$

Alanine may be sublimed by cautiously heating it. By dry distillation, it breaks up into carbon dioxide and ethylamine.

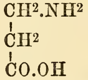
$$C^3H^7NO^2 = CO^2 + C^2H^5.NH^2$$

It is isomeric with lactamide and with an acid amide which is obtained by the action of ammonia on β–iodopropionic acid. The following formulæ account for these isomerides:



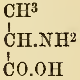
$$\begin{array}{l} CH^3 \\ | \\ CH.OH \\ | \\ CO.NH^2 \end{array}$$

Lactamide.



$$\begin{array}{l} CH^2.NH^2 \\ | \\ CH^2 \\ | \\ CO.OH \end{array}$$

β–amidopropionic acid.



$$\begin{array}{l} CH^3 \\ | \\ CH.NH^2 \\ | \\ CO.OH \end{array}$$

Alanine.

β–amidopropionic acid, which is formed in the reaction just indicated, crystallizes in transparent and colorless oblique rhombic prisms. It is very soluble in water and but slightly soluble in alcohol. It melts at 196°, partly subliming in needles, and partly decomposing into ammonia and acrylic acid.

LEUCINE.

$$C^6H^{13}NO^2$$

This body was discovered by Proust, in 1818, in old cheese. It seems to be identical with a substance obtained from cadaveric fat, and named by Fourcroy *aposepedine*. It is a product of the putrefaction of animal matters. It is also formed when horn, gelatinous tissues, or albuminous matters are boiled with dilute sulphuric acid, or fused with caustic alkalies. In these reactions, tyrosine, and sometimes glycocoll, is formed at the same time.

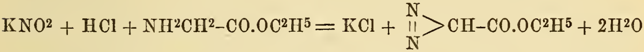
Leucine exists already formed in the economy. It is met with in the tissues of the liver, spleen, lungs, pancreas, salivary glands, etc., and may be formed artificially, by a process analogous to that described for the synthesis of alanine.

Properties.—Leucine crystallizes in white plates. It dissolves in 27 parts of cold water and much more abundantly in boiling water. It melts at 270°, and decomposes at a higher temperature into carbon dioxide and amylamine.

$$C^6H^{13}NO^2 = CO^2 + C^5H^{11}.NH^2$$

DIAZO-ACIDS.

A series of interesting and important acids has recently been discovered by Curtius as products of the action of potassium nitrite on hydrochloric acid solutions of the amido-acid ethers. While it has not been possible to isolate the free acids on account of their tendency to decompose with liberation of nitrogen, their ethers are formed quite readily. Thus, the action of potassium nitrite on ethyl amido-acetate in presence of hydrochloric acid yields *ethyl diazoacetate.*



$$KNO^2 + HCl + NH^2CH^2\text{-}CO.OC^2H^5 = KCl + \begin{matrix} N \\ \| \\ N \end{matrix}\!\!>CH\text{-}CO.OC^2H^5 + 2H^2O$$

This ether is a lemon-yellow oil, which may be distilled in vacuum, but is decomposed with explosive violence when heated under ordinary pressures or on contact with sulphuric acid. Nascent hydrogen converts the diazoethers into hydrazine derivatives. Diamide and hydrazoic acid (page 160) were first obtained with the aid of these ethers.

OXALIC ACID.

$$C^2H^2O^4 = CO(OH)\text{-}CO(OH)$$

Natural State and Modes of Formation.—This important acid exists in many vegetables. Wiegleb and Scheele extracted it from salt of sorrel, which is an acid oxalate of potassium.

The process of Scheele has become classic. It consists in precipitating a solution of salt of sorrel with acetate of lead, and decomposing the precipitated lead oxalate by hydrogen sulphide. The great Swedish chemist demonstrated the identity of the acid thus formed and that which Bergman had previously obtained by treating sugar with nitric acid.

Oxalic acid is met with in the animal economy. Urine often deposits little crystals of calcium oxalate, which salt is sometimes deposited in the bladder and there forms rough concretions known as mulberry calculi.

Oxalic acid is formed by the action of nitric acid or fused caustic potash on a great number of organic matters.

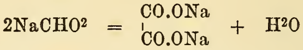
Cyanogen yields oxalic acid by its decomposition in contact with water (page 464).

We have already studied the relations which exist between oxalic acid and glycol (page 579).

Drechsel has made a synthesis of oxalic acid by passing carbon dioxide over metallic sodium disseminated in very dry sand and heated to 350°. The product was sodium oxalate.

$$2CO^2 + Na^2 = \underset{\text{Sodium oxalate.}}{Na^2C^2O^4}$$

An oxalate also results when sodium or potassium formate is rapidly heated to 440°.



$$2NaCHO^2 = \begin{matrix} CO.ONa \\ | \\ CO.ONa \end{matrix} + H^2O$$

Preparation.—Oxalic acid is prepared in the arts by two processes. One consists in the oxidation of molasses of an inferior quality by nitric acid. The operation gives rise to an abundant disengagement of nitrous vapors and carbon dioxide. It is conducted in leaden boilers that are not attacked in presence of a great excess of oxidizable organic matter.

Another process consists in the reaction of potassium hydrate on saw-dust at a high temperature. The mass is exhausted with water which dissolves out potassium oxalate, and the solution is treated with milk of lime. Calcium oxalate is precipitated and potassium hydrate regenerated. The precipitated calcium oxalate is decomposed by sulphuric acid, calcium sulphate, which is almost insoluble, being formed, and oxalic acid remaining in solution in the water. When the latter is sufficiently concentrated, the acid is deposited in crystals. The potassium hydrate which remains in the first solution is evaporated, and serves for new operations.

Properties.—Oxalic acid crystallizes from its aqueous solution in large, transparent prisms, containing 2 molecules of water. When exposed to the air, these crystals effloresce, and they completely lose their water at 100° or in a vacuum over sulphuric acid. One part of oxalic acid dissolves in 15.5 parts of water at 10°. It is also very soluble in alcohol.

It melts in its water of crystallization at 98°, begins to disengage gases at 132°, and between 155 and 160° breaks up into water, carbon monoxide, carbon dioxide, and formic acid.

$$C^2H^2O^4 = CO^2 + CH^2O^2$$
$$C^2H^2O^4 = CO^2 + CO + H^2O$$

At the same time, a portion of the dry acid escapes decomposition and sublimes.

When oxalic acid is heated with sulphuric acid, it is decomposed into carbon monoxide, carbon dioxide, and water, according to the equation given above.

Certain chlorides are reduced by ebullition with a solution of oxalic acid: hydrochloric acid is formed, and carbon dioxide disengaged. Under such circumstances, auric chloride deposits metallic gold; mercuric chloride is reduced to mercurous chloride.

Oxalic acid is a violent poison. In doses of 8, 12, to 20 grammes, it produces poisonous effects which may prove fatal. It acts upon the heart, retarding its movements, and upon the nerve centres, of which it rapidly depresses the functions. Its antidote is chalk or precipitated calcium carbonate.

If a solution of oxalic acid, or better, ammonium oxalate, be added to a solution of calcium chloride, a white precipitate of calcium oxalate is formed. This precipitate is formed even in very dilute solutions, and is insoluble in acetic acid.

If a small quantity of silver oxalate be heated in a small test-tube, the salt decomposes with explosive violence into carbon dioxide and metallic silver: a portion of the latter is projected from the tube, while the remainder is left as a gray powder.

These reactions characterize oxalic acid.

Oxalates.—Oxalic acid is dibasic. Its two atoms of hydrogen may be replaced by two atoms of a univalent metal, or by one atom of a bivalent. Acid oxalates and neutral oxalates are known.

Potassium Acid Oxalate, $KHC^2O^4 + H^2O$.—This salt constitutes the greater part of the salt of sorrel of commerce. It is extracted from the juice of various kinds of *Rumex* and *Oxalis*, the juice of which is clarified with clay and then evaporated to crystallization. It is but slightly soluble in water.

If a concentrated solution of oxalic acid be agitated with a solution of potassium neutral oxalate, a precipitate of potassium acid oxalate will be formed.

If a concentrated solution of oxalic acid be agitated with a solution of potassium acid oxalate, a white precipitate of potassium quadroxalate, a combination of the acid salt and oxalic acid, will be deposited. It contains $C^2H^2O^4 + KHC^2O^4 + 2H^2O$.

Neutral Potassium Oxalate, $K^2C^2O^4 + H^2O$, is obtained by neutralizing a solution of the acid salt with potassium carbonate and evaporating. It crystallizes in oblique rhombic prisms, very soluble in water.

Ammonium Oxalate, $(NH^4)^2C^2O^4 + H^2O$, which is frequently used as a reagent, is prepared by neutralizing oxalic acid with ammonia. The concentrated solution deposits colorless crystals belonging to the type of the right rhombic prism. There is also an acid oxalate of ammonium, $(NH^4)HC^2O^4$.

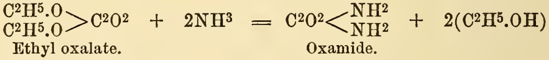
Methyl Oxalate, $(CH^3)^2C^2O^4$, forms colorless crystals melting at 54°. It is prepared by heating anhydrous oxalic acid with methyl alcohol.

Ethyl Oxalate, or Oxalic Ether, $(C^2H^5)^2C^2O^4$.—This ether may be prepared by distilling a mixture of potassium acid oxalate, alcohol, and concentrated sulphuric acid. It is a colorless oily liquid, heavier than water, and having an aromatic odor. It boils at 186°.

OXAMIDE.

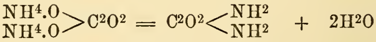
$C^2O^2(NH^2)^2$

If solution of ammonia be added to ethyl oxalate, the latter immediately solidifies to a white mass formed of a crystalline powder. This is oxamide.



$$\underset{\text{Ethyl oxalate.}}{\begin{matrix} C^2H^5.O \\ C^2H^5.O \end{matrix}\!\!>C^2O^2} \quad + \quad 2NH^3 \quad = \quad \underset{\text{Oxamide.}}{C^2O^2\!\!<\!\!\begin{matrix} NH^2 \\ NH^2 \end{matrix}} \quad + \quad 2(C^2H^5.OH)$$

Oxamide is also formed by the dry distillation of ammonium oxalate.

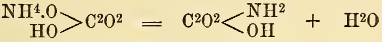


$$\begin{matrix} NH^4.O \\ NH^4.O \end{matrix}\!\!>C^2O^2 = C^2O^2\!\!<\!\!\begin{matrix} NH^2 \\ NH^2 \end{matrix} \quad + \quad 2H^2O$$

The latter reaction, studied in 1830 by Dumas, led to the discovery of the amides.

Oxamide is a white, crystalline powder, very slightly soluble in cold water, insoluble in alcohol, somewhat soluble in boiling water, from which it is deposited on cooling. Like all of the amides, it is decomposed by boiling caustic alkalies, ammonia being disengaged and potassium oxalate formed.

Oxamic Acid.—This body is formed when ammonium acid oxalate is heated to between 220 and 238° (Balard).

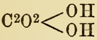


$$\begin{matrix}NH^4.O\\HO\end{matrix}\!>C^2O^2 = C^2O^2<\begin{matrix}NH^2\\OH\end{matrix} + H^2O$$

Ammonium acid oxalate. Oxamic acid.

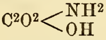
It is a yellowish, granular powder which boiling water converts into ammonium acid oxalate by the direct addition of one molecule of water.

The following formulæ express clearly the relations existing between oxalic acid, oxamic acid, and oxamide:



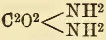
$$C^2O^2<\begin{matrix}OH\\OH\end{matrix}$$

Oxalic acid.



$$C^2O^2<\begin{matrix}NH^2\\OH\end{matrix}$$

Oxamic acid.



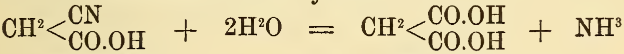
$$C^2O^2<\begin{matrix}NH^2\\NH^2\end{matrix}$$

Oxamide.

MALONIC ACID.

$$C^3H^4O^4 = CH^2<\begin{matrix}CO.OH\\CO.OH\end{matrix}$$

Malonic acid is the next higher homologue of oxalic acid, and was first obtained by the oxidation of malic acid by potassium dichromate and sulphuric acid. It also results from the hydration of cyanacetic acid when that compound is heated with alkalies or with hydrochloric acid.



$$CH^2<\begin{matrix}CN\\CO.OH\end{matrix} + 2H^2O = CH^2<\begin{matrix}CO.OH\\CO.OH\end{matrix} + NH^3$$

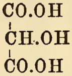
Cyanacetic acid. Malonic acid.

It crystallizes in colorless thin plates, readily soluble in water and alcohol, and fusible at 132°. At a high temperature it decomposes into carbon dioxide and acetic acid.

It is dibasic, like oxalic acid forming two series of salts in which either one or both atoms of basic hydrogen are replaced by an equivalent quantity of metal.

Ethyl Malonate, $(C^2H^5)^2C^3H^2O^4$, can be prepared by the action of hydrochloric acid gas on a mixture of alcohol and calcium malonate. It is a colorless liquid, boiling at 198°. When heated with water to 150°, it is decomposed into ethyl acetate, carbon dioxide, and ethylene. The hydrogen atoms in the acid radical of ethyl malonate can be successively replaced by sodium, and the reactions of the sodium malonic ethers so formed render them valuable agents in many syntheses (see Succinic Acid).

Oxymalonic or Tartronic Acid, $C^3H^4O^5$, is one of the products of the decomposition of tartaric acid by nitric acid, page 617. Its formula is



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

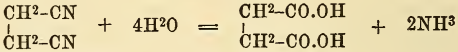
It forms large colorless prisms, fusible at 184°.

SUCCINIC ACID.

$$C^4H^6O^4 = CO.OH\text{-}CH^2\text{-}CH^2\text{-}CO.OH$$

This acid, which was first obtained by the distillation of amber, is one of the products of oxidation by nitric acid of the complex fatty acids, such as palmitic and stearic acids. It is also formed in the alcoholic fermentation of sugar (see page 648), in the fermentation of calcium malate, and by the reduction of malic and tartaric acids by hydriodic acid.

Maxwell Simpson obtained it synthetically by decomposing ethylene dicyanide with potassium hydroxide.



$$\begin{array}{l} CH^2\text{-}CN \\ | \\ CH^2\text{-}CN \end{array} + 4H^2O = \begin{array}{l} CH^2\text{-}CO.OH \\ | \\ CH^2\text{-}CO.OH \end{array} + 2NH^3$$

Ethylene dicyanide. Succinic acid.

In this reaction the nitrogen of each cyanogen group unites with H^3, and is replaced by $O^2H = 2(H^2O) - H^2$. Succinic acid thus contains two groups CO^2H, combined with ethylene.

When the monosodium compound of malonic ether reacts with chloracetic ether the ethyl ether of ethenyltricarboxylic acid is formed.

$$\underset{\text{Sodium malonic ether.}}{CHNa{=}(COOC^2H^5)^2} + \underset{\text{Chloracetic ether.}}{CH^2Cl\text{-}COOC^2H^5} =$$

$$NaCl + \underset{\text{Ethenyltricarboxylic ether.}}{COO(C^2H^5)\text{-}CH^2\text{-}CH{=}(COOC^2H^5)^2}$$

By the action of heat the free acid obtained by saponification of the latter ether is decomposed into carbon dioxide and succinic acid. All acids containing two carboxyl groups combined with the same carbon atom are decomposed with loss of carbon dioxide in an analogous manner.

Preparation.—Succinic acid is manufactured by the dry distillation of amber and purifying the solid product of this distillation.

Properties.—Succinic acid forms large, colorless crystals, unaltered by the air, and fusible at 180°. At 235° it boils and breaks up into *succinic anhydride* and water.

$$\underset{\text{Succinic acid.}}{C^4H^6O^4} = \underset{\text{Succinic anhydride.}}{C^4H^4O^3} + H^2O$$

It is fairly soluble in water, less so in alcohol, and almost insoluble in ether.

Succinic anhydride, $C^4H^4O^3$, which is formed as above mentioned by the dry distillation of succinic acid, forms a white, crystalline mass. It is converted by phosphorus pentachloride into succinyl chloride, $C^4H^4O^2Cl^2$.

$$\begin{array}{l}CH^2\text{–}CO\\ \vert\\ CH^2\text{–}CO\end{array}\!\!>O + PCl^5 = POCl^3 + \begin{array}{l}CH^2\text{–}COCl\\ \vert\\ CH^2\text{–}COCl\end{array}$$

Succinic anhydride. Succinyl chloride.

Kekulé has obtained *monobromo-succinic* and *dibromo-succinic* acids by heating moistened succinic acid with bromine in sealed tubes.

Monobromo-succinic acid is converted into malic acid when treated with water and silver oxide.

$$C^2H^3Br\!<\!\begin{array}{l}CO^2H\\ CO^2H\end{array} + AgOH = C^2H^3(OH)\!<\!\begin{array}{l}CO^2H\\ CO^2H\end{array} + AgBr$$

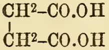
Monobromo-succinic acid. Malic acid.

Under the same circumstances, dibromo-succinic acid is converted into tartaric acid.

$$C^2H^2Br^2\!<\!\begin{array}{l}CO^2H\\ CO^2H\end{array} + 2AgOH = C^2H^2(OH)^2\!<\!\begin{array}{l}CO^2H\\ CO^2H\end{array} + 2AgBr$$

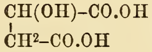
Dibromo-succinic acid. Tartaric acid.

These reactions, which were discovered by Kekulé, establish very close relations between succinic, malic, and tartaric acids.



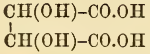
$$\begin{array}{l}CH^2\text{–}CO.OH\\ \vert\\ CH^2\text{–}CO.OH\end{array}$$

succinic acid.



$$\begin{array}{l}CH(OH)\text{–}CO.OH\\ \vert\\ CH^2\text{–}CO.OH\end{array}$$

malic acid.



$$\begin{array}{l}CH(OH)\text{–}CO.OH\\ \vert\\ CH(OH)\text{–}CO.OH\end{array}$$

tartaric acid.

Malic acid is oxysuccinic acid, and tartaric acid is dioxysuccinic acid. By reducing agents, the latter acids can be converted into succinic acid. When either of them is heated with a large excess of hydriodic acid, water is formed, iodine is deposited, and the liquid will be found to contain succinic acid (Schmitt and Dessaignes).

Isosuccinic Acid, $CH^3\text{–}CH{<}\begin{smallmatrix}CO.OH\\CO.OH\end{smallmatrix}$, isomeric with succinic acid, is obtained by boiling with potassium hydrate the *cyanide of ethylidene*, $CH^3\text{–}CH(CN)^2$, corresponding to the chloride $CH^3\text{–}CHCl^2$. It crystallizes in needles, fusible at 130°, and more soluble in water than succinic acid.

MALIC ACID.

$$C^4H^6O^5 = CO.OH\text{–}CH^2\text{–}CH(OH)\text{–}CO.OH$$

This acid, which exists in a number of vegetables, was extracted by Scheele from apple-juice. It is generally prepared from the berries of the mountain-ash, gathered before their complete maturity; they are strongly pressed, and the juice is boiled, filtered, and neutralized with milk of lime at the ordinary temperature. Calcium malate is deposited, and this is converted into the acid malate by dissolving it in boiling water acidulated with nitric acid. The calcium acid malate may be readily purified by crystallization, after which it is converted into malate of lead by double decomposition with lead acetate. The lead salt is suspended in pure water and decomposed by hydrogen sulphide; the filtered solution is then evaporated.

Properties.—Malic acid crystallizes in little needles grouped in rounded grains. These deliquesce when exposed to the air.

This acid presents three isomerides. Their solutions have a sour taste; one of them, the natural acid, rotates the plane of polarized light to the left, another to the right, and the third is optically inactive. They are identical in structure, and must be regarded as stereoisomeric (see page 614). Malic acid solutions do not produce a cloud in lime-water, neither in the cold, nor on boiling.

When malic acid is heated, it begins to lose water at 130°, and between 150 and 200° is converted into two acids which are isomeric with each other, and are known as maleic and fumaric acids.

$$\underset{\text{Malic acid.}}{C^4H^6O^5} = \underset{\text{Maleic and fumaric acids.}}{C^4H^4O^4} + H^2O$$

Fumaric acid forms colorless prisms, not very soluble in cold water, and not fusible but volatilizing with partial decomposition above 200°. Nascent hydrogen converts it into succinic acid.

Maleic acid resembles fumaric acid, but is much more soluble in water. It melts at 130°, and at 160° decomposes into maleic anhydride and water. The differences in the constitution of these two acids are not clearly understood. Both are probably represented by the formula CO.OH–CH=CH–CO.OH; they may be stereoisomeric.

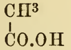
By the action of potassium hydrate at about 150°, malic acid is decomposed into oxalic and acetic acids.

$$\underset{\text{Malic acid.}}{C^4H^6O^5} + H^2O = \underset{\text{Oxalic acid.}}{C^2H^2O^4} + \underset{\text{Acetic acid.}}{C^2H^4O^2} + H^2$$

ASPARAGIN AND ASPARTIC ACID.

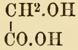
Succinic and malic acids present simple and remarkable relations with two nitrogenized bodies which have long been known; they are asparagin and aspartic acids.

The latter body is amidosuccinic acid, and bears the same relations to succinic acid that glycocoll (amido-acetic acid) bears to acetic acid. On the other hand, its relations to malic acid are analogous to those of glycocoll to glycollic acid.



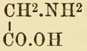
$$\begin{array}{l} CH^3 \\ | \\ CO.OH \end{array}$$

Acetic acid.



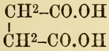
$$\begin{array}{l} CH^2.OH \\ | \\ CO.OH \end{array}$$

Glycollic acid.



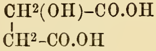
$$\begin{array}{l} CH^2.NH^2 \\ | \\ CO.OH \end{array}$$

Glycocoll.



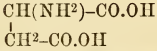
$$\begin{array}{l} CH^2\text{–}CO.OH \\ | \\ CH^2\text{–}CO.OH \end{array}$$

Succinic acid.



$$\begin{array}{l} CH^2(OH)\text{–}CO.OH \\ | \\ CH^2\text{–}CO.OH \end{array}$$

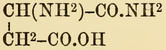
Malic acid.



$$\begin{array}{l} CH(NH^2)\text{–}CO.OH \\ | \\ CH^2\text{–}CO.OH \end{array}$$

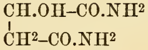
Aspartic or amidosuccinic acid.

Asparagin is the monamide of aspartic or amidosuccinic acid; it is isomeric with the diamide of malic acid.



$$\begin{array}{l} CH(NH^2)\text{–}CO.NH^2 \\ | \\ CH^2\text{–}CO.OH \end{array}$$

Asparagin.



$$\begin{array}{l} CH.OH\text{–}CO.NH^2 \\ | \\ CH^2\text{–}CO.NH^2 \end{array}$$

Malamide.

Asparagin, $C^4H^8N^2O^3$.—This body exists naturally in asparagus, black salsify, the roots of marsh-mallow, licorice wood, and in the buds of cereals, peas, vetches, and beans before they flower. To extract it from these vegetables, they are expressed while fresh, and the juice is clarified and concentrated. The asparagin is deposited in colorless crystals. It is only slightly soluble in cold water and alcohol, but is more soluble in hot water. It forms combinations with both bases and acids.

When boiled with these agents, it loses ammonia and is converted into aspartic acid.

$$\underset{\text{Asparagin.}}{C^4H^8N^2O^3} + H^2O = NH^3 = \underset{\text{Aspartic acid.}}{C^4H^7NO^4}$$

Aspartic Acid, $C^4H^7NO^4$, forms rhombic crystals, slightly soluble in cold, and more soluble in hot water. Like glycocoll, aspartic acid can form compounds with both acids and bases.

TARTARIC ACID, OR DIOXYSUCCINIC ACID.

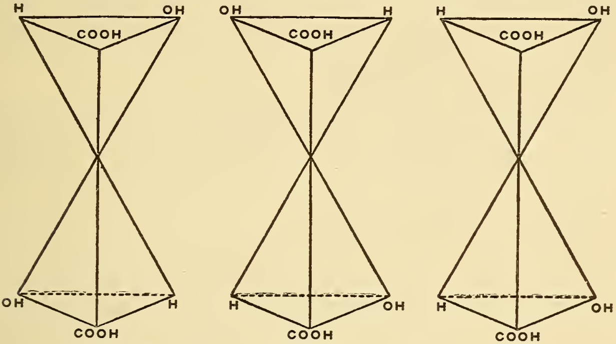
$$C^4H^6O^6 = CO.OH\text{-}CH(OH)\text{-}CH(OH)\text{-}CO.OH$$

This acid exists in four distinct modifications,—namely, dextrotartaric acid, levotartaric acid, mesotartaric acid, and racemic acid. They all have the same molecular structure: they are symmetrical dioxyderivatives of succinic acid, and must be regarded as *stereoisomeric.*

This kind of isomerism, which has been mentioned before, is believed to be due to differences in the spatial arrangement of the atoms within the molecules. It cannot be expressed by the ordinary structural formulas. Van't Hoff has shown that optical activity (power to rotate the plane of polarization) is confined to substances containing one or more carbon atoms of which the four atomicities are satisfied by four distinctly different atoms or radicals. Such carbon atoms he designates as *asymmetric.* He conceives the carbon atom placed in the centre of a tetrahedron, and the four atoms or radicals combined with it at the angles of the tetrahedron. Two different arrangements of the different groups with reference to the carbon atom are possible, and the resulting configurations are to each other as an object is to its mirror-image: they are *enantiomorphous.* They would have opposite rotatory power, but their chemical properties would be identical.

Lactic and malic acids, for example, both contain an asymmetric carbon atom, and both exist in three modifications differing in their behavior toward polarized light and in other physical properties.

The molecule of tartaric acid contains two such asymmetric carbon atoms, directly united, and each of these is combined with a hydrogen atom, a hydroxyl group, and a carbonyl group. Three configurations are possible,—a dextro-form, in which both asymmetric carbon atoms are positive, a levo-form, in which both are negative, and an inactive variety, in which one is positive and the other negative.



a. Dextrotartaric acid. *b.* Levotartaric acid. *c.* Mesotartaric acid.

a and *b* are optically active: each contains two similar asymmetric carbon atoms; *c* is inactive because the two asymmetric atoms neutralize each other (*internal compensation*).

There is possible still another inactive modification formed by the union of equal molecular proportions of the two active varieties (*external compensation*). This is racemic acid; it is capable of being split up into dextro- and levo-tartaric acids.

Dioxysuccinic acid has been obtained synthetically in several ways. By heating succinic acid with bromine and water, dibromosuccinic acid is obtained; when this is boiled with water and silver oxide, it is converted into the dioxyderivative, thus:

$$\begin{array}{l}\mathrm{CHBr{-}COOH}\\ |\\ \mathrm{CHBr{-}COOH}\end{array} + 2\mathrm{AgOH} = \begin{array}{l}\mathrm{CH(OH){-}COOH}\\ |\\ \mathrm{CH(OH){-}COOH}\end{array} + 2\mathrm{AgBr}$$

The synthesis of racemic acid was effected by Strecker; he converted glyoxal into the corresponding dicyanohydrin, which he then decomposed by hydrochloric acid.

$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{CHO}\end{array} + 2\mathrm{HCN} = \begin{array}{l}\mathrm{CH(OH){-}CN}\\ |\\ \mathrm{CH(OH){-}CN}\end{array}$$

$$\begin{array}{l}\mathrm{CH(OH){-}CN}\\ |\\ \mathrm{CH(OH){-}CN}\end{array} + 4\mathrm{H^2O} = \begin{array}{l}\mathrm{CH(OH){-}COOH}\\ |\\ \mathrm{CH(OH){-}COOH}\end{array} + 2\mathrm{NH^3}$$

DEXTROTARTARIC ACID (ORDINARY TARTARIC ACID).

This is one of the most widely distributed of the vegetable acids. It was discovered by Scheele in the tartar, or *argol*, which is deposited in casks in which wine is kept. It is prepared from purified tartar, called *cream of tartar*, which is acid tartrate of potassium.

Preparation.—The salt is dissolved in boiling water, and chalk is added until all effervescence, due to the disengagement of carbon dioxide, ceases. Insoluble calcium tartrate is deposited, and potassium neutral tartrate remains in solution. The calcium tartrate is collected on a filter, and the filtrate is precipitated by calcium chloride. A new portion of insoluble calcium tartrate is thus obtained, and is washed and united with the first portion. This salt is then suspended in water and exactly decomposed by dilute sulphuric acid; calcium sulphate is precipitated, and separated by filtration, and the filtered liquid, when sufficiently concentrated and allowed to evaporate in a warm place, deposits crystals of tartaric acid.

Properties.—Tartaric acid crystallizes in large, oblique rhombic prisms, which often present hemihedral facettes. They are unaltered by the air, and dissolve in about half their weight of cold water and still more abundantly in boiling water. They dissolve also in alcohol, but not in ether.

The aqueous solution of tartaric acid turns the plane of polarization to the right. It forms white precipitates in lime-water and baryta-water, but an excess of the acid redissolves these precipitates.

If an excess of tartaric acid be added to a solution of cupric sulphate, the liquid may be saturated with caustic potash, but no precipitation of cupric hydroxide will take place. The liquid will remain transparent and will assume a beautiful dark-blue color; it is known as *Fehling's solution.* In the same manner, ferric chloride, to which tartaric acid has been added, is not precipitated by alkaline hydroxides.

When tartaric acid is fused with caustic potash, it is decomposed into acetic and oxalic acids.

$$C^4H^6O^6 = C^2H^4O^2 + C^2H^2O^4$$

Action of Heat on Tartaric Acid.—1. Tartaric acid fuses between 167 and 170°, and when the action of the heat is not prolonged, it is converted into isomeric mesotartaric acid.

Prolonged heating to 165° in sealed tubes, of tartaric acid with a small quantity of water, transforms it into mesotartaric and racemic acids.

2. If the acid be maintained for some time in fusion, it loses water and is converted into *ditartaric acid.*

$$2C^4H^6O^6 = \underset{\text{Ditartaric acid.}}{C^8H^{10}O^{11}} + H^2O$$

3. When 15 or 20 grammes of tartaric acid are suddenly heated over a naked flame for four or five minutes, the mass swells up and a deliquescent, yellow, spongy mass is obtained, which constitutes what is called *tartaric anhydride.*

$$C^4H^6O^6 = \underset{\text{Tartaric anhydride.}}{C^4H^4O^5} + H^2O$$

When heated for some time to 150° in a hot-air oven, tartaric anhydride becomes insoluble.

4. When tartaric acid is distilled by heating it gradually in a retort to 300°, it yields besides other products two pyrogenous acids, *pyruvic* and *pyrotartaric* acids.

$$C^4H^6O^6 = \underset{\text{Pyruvic acid.}}{C^3H^4O^3} + CO^2 + H^2O$$

$$2C^4H^6O^6 = \underset{\text{Pyrotartaric acid.}}{C^5H^8O^4} + 3CO^2 + 2H^2O$$

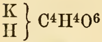
Action of Nitric Acid upon Tartaric Acid.—Very concentrated nitric acid converts tartaric acid into *nitrotartaric acid,* $C^4H^4(NO^2)^2O^6$ (Dessaignes). This body may be obtained in crystals, but it is not stable. Its aqueous solution decomposes between 40 and 50°, with a brisk effervescence of carbon dioxide, and formation of oxalic acid. When the decomposition takes place below 36°, a peculiar, crystallizable acid is formed, which Dessaignes has named *tartronic acid.* Its composition corresponds to the formula $C^3H^4O^5$ (see page 610).

TARTRATES.

Tartaric acid is dibasic; it contains two hydrogen atoms which are replaceable by an equivalent quantity of metal. Neutral tartrates and acid tartrates are known.

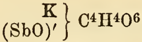
$\left.\begin{matrix}H\\H\end{matrix}\right\}C^4H^4O^6$	$\left.\begin{matrix}H\\M'\end{matrix}\right\}C^4H^4O^6$	$\left.\begin{matrix}M'\\M'\end{matrix}\right\}C^4H^4O^6$, or $R''C^4H^4O^6$
Tartaric acid.	Acid tartrates.	Neutral tartrates.

Neutral tartrates are known in which one atom of metal is replaced by a monatomic oxidized group, such as $(SbO)'$, $(FeO)'$, $(BO)'$.



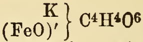
$\left.\begin{matrix}K\\H\end{matrix}\right\}C^4H^4O^6$

Potassium acid tartrate.



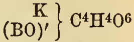
$\left.\begin{matrix}K\\(SbO)'\end{matrix}\right\}C^4H^4O^6$

Tartar-emetic.



$\left.\begin{matrix}K\\(FeO)'\end{matrix}\right\}C^4H^4O^6$

Ferro-potassium tartrate.



$\left.\begin{matrix}K\\(BO)'\end{matrix}\right\}C^4H^4O^6$

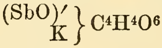
Boro-potassium tartrate.

Potassium Acid Tartrate, or Cream of Tartar, $KHC^4H^4O^6$, is prepared from the crude tartar of wine-casks by subjecting that product to several crystallizations in boiling water. It crystallizes in right rhombic prisms, very slightly soluble in water. If a concentrated solution of tartaric acid be added to a saturated solution of potassium chloride, a precipitate of potassium acid-tartrate will be formed on agitating the liquid. This reaction serves as a characteristic test for tartaric acid.

Potassium Neutral Tartrate, $K^2C^4H^4O^6$.—This salt is prepared by neutralizing a boiling solution of cream of tartar with potassium carbonate. The evaporated solution deposits on cooling oblique rhombic prisms, very soluble in water.

Potassium and Sodium Tartrate, $\left.\begin{matrix}K\\Na\end{matrix}\right\}C^4H^4O^6 + 4H^2O$.—This salt, which is much used in medicine, was discovered in 1672 by Seignette, a pharmacist of Rochelle; hence it is often called Rochelle salt, or Seignette's salt. It is prepared by neutralizing a boiling solution of cream of tartar with sodium carbonate, and evaporating the solution. On cooling, the double tartrate is deposited in large, beautiful crystals, eight-sided right rhombic prisms.

POTASSIUM ANTIMONYL TARTRATE, OR TARTAR EMETIC.



$$\left.\begin{matrix}(SbO)'\\K\end{matrix}\right\}C^4H^4O^6$$

This salt is prepared by boiling cream of tartar with water and oxide of antimony, which dissolves abundantly in the liquid. After filtration and cooling, the salt is deposited in crystals which are purified by a second crystallization.

Tartar-emetic crystallizes in rhombic octahedra, and the crystals, which contain one molecule of water of crystallization for two molecules of salt, effloresce in dry air.

Its taste is astringent and nauseating. It dissolves in 14.5

parts of cold water and in about two parts of boiling water. It is insoluble in alcohol.

When heated to 200° it loses the elements of water and is converted into a double tartrate of antimony and potassium, in which the trivalent antimony replaces 3 atoms of hydrogen in the tartaric acid.

$$C^4H^4(SbO)'KO^6 = C^4H^2Sb'''HKO^6 + H^2O$$

When heated to redness in a small, covered crucible, tartar-emetic leaves an alloy of potassium and antimony, disseminated in a mass of charcoal. When this mass is exposed to moist air, it suddenly takes fire and explodes, projecting brilliant sparks.

The following are the characteristics of a solution of tartar-emetic:

Hydrogen sulphide forms an orange precipitate of antimony sulphide.

A few drops of hydrochloric acid cause the appearance of a white precipitate of antimony oxychloride, which disappears in an excess of acid.

Potassium hydroxide produces a white precipitate of antimony oxide, which redissolves in an excess of alkali.

A plate of tin immersed in a solution of emetic precipitates metallic antimony as a black deposit.

Tartar-emetic is a much employed medicine. In large doses, or smaller ones frequently repeated, it is an energetic poison. It is also used as a mordant in calico-printing.

Ferro-Potassium Tartrate.—This salt is prepared by dissolving ferric hydrate in cream of tartar, and evaporating the solution. It forms brown, amorphous scales, very soluble in water. It is used in medicine.

Boro-potassium Tartrate is formed when boric acid is dissolved in a boiling solution of cream of tartar. It is an amorphous salt, very soluble in water.

RACEMIC ACID (PARATARTARIC ACID).

$$C^8H^{12}O^{12} + 2H^2O$$

This acid was discovered in 1822 by Kestner, and has been studied by Berzelius and by Pasteur.

It crystallizes in transparent, triclinic prisms, which effloresce in the air, losing their water of crystallization. It dissolves in 5.7 parts of water at 15°. Its solution does not change the plane of polarized light, but Pasteur has succeeded in separating it into two other acids, both of which are optically active. One of them turns the plane of polarization to the right, and is ordinary tartaric acid; the other deflects it to the left, and is levo-tartaric acid. These two acids, which are isomeric with each other, reproduce racemic acid when they are mixed in equivalent proportions. It is somewhat remarkable that the mixture of their solutions is attended by a development of heat (Pasteur).

The solution of racemic acid precipitates solutions of sulphate, nitrate, and chloride of calcium, a character which tartaric acid does not possess.

Mesotartaric Acid, or inactive tartaric acid, has no action on polarized light, but cannot be split up into the active varieties. It is also more soluble than racemic acid, and its salts are well characterized.

PYROGENOUS ACIDS DERIVED FROM TARTARIC ACID.

Pyruvic Acid, $C^3H^4O^3 = CH^3\text{–}CO\text{–}CO.OH$.—This acid, which is produced by the dry distillation of glycerol, tartaric and pyrotartaric acids, is formed synthetically by the action of concentrated hydrochloric acid on acetyl cyanide.

$$\begin{matrix} CH^3 \\ | \\ CO.CN \end{matrix} + 2H^2O = CO\begin{matrix} \diagup CH^3 \\ \diagdown CO.OH \end{matrix} + NH^3$$

Acetyl cyanide. Pyruvic acid.

This reaction determines the constitution of pyruvic acid, and shows that it contains the group carbonyl, CO, like acetone, $CH^3\text{–}CO\text{–}CH^3$. All acids containing the group CO are called *ketonic* acids.

Pyruvic acid is a liquid, soluble in water, alcohol, and ether; its odor is like that of acetic acid. It boils at 165–170°, being partially decomposed into carbon dioxide and pyrotartaric acid.

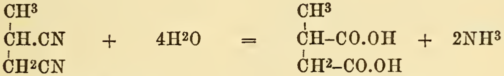
$$\underset{\text{Pyruvic acid.}}{2C^3H^4O^3} = CO^2 + \underset{\text{Pyrotartaric acid.}}{C^5H^8O^4}$$

With sodium acid sulphite it forms a crystallizable compound, an evidence of its ketonic nature, as is also its behavior towards hydroxylamine and phenylhydrazine. With the latter it gives a very characteristic hydrazone, $CH^3C(N^2HC^6H^5)$ COOH.

Under the influence of nascent hydrogen it yields ordinary lactic acid.

$$CH^3\text{–}CO\text{–}CO.OH + H^2 = CH^3\text{–}CH.OH\text{–}CO.OH$$

Methyl-succinic, or **Pyrotartaric Acid,** $C^5H^8O^4.CH^3\text{–}CH(CO.OH)\text{–}CH^2\text{–}CO.OH$.—This acid, of which the mode of formation has been already indicated, is one of the four acids of the formula $C^5H^8O^4$, of which theory predicts the existence, and all of which are actually known. It has been obtained synthetically by the action of boiling potassium hydroxide on propylene cyanide.



$$\begin{matrix}CH^3\\|\\CH.CN\\|\\CH^2CN\end{matrix} + 4H^2O = \begin{matrix}CH^3\\|\\CH\text{–}CO.OH\\|\\CH^2\text{–}CO.OH\end{matrix} + 2NH^3$$

Propylene cyanide. Pyrotartaric acid.

It is prepared by rapidly distilling a dry mixture of tartaric acid and pumice-stone.

It crystallizes in small prisms, soluble in water, alcohol, and ether. It melts at 112°. When heated for a long time to about 210°, it decomposes into carbon dioxide and butyric acid.

$$C^5H^8O^4 = CO^2 + C^4H^8O^2$$

Glutaric Acid, $CH^2<\begin{matrix}CH^2\text{–}CO.OH\\CH^2\text{–}CO.OH\end{matrix}$, is formed when trimethylene cyanide, $CH^2.CN\text{–}CH^2\text{–}CH^2\text{–}CN$, derived from trimethylene chloride, is boiled with potassium hydrate.

It crystallizes in large clinorhombic tables, fusible at 97°, soluble in 1.2 parts of water at 14°. It distils almost unaltered towards 300° (Reboul).

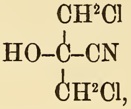
CITRIC ACID.

$C^6H^8O^7$

This acid, discovered by Scheele in 1784, is widely diffused throughout the vegetable kingdom. It exists in lemons, oranges, limes, currants, raspberries, cherries, etc.

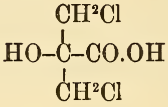
It may be advantageously prepared from lemon-juice, which is allowed to stand until it begins to ferment, and is then filtered, and saturated with chalk while boiling. The precipitate of calcium citrate is washed with boiling water, and decomposed by a slight excess of dilute sulphuric acid. The liquid separated from the calcium sulphate yields crystals of citric acid after concentration.

Grimaux and Adam have made the synthesis of citric acid from dichloracetone, $CH^2Cl{-}CO{-}CH^2Cl$, which is produced by the dehydration of *α* dichlorhydrin (page 588) by a mixture of potassium dichromate and sulphuric acid. Like all of its analogues, this acetone combines directly with hydrocyanic acid, yielding the cyanide



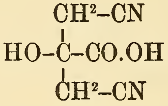
$$\begin{array}{c} CH^2Cl \\ HO{-}\overset{|}{\underset{|}{C}}{-}CN \\ CH^2Cl, \end{array}$$

which by the action of alkalies or acids (hydrochloric acid answers best) yields the acid



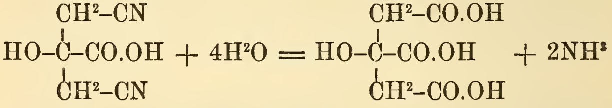
$$\begin{array}{c} CH^2Cl \\ HO{-}\overset{|}{\underset{|}{C}}{-}CO.OH \\ CH^2Cl \end{array}$$

An alcoholic solution of the sodium salt of the latter acid (dichloroxisobutyric) heated with potassium cyanide furnishes the cyanide



$$\begin{array}{c} CH^2{-}CN \\ HO{-}\overset{|}{\underset{|}{C}}{-}CO.OH \\ CH^2{-}CN \end{array}$$

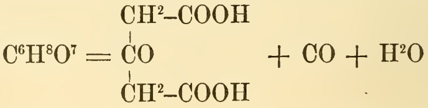
This is saturated with hydrochloric acid gas, and a solution containing citric acid is obtained, from which calcium citrate is precipitated when the liquid is neutralized with milk of lime.



$$\begin{array}{c} CH^2{-}CN \\ HO{-}\overset{|}{\underset{|}{C}}{-}CO.OH \\ CH^2{-}CN \end{array} + 4H^2O = \begin{array}{c} CH^2{-}CO.OH \\ HO{-}\overset{|}{\underset{|}{C}}{-}CO.OH \\ CH^2{-}CO.OH \end{array} + 2NH^3$$

Properties.—This acid forms large, colorless crystals, derived from a right rhombic prism. It dissolves in three-fourths its weight of cold and half its weight of boiling water.

Careful heating with sulphuric acid converts citric acid into *acetone-dicarboxylic acid*, carbon monoxide being disengaged.



$$C^6H^8O^7 = \begin{array}{l} CH^2{-}COOH \\ \overset{|}{\underset{|}{C}}O \\ CH^2{-}COOH \end{array} + CO + H^2O$$

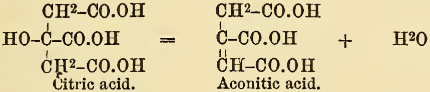
The solution of citric acid has an acid reaction and a very sour taste. It does not precipitate lime-water in the cold, but the solution upon heating deposits a crystalline precipitate.

Citric acid is tribasic.

Magnesium citrate, which is soluble, is employed in medicine; it is a purgative, having a sweetish taste. Ferric citrate also is used in medicine.

PYROGENOUS ACIDS DERIVED FROM CITRIC ACID.

Aconitic Acid, $\mathrm{C^6H^6O^6}$.—When citric acid is heated, it melts; at 176° it disengages water and is converted into aconitic acid.



$$\begin{array}{l}\mathrm{CH^2{-}CO.OH}\\ \mathrm{HO{-}\overset{|}{C}{-}CO.OH}\\ \mathrm{\overset{|}{C}H^2{-}CO.OH}\\ \text{Citric acid.}\end{array} = \begin{array}{l}\mathrm{CH^2{-}CO.OH}\\ \mathrm{\overset{|}{C}{-}CO.OH}\\ \mathrm{\overset{\|}{C}H{-}CO.OH}\\ \text{Aconitic acid.}\end{array} + \mathrm{H^2O}$$

Citric acid. Aconitic acid.

Aconitic acid was first obtained from aconite (*Aconitum Napellus*). It also exists in shave-grass (*Equisetum fluviatile*) and in sugar-cane. It crystallizes in little scales, soluble in water, alcohol and ether. It fuses at 191°, and when further heated it loses carbon dioxide, and is converted into itaconic acid and citraconic anhydride.

$$\mathrm{C^6H^6O^6} = \mathrm{CO^2} + \underset{\text{Itaconic and citraconic acids.}}{\mathrm{C^5H^6O^4}}$$

$$\mathrm{C^5H^6O^4} = \underset{\text{Citraconic anhydride.}}{\mathrm{C^5H^4O^3}} + \mathrm{H^2O}$$

Aconitic acid, being unsaturated, is converted by the action of sodium amalgam into tricarballylic acid by combining with two atoms of hydrogen.

$$\begin{array}{l}\mathrm{CH{-}CO.OH}\\ \mathrm{\overset{\|}{C}{-}CO.OH}\\ \mathrm{\overset{|}{C}H^2{-}CO.OH}\end{array} + \mathrm{H^2} = \begin{array}{l}\mathrm{CH^2{-}CO.OH}\\ \mathrm{\overset{|}{C}H{-}CO.OH}\\ \mathrm{\overset{|}{C}H^2.CO.OH}\end{array}$$

Aconitic acid. Tricarballylic acid.

The latter acid is so named because it was first obtained by the hydration of allyl tricyanide, $\mathrm{C^3H^5(CN)^3}$, corresponding to allyl tribromide, or tribromhydrin (page 589).

Itaconic, Citraconic, and Mesaconic Acids, $\mathrm{C^5H^6O^4}$.—These three acids are isomeric. The first two are formed by the action of heat on citric and aconitic acids; and they both are by dehydration converted into citraconic anhydride. Citraconic acid is converted into mesaconic acid when it is boiled with dilute nitric acid, or when heated to 100° with concentrated hydrochloric acid. The three acids are unsaturated, and can combine with nascent hydrogen, forming pyrotartaric acid.

$$C^5H^6O^4 + H^2 = C^5H^8O^4$$

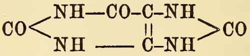
Itaconic acid crystallizes in rhomboidal octahedra, fusible at 161°, soluble in seventeen parts of water at 10°. When strongly heated it yields citraconic anhydride, which distils.

Citraconic acid crystallizes in quadratic tables, fusible at 80°. It is much more soluble in water than itaconic acid, and deliquesces in moist air. Its anhydride, $C^5H^4O^3$, is an oily liquid, boiling at 213–214°. On contact with water it regenerates citraconic acid.

Mesaconic acid forms brilliant prisms, fusible at 202°, only slightly soluble in cold water. At 250° it decomposes into water and citraconic anhydride.

The isomerism of citraconic and mesaconic acids is analogous to that of maleic and fumaric acids, and is probably a case of stereoisomerism.

URIC ACID.



$$CO{<}\begin{array}{l}NH{-}CO{-}C{-}NH\\ \qquad\qquad\quad \| \\ NH \text{——} C{-}NH\end{array}{>}CO$$

This body is related to the complex organic acids which have just been studied. Among the numerous products derived from its oxidation, we may mention oxalic acid, $\begin{array}{c}COOH\\ | \\ COOH\end{array}$, and an acid, $CO(COOH^2) + H^2O$ or $C(OH)^2(COOH)^2$, which has been called mesoxalic.

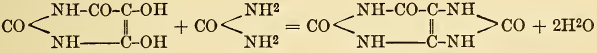
Uric acid was discovered by Scheele, and its numerous metamorphoses were the subject of a classic research by Liebig and Wöhler, and have been more recently studied by Baeyer and other chemists.

Preparation.—Uric acid may be extracted from the excrements of serpents, from guano, and from certain urinary calculi, which are almost entirely composed of it. These substances are reduced to a fine powder, boiled with potassium carbonate and lime, and the solution filtered. The colored solution of potassium urate is mixed with a solution of ammonium chloride, which produces a white precipitate of ammonium urate. This salt is well washed, and treated with hydrochloric acid, which sets free uric acid.

J. Horbaczewski has made the synthesis of uric acid by heating a mixture of urea and glycocoll to 200–230°.

$$\underset{\text{Urea.}}{3CON^2H^4} + \underset{\text{Glycocoll.}}{C^2H^5NO^2} = \underset{\text{Uric acid.}}{C^5H^4N^4O^3} + 3NH^3 + 2H^2O$$

According to Behrend and Roosen, it is also obtained, and in much larger quantity, by heating a mixture of isodialuric acid, urea, and sulphuric acid.



$$CO\left<\begin{array}{l} NH-CO-C-OH \\ \qquad\qquad\quad \| \\ NH\text{——}C-OH \end{array}\right. + CO\left<\begin{array}{l} NH^2 \\ NH^2 \end{array}\right. = CO\left<\begin{array}{l} NH-CO-C-NH \\ \qquad\qquad\quad \| \\ NH\text{——}C-NH \end{array}\right>CO + 2H^2O$$

Isodialuric acid. Urea. Uric acid.

Properties.—Pure uric acid is a light, white powder, which has a crystalline aspect under the microscope. When slowly separated from dilute solutions, it sometimes forms larger crystals, containing 2 molecules of water of crystallization. It is often deposited from urine in small rhomboidal tables of a brownish-yellow color.

Uric acid is insoluble in alcohol and in ether. It requires 15,000 parts of cold water, or 1800 parts of boiling water, for its solution. It dissolves in solutions of the alkalies, forming neutral urates containing two atoms of the alkaline metal. It is therefore a dibasic acid. When carbonic acid gas is passed into a solution of a neutral urate, an acid urate, which is almost insoluble, is precipitated.

Hydrochloric acid forms a thick, white, gelatinous precipitate of uric acid when added to the solution of a urate.

When uric acid is heated to 160 or 170° with an excess of hydriodic acid, it absorbs water, and is decomposed into glycocoll, carbonic acid gas, and ammonia (Strecker).

$$\underset{\text{Uric acid.}}{C^5H^4N^4O^3} + 5H^2O = \underset{\text{Glycocoll.}}{C^2H^5NO^2} + 3CO^2 + 3NH^3$$

If a small quantity of uric acid be gently heated with nitric acid in a porcelain capsule, it is dissolved with a disengagement of red vapors, and the solution, evaporated at a gentle heat, leaves a residue which assumes a purple color on the addition of a drop of ammonia.

This test is characteristic of uric acid, and permits the detection of the least traces of that substance. The purple body formed is called *murexide*.

DERIVATIVES OF URIC ACID.

Among the numerous compounds which may be derived from uric acid, some are closely related to oxalic acid, or other acid containing two carbon atoms; others are derived from mesoxalic acid (see farther on), which contains three carbon atoms. All of these derivatives are more or less closely related to urea; they are substituted ureas, and are more specially designated by the name *ureides.* Those related to mesoxalic acid are the more direct derivatives.

Alloxan, $C^4H^2N^2O^4$.—This body is one of the products of the oxidation of uric acid by nitric acid; urea is formed at the same time.

$$\underset{\text{Uric acid.}}{C^5H^4N^4O^3} + H^2O + O = \underset{\text{Alloxan.}}{C^4H^2N^2O^4} + \underset{\text{Urea.}}{CH^4N^2O}$$

It may be prepared by introducing uric acid, in successive small quantities, into nitric acid of a density of 1.41–1.42, as long as it dissolves producing red vapors. The alloxan finally separates in a mass of delicate needles; in about twenty-four hours they are drained and dissolved in water at 60 or 65°. On cooling, the alloxan separates in voluminous crystals containing 4 molecules of water of crystallization. They effloresce in dry air.

When crystallized from a hot solution, alloxan forms rhombic octahedra, containing but a single molecule of water.

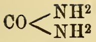
It is very soluble in water, and the solution is acid. By the action of alkalies, baryta-water for example, alloxan is converted into *alloxanic acid*, which is formed by the direct combination of the elements of one molecule of water with alloxan.

$$\underset{\text{Alloxan.}}{C^4H^2N^2O^4} + H^2O = \underset{\text{Alloxanic acid.}}{C^4H^4N^2O^5}$$

The alloxanates are decomposed by boiling into mesoxalic acid and urea. Thus if a solution of alloxanic acid, or even alloxan, be added to a boiling solution of lead acetate, a precipitate of lead mesoxalate is formed.

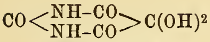
$$\underset{\text{Alloxanic acid.}}{C^4H^4N^2O^5} + H^2O = \underset{\text{Mesoxalic acid.}}{C^3O^5H^2} + \underset{\text{Urea.}}{CH^4N^2O}$$

Mesoxalic acid, $C^3O^3(OH)^2 = CO.OH\text{–}CO\text{–}CO.OH$, is a dibasic acid. According to Baeyer, its diatomic radical, mesoxalyl, exists in alloxan itself, which is mesoxalylurea, that is, urea in which two atoms of hydrogen are replaced by the diatomic radical $[(CO)^2\text{–}C(OH)^2]''$.



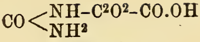
$$CO<\begin{matrix}NH^2\\NH^2\end{matrix}$$

Urea.



$$CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>C(OH)^2$$

Mesoxalyl-urea (alloxan).



$$CO<\begin{matrix}NH-C^2O^2-CO.OH\\NH^2\end{matrix}$$

Alloxanic or mesoxaluric acid.

Dialuric Acid, $C^4H^4N^2O^4$, is the product of the prolonged action of hydrogen sulphide on a hot solution of alloxan or alloxantin.

$$\underset{\text{Alloxan.}}{C^4H^2N^2O^4} + H^2S = \underset{\text{Dialuric acid.}}{C^4H^4N^2O^4} + S$$

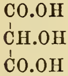
It is also formed by the action of sodium amalgam on the same solutions.

It crystallizes in long needles, quite soluble in water; these crystals assume a red color in the air, and are gradually transformed into alloxantin.

When a solution of alloxan is added to a solution of dialuric acid, alloxantin is formed.

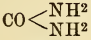
$$\underset{\text{Dialuric acid.}}{C^4H^4N^2O^4} + \underset{\text{Alloxan.}}{C^4H^2N^2O^4} = \underset{\text{Alloxantin.}}{C^8H^4N^4O^7} + H^2O$$

Baeyer regards dialuric acid as tartronyl-urea, that is, urea in which two atoms of hydrogen are replaced by the diatomic radical of tartronic acid.



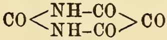
$$\begin{matrix}CO.OH\\|\\CH.OH\\|\\CO.OH\end{matrix}$$

Tartronic acid.



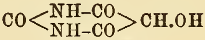
$$CO<\begin{matrix}NH^2\\NH^2\end{matrix}$$

Urea.



$$CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>CO$$

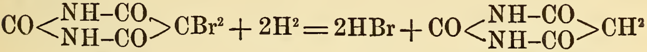
Alloxan.



$$CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>CH.OH$$

Dialuric acid (tartronyl-urea).

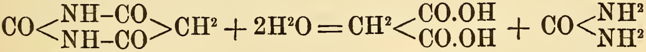
Barbituric Acid, $C^4H^4N^2O^3$.—This acid, which is malonyl-urea, is formed by the action of nascent hydrogen on dibromalloxan.



$$CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>CBr^2 + 2H^2 = 2HBr + CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>CH^2$$

Dibromalloxan. Barbituric acid.

It crystallizes in large prisms, slightly soluble in cold and more soluble in boiling water. Ebullition with alkalies converts it into malonic acid and urea.

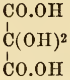


$$CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>CH^2 + 2H^2O = CH^2<\begin{matrix}CO.OH\\CO.OH\end{matrix} + CO<\begin{matrix}NH^2\\NH^2\end{matrix}$$

Malonyl-urea. Malonic acid. Urea.

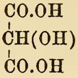
Alloxan, dialuric and barbituric acids, which have been described, are *ureides* derived from a single molecule of urea by the substitution of the radical of a dibasic acid for two atoms of hydrogen. The groups C^2O^2,$[(CO^2-C(OH)^2]$,$C^2O^2-CH.OH$,

C^2O^2–CH^2, which in oxalic, mesoxalic, tartronic, and malonic acids are united to two hydroxyls, are diatomic.



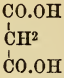
$$\begin{array}{c} CO.OH \\ | \\ C(OH)^2 \\ | \\ CO.OH \end{array}$$

Mesoxalic acid.



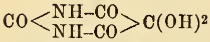
$$\begin{array}{c} CO.OH \\ | \\ CH(OH) \\ | \\ CO.OH \end{array}$$

Tartronic acid.



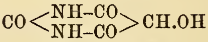
$$\begin{array}{c} CO.OH \\ | \\ CH^2 \\ | \\ CO.OH \end{array}$$

Malonic acid.



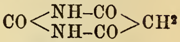
$$CO<\begin{matrix} NH-CO \\ NH-CO \end{matrix}>C(OH)^2$$

Mesoxalyl-urea (alloxan).



$$CO<\begin{matrix} NH-CO \\ NH-CO \end{matrix}>CH.OH$$

Tartronyl-urea (dialuric acid).



$$CO<\begin{matrix} NH-CO \\ NH-CO \end{matrix}>CH^2$$

Malonyl-urea (barbituric acid).

The following compounds are diureides; they are derived from two molecules of urea in which four atoms of hydrogen are replaced by two dibasic acid radicals, each of which contains three atoms of carbon and is related to mesoxalyl:

Alloxantin, $C^8H^4N^4O^7$.—This body is produced by the reduction of alloxan. When a current of hydrogen sulphide is passed through a cold solution of alloxan, sulphur separates, and a crystalline precipitate of alloxantin soon forms.

$$\underset{\text{Alloxan.}}{2C^4H^2N^2O^4} + H^2S = \underset{\text{Alloxantin.}}{C^8H^4N^4O^7} + H^2O + S$$

Alloxantin is also formed directly, at the same time as alloxan, by the action of weak nitric acid on uric acid. It crystallizes in small, colorless prisms containing 3 molecules of water of crystallization. It is but slightly soluble in cold water. Nitric acid converts it into alloxan, and reducing agents transform it into dialuric acid.

Purpuric Acid and Murexide.—Scheele had already observed murexide, which Prout studied and described as *purpurate of ammonia*. It is, indeed, the ammonium salt of a nitrogenized acid, $C^8H^5N^5O^6$, for which it is convenient to preserve the name purpuric acid (Beilstein).

Murexide is formed by the action of ammonia on dry alloxantin heated to 100°, or again, when ammonia or ammonium carbonate is added to a hot solution of alloxantin or alloxan.

$$\underset{\text{Alloxantin.}}{C^8H^4N^4O^7} + 2NH^3 = \underset{\text{Murexide (ammonium purpurate).}}{C^8H^4(NH^4)N^5O^6} + H^2O$$

Murexide crystallizes in quadrangular prisms, or in tables which are green by reflected and red by transmitted light. These crystals, which contain one molecule of water, present the magnificent metallic reflections shown by the wings of cantharides. They dissolve in water with a rich purple color.

Allantoin, $C^4H^6N^4O^3$.—This body was discovered in 1800, by Vauquelin and Buniva, in the allantoic liquid of the cow, that is, the urine of the fœtal calf. It occurs also in the urine of young calves. In 1836, Liebig and Wöhler obtained it by oxidizing uric acid with lead dioxide. Gorup-Besanez has observed its formation in the action of ozone upon uric acid.

Grimaux has made the synthesis of allantoin by heating one part of glyoxylic acid with two parts of urea, for eight or ten hours.

$$\underset{\text{Glyoxylic acid.}}{C^2H^2O^3} + \underset{\text{Urea.}}{2(CH^4N^2O)} = \underset{\text{Allantoin.}}{C^4H^6N^4O^3} + 2H^2O$$

From this remarkable synthesis, it appears that allantoin is derived from two molecules of urea; it is the diureide of glyoxylic acid.

Allantoin may be prepared by boiling uric acid with water, and adding lead dioxide, in small quantities, as long as that oxide continues to be converted into a white powder, which is lead carbonate. The filtered liquid, freed from lead by hydrogen sulphide, yields crystals of allantoin on evaporation.

$$\underset{\text{Uric acid.}}{C^5H^4N^4O^3} + H^2O + O = \underset{\text{Allantoin.}}{C^4H^6N^4O^3} + CO^2$$

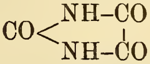
Allantoin crystallizes in brilliant, colorless prisms. It dissolves in 30 parts of boiling water and in 160 parts of cold water; it is also soluble in alcohol, but is insoluble in ether. It forms crystallizable compounds with certain metallic oxides.

The following compounds are ureides of oxalic and glycollic acids:

Parabanic Acid, $C^3H^2N^2O^3$.—This body is formed by the action of an excess of nitric acid on alloxan, which thus gives up the elements of carbon dioxide.

$$\underset{\text{Alloxan.}}{C^4H^2N^2O^4} + O = CO^2 + \underset{\text{Parabanic acid.}}{C^3H^2N^2O^3}$$

Parabanic acid forms thin, transparent prisms, which are very soluble in water. By boiling with acids, it is transformed into oxalic acid and urea. Baeyer regards it as oxalylurea.



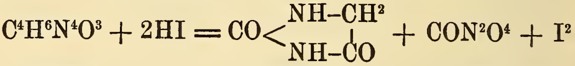
$$CO\begin{matrix}\diagup NH-CO\\ \diagdown NH-CO\end{matrix}$$

When parabanic acid is heated with ammonia, *ammonium oxalurate* is formed, and separates in fine needles. In this case the parabanic acid is converted into oxaluric acid by directly combining with the elements of water.

$$\underset{\text{Parabanic acid.}}{C^3H^2N^2O^3} + H^2O = \underset{\text{Oxaluric acid.}}{C^3H^4N^2O^4}$$

It is seen that oxaluric acid is related to parabanic acid, as alloxanic acid is to alloxan.

Hydantoin, or Glycolyl Urea.—The relations between this compound and parabanic acid are the same as those between glycollic and oxalic acids. It is glycolyl urea, $C^3H^4N^2O^2$, and is formed by the action of hydriodic acid on allantoin.



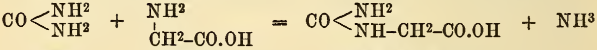
$$C^4H^6N^4O^3 + 2HI = CO{<}\begin{matrix}NH{-}CH^2\\ \vert\\ NH{-}CO\end{matrix} + CON^2O^4 + I^2$$

Allantoin. Hydantoin. Urea.

It crystallizes in needles, fusible at 215°, very soluble in hot water. Its solution is neutral. When hydantoin is heated with baryta-water, it is converted into hydantoic acid.

$$\underset{\text{Hydantoin.}}{C^3H^4N^2O^2} + H^2O = \underset{\text{Hydantoic acid.}}{C^3H^6N^2O^3}$$

Hydantoic Acid, $C^3H^6N^2O^3$, may be obtained synthetically by heating urea with glycocoll; ammonia is disengaged.

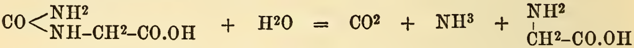


$$CO{<}\begin{matrix}NH^2\\ NH^2\end{matrix} + \begin{matrix}NH^2\\ \vert\\ CH^2{-}CO.OH\end{matrix} = CO{<}\begin{matrix}NH^2\\ NH{-}CH^2{-}CO.OH\end{matrix} + NH^3$$

Urea. Glycocoll. Hydantoic acid.

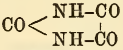
Indeed, hydantoic acid is formed by the replacement of one atom of hydrogen in urea by the group $CH^2{-}CO.OH$, which is acetic acid less one atom of hydrogen.

It crystallizes in large, rhomboidal prisms, soluble in water. It is monobasic. When heated with hydriodic acid it is converted into glycocoll.



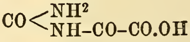
$$CO{<}\begin{matrix}NH^2\\ NH{-}CH^2{-}CO.OH\end{matrix} + H^2O = CO^2 + NH^3 + \begin{matrix}NH^2\\ \vert\\ CH^2{-}CO.OH\end{matrix}$$

Hydantoin and hydantoic acid present evident relations with parabanic and oxaluric acids.



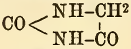
$$CO{<}\begin{matrix}NH{-}CO\\ \vert\\ NH{-}CO\end{matrix}$$

Parabanic acid.



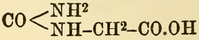
$$CO{<}\begin{matrix}NH^2\\ NH{-}CO{-}CO.OH\end{matrix}$$

Oxaluric acid.



$$CO{<}\begin{matrix}NH{-}CH^2\\ \vert\\ NH{-}CO\end{matrix}$$

Hydantoin.



$$CO{<}\begin{matrix}NH^2\\ NH{-}CH^2{-}CO.OH\end{matrix}$$

Hydantoic acid.

We cannot further continue the study of the numerous derivatives of uric acid. This study has already thrown much light upon the constitution of the acid, without definitely determining it. The syntheses indicated by Horbaczewski (page

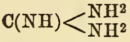
625), and by Behrend and Roosen, as well as more recent investigations of E. Fischer, afford additional proof for the correctness of the formula of uric acid given above.

DERIVATIVES OF GUANIDINE.

There are interesting structural relations between urea and guanidine; the latter is urea in which the oxygen is replaced by the imidogen group NH.

$$\mathrm{CO}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix}$$

Urea.

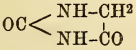


$$\mathrm{C(NH)}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH^2}\end{matrix}$$

Guanidine.

This analogy is borne out in the guanidine derivatives corresponding to the ureides just described.

Hydantoin, or glycolyl-urea, corresponds to a glycolyl-guanidine which has been named glycocyamidine.



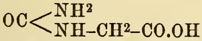
$$\mathrm{OC}<\begin{array}{l}\mathrm{NH{-}CH^2}\\ \qquad\;\; |\\ \mathrm{NH{-}CO}\end{array}$$

Hydantoin.

$$\mathrm{HN{=}C}<\begin{array}{l}\mathrm{NH{-}CH^2}\\ \qquad\;\; |\\ \mathrm{NH{-}CO}\end{array}$$

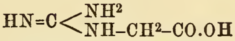
Glycocyamidine.

Hydantoic or uracetic acid corresponds to a guanidine acetic acid called glycocyamine.



$$\mathrm{OC}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH{-}CH^2{-}CO.OH}\end{matrix}$$

Hydantoic or uracetic acid.



$$\mathrm{HN{=}C}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH{-}CH^2{-}CO.OH}\end{matrix}$$

Glycocyamine or guanidine-acetic acid.

Glycocyamine is formed by the mixture of aqueous solutions of glycocoll and cyanamide.

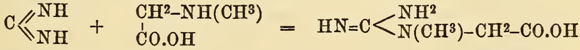
$$\mathrm{C}\ll\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix} + \begin{array}{l}\mathrm{CH^2{-}NH^2}\\ |\\ \mathrm{CO.OH}\end{array} = \mathrm{HN{=}C}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{NH{-}CH^2{-}CO.OH}\end{matrix}$$

Cyanamide. Glycocoll. Glycocyamine.

Our space only permits the mention of these bodies, but we must describe their important homologues, creatine and creatinine, which have long been known.

CREATINE AND CREATININE.

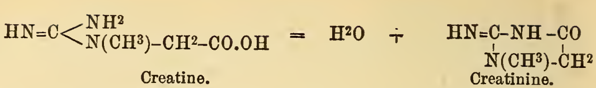
Creatine results from the direct combination of cyanamide and methylglycocoll (sarcosine), a reaction discovered by Volhard, and entirely analogous to that which yields glycocyamine (see above).



$$\mathrm{C}\ll\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix} + \begin{array}{l}\mathrm{CH^2{-}NH(CH^3)}\\ |\\ \mathrm{CO.OH}\end{array} = \mathrm{HN{=}C}<\begin{matrix}\mathrm{NH^2}\\ \mathrm{N(CH^3){-}CH^2{-}CO.OH}\end{matrix}$$

Cyanamide. Methylglycocoll. Creatine.

Creatinine, or methylglycocyamidine, results from the dehydration of creatine.



$$HN{=}C\left<\begin{array}{l}NH^2\\ N(CH^3){-}CH^2{-}CO.OH\end{array}\right. = H^2O + \begin{array}{l}HN{=}C{-}NH{-}CO\\ \quad\; N(CH^3){-}CH^2\end{array}$$

Creatine. Creatinine.

Creatine, $C^4H^9N^3O^2 + H^2O$.—This body was discovered by Chevreul in meat broth. It exists ready formed in the muscles, and passes into the extract of meat. It may be prepared by treating the solution of this extract with basic acetate of lead, filtering, freeing the filtrate from excess of lead by hydrogen sulphide, and evaporating the solution at a gentle heat until it crystallizes. The crystals are separated from the mother-liquor, and alcohol added to the latter precipitates a fresh quantity of creatine (Neubauer).

Creatine crystallizes in brilliant, colorless, oblique rhombic prisms, containing one molecule of water, which they lose at 100°, becoming opaque.

By the action of acids or by long boiling with water, creatine is converted into *creatinine*.

$$\underset{\text{Creatine.}}{C^4H^9N^3O^2} = \underset{\text{Creatinine.}}{C^4H^7N^3O} + H^2O$$

When creatine is boiled with baryta-water, it is converted into *sarcosine*, ammonia being disengaged and barium carbonate precipitated at the same time. It is generally considered that the ammonia and carbon dioxide are produced in this case at the expense of urea, which is formed directly by the decomposition of creatine.

$$\underset{\text{Creatine.}}{C^4H^9N^3O^2} + H^2O = \underset{\text{Sarcosine.}}{C^3H^7NO^2} + \underset{\text{Urea.}}{CH^4N^2O}$$

Sarcosine is methylglycocoll (page 603), isomeric with lactamide and alanine.

Creatinine, $C^4H^7N^3O$.—This body exists in muscular tissue independently of creatine. It may be precipitated from the mother-liquor from which the latter body has deposited, by adding an alcoholic solution of zinc chloride, which forms a crystalline combination with the creatinine.

Creatinine crystallizes in oblique rhombic prisms. It is much more soluble in alcohol than creatine. It has basic properties, and forms a crystallizable compound with hydrochloric acid.

Creatine and creatinine have been found not only in the muscles, but in small quantities in the brain, blood, and urine.

POLYHYDRIC ALCOHOLS.

The only tetrahydric alcohol of importance is erythritol, and rhamnitol represents the pentahydric alcohols.

The best characterized hexahydric alcohol is mannitol, a sweet, crystallizable substance, which is extracted from manna. Glucose is related to mannitol, from which it differs only by two atoms of hydrogen. The constitution of mannitol may be expressed by the following formula:

$$C^6H^{14}O^6 = C^6H^{8vi}(OH)^6$$

It appears from the experiments of Linnemann that various saccharine matters, possessing the composition $C^6H^{12}O^6$, fix H^2 directly under the influence of sodium amalgam and water, and are converted into mannitol. The latter body is characterized as a hexahydric alcohol by the property which it possesses of forming neutral compounds with 6 molecules of a monobasic acid, such as acetic acid. In other words, this body contains 6 hydroxyl groups, or six atoms of hydrogen capable of being replaced by 6 monobasic acid radicals.

Six isomeric alcohols of the composition $C^6H^{14}O^6$ are known, and theory indicates the possible existence of fourteen.

ERYTHRITOL.

$$C^4H^{10}O^4 = C^4H^6(OH)^4$$

This beautiful body was discovered in 1849 by Stenhouse, who found it among the decomposition products of erythric acid or erythrin, a substance contained in certain lichens. In 1852, Lamy obtained from an alga, the *Protococcus vulgaris*, a substance which he first named phycite, but which he afterwards recognized to be identical with erythritol.

Preparation.—De Luynes first extracts erythrin from a lichen, the *Rocella Montagnei*, and decomposes it, while still moist, by slaked lime in closed vessels at a temperature of 150°. Under these conditions, erythrin is decomposed into carbonic acid which is at once taken up by the lime, orcinol, and erythritol, which are separated by crystallization, the orcinol being deposited first. The erythritol is purified by washing with ether, which removes a trace of orcinol.

Properties.—Erythritol crystallizes in tetragonal prisms. The crystals are hard, have a feeble, sweet taste, and are very soluble in water, soluble in boiling absolute alcohol, and insoluble in ether. They melt at 126°. Erythritol reacts with the acids, forming neutral bodies analogous to the ethers (Berthelot).

When heated with a concentrated solution of hydriodic acid, it is converted into secondary butyl iodide (de Luynes.)

$$\underset{\text{Erythritol.}}{C^4H^{10}O^4} + 7HI = \underset{\text{Secondary butyl iodide.}}{C^4H^9I} + 4H^2O + 3I^2$$

MANNITOL.

$$C^6H^{14}O^6 = C^6H^8(OH)^6$$

This body, discovered by Proust in 1806, exists in a great number of vegetables. It is the most abundant constituent of manna, a substance which flows from several species of ash, either naturally or from incisions. It is prepared by dissolving manna in distilled water, in which the white of an egg has previously been beaten up. The solution is boiled several minutes and then filtered through a woollen cloth and allowed to cool. The liquid then solidifies to a mass of crystals which are purified by recrystallization after treatment with animal charcoal.

Mannitol forms large, right rhombic prisms. Its taste is sweet, and it is soluble in water and hot alcohol.

When heated with a concentrated solution of hydriodic acid, it is reduced to a secondary hexyl iodide.

$$\underset{\text{Mannite.}}{C^6H^{14}O^6} + 11HI = \underset{\beta\text{-secondary hexyl iodide.}}{CH^3\text{–}CH^2\text{–}CH^2\text{–}CHI\text{–}CH^2\text{–}CH^3} + 6H^2O + 5I^2$$

It forms a hexacetate, a hexanitrate, and a hexastearate. By oxidation with nitric acid it yields mannose, an aldehyde, and fructose, a ketone.

There are several stereoisomers of mannitol.

Dulcitol, $C^6H^{14}O^6$, which has been obtained from Madagascar manna, exists in certain plants, such as *Melampyrum nemorosum* and *Evonymus europæus.* It forms large, oblique rhombic prisms, and is less soluble in water than mannitol; it is but slightly soluble in alcohol. It melts at 188.5°. Like its isomer, mannitol, it is reduced by hydriodic acid to a secondary hexyl iodide.

Sorbitol, $C^6H^{14}O^6$, obtained by J. Boussingault from the fermented juice of the mountain-ash, is another isomer of mannitol.

It forms small acicular crystals containing water of crystallization. Hydriodic acid reduces it to normal secondary hexyl iodide. Sorbitol has been obtained from glucose by reduction.

Perseitol, $C^7H^{16}O^7$, or Mannoheptitol, is a heptahydric alcohol which occurs in the leaves and berries of *Laurus persea*, and has been synthetically prepared from mannose; it crystallizes in microscopic needles, melting at 188°.

SUGARS, STARCHES, AND CELLULOSES.

Among the more widely distributed products of the vegetable kingdom must be included the various kinds of sugar, starch, the gums, and the matter of young vegetable cells, or cellulose.

These compounds contain carbon, hydrogen, and oxygen in such proportions that the oxygen is present in exactly sufficient quantity to form water with the hydrogen. Their composition is then expressed by the general formula $C^m(H^2O)^n$. If all of the oxygen and hydrogen were removed in the form of water, only carbon would remain. Hence the name *hydrates of carbon*, often applied to this class of bodies.

They can be arranged in three different classes, of which the types are glucose, saccharose, and starch.

The first of these, termed *monosaccharides*, comprises a number of aldehyde alcohols (aldoses) and ketone alcohols (ketoses); their molecules contain a carbonyl group (CO) and several hydroxyl (OH) groups. According to the number of oxygen atoms contained in the molecule, they are designated trioses, tetroses, pentoses, hexoses, etc. The second class, embracing *di-* and *trisaccharides*, may be considered to be ether-like anhydrides of the monosaccharides, formed by the condensation of two or more molecules of the latter, with elimination of the elements of one or several molecules of water. Hydrolysis resolves them into their monosaccharide components. The known disaccharides are all derived from the hexoses; according to the number of monosaccharide molecules that can be obtained from them, they are distinguished as hexobioses, hexotrioses, etc.

The *polysaccharides*, to which starch and cellulose belong, are very different in their physical properties from the sugars: they are non-crystalline and insoluble. They yield sugars by hydrolysis, but their molecules are much more complex than those of the disaccharides.

	MONOSACCHARIDES.	DI- AND TRI-SACCHARIDES.	POLYSACCHARIDES.
	Glycerose, $C^3H^6O^3$	Saccharose, $C^{12}H^{22}O^{11}$	Starch, $(C^6H^{10}O^5)^n$
	Erythrose, $C^4H^8O^4$	Lactose, $C^{12}H^{22}O^{11}$	Inulin, $(C^6H^{10}O^5)^n + H^2O$
	Arabinose, $C^5H^{10}O^5$	Maltose, $C^{12}H^{22}O^{11}$	Glycogen, $(C^6H^{10}H^5)^n$
	Xylose, $C^5H^{10}O^5$	Isomaltose, $C^{12}H^{22}O^{11}$	Cellulose, $(C^6H^{10}O^5)^n$
	Rhamnose, $C^6H^{12}O^5$	Melitose, $C^{18}H^{32}O^{16}$	Dextrin, $(C^6H^{10}O^5)^n$
Aldoses	Mannose, $C^6H^{12}O^6$	Melizitose, $C^{18}H^{32}O^{16}$	Gums, $(C^6H^{10}O^5)^n$
	Glucose, $C^6H^{12}O^6$		
	Galactose, $C^6H^{12}O^6$		
Ketose	Fructose, $C^6H^{12}O^6$		

ARABINOSE.

$$C^5H^{10}O^5 = CH^2.OH\text{–}[CH.OH]^3\text{–}CHO$$

This is the sugar of gum. It is formed when arabin, or gum arabic, is boiled with dilute nitric acid. It crystallizes in brilliant rhomboidal prisms, fusible at 160°. Its aqueous solution has a sweet taste and is dextrogyrate. It reduces Fehling's solution, but is not fermentable. By an interesting but complicated process arabinose can be obtained from glucose (Wohl).

Xylose is stereoisomeric with arabinose. It is obtained by heating wood-gum with dilute sulphuric acid.

Rhamnose, $C^6H^{12}O^5$, is another pentose. It contains a methyl group, and results from the hydrolysis of certain glucosides.

Mannose, $C^6H^{12}O^6 = CH^2.OH\text{–}[CH.OH]^4\text{–}CHO$. — Mannose was first obtained as a product of the oxidation of mannitol (Fischer). It has since been observed among the substances which result from the hydrolysis of certain naturally occurring hydrates of carbon, such as reserve-cellulose. Mannose forms friable masses which are very soluble in water, difficultly soluble in alcohol, and insoluble in ether. It is dextro-rotatory, and fermentable with brewer's yeast. With phenylhydrazine it yields a characteristic and difficultly crystallizable compound, $C^{12}H^{18}N^2O^2$, melting at 195°. With an excess of phenylhydrazine, it yields the same product as glucose and fructose,—normal phenylglucosazone. Nascent hydrogen converts mannose into mannitol, and bromine water oxidizes it into mannonic acid. It must, therefore, be regarded as the aldehyde of mannitol.

GLUCOSE.

$C^6H^{12}O^6$

This important body, which forms the solid and crystallizable part of honey, exists in a great number of dried fruits, on the surface of which it forms a well-known white efflorescence.

It is also found in the urine in the disease known as diabetes.

It may be made artificially by the action of dilute sulphuric acid on starch (Kirchoff), or on cellulose (Braconnot).

Its synthesis was achieved when it was obtained by reduction of the lactone of gluconic acid (E. Fischer).

Preparation.—Glucose is prepared in the arts by the following process:

6000 litres of water and 42 kilogrammes of sulphuric acid are introduced into a large wooden trough, and the liquid is heated by jets of superheated steam. When it is in full ebullition, 2000 kilogrammes of starch suspended in 2000 litres of warm water are allowed to run in gradually, and in thirty or forty minutes the saccharification is complete. The sulphuric acid is then saturated with pulverized chalk, the insoluble calcium sulphate is separated, and the liquid concentrated in boilers heated by steam until it marks 40 or 41° Baumé. It is then allowed to crystallize, and solidifies to an opaque, yellowish, crystalline mass, which is glucose.

The sulphuric acid has recently been replaced by hydrochloric acid, which produces a whiter product. The small quantity of calcium chloride formed does not prevent the crystallization of the glucose.

Properties.—This body crystallizes in small, white, rounded masses, agglomerated like cauliflowers. The crystals contain one molecule of water of crystallization ($C^6H^{12}O^6 + H^2O$). They remain unchanged in the air. They melt when heated on a water-bath, and lose their water at 100°. Anhydrous glucose, deposited from alcoholic solution, melts at 146°.

Glucose dissolves in a little more than its own weight of water at 17°. It is three times less soluble than cane-sugar, and in solutions of equal concentration it is three times less sweet. It is much less soluble in alcohol than in water.

The solution of glucose rotates the plane of polarization to the right. The deviation caused by a recently-prepared solution diminishes after a time as much as fifty per cent.; it varies with the concentration. The specific rotatory power is $[\alpha]_D = 52.6°$.

A levo-form and an inactive variety of glucose are also known.

Glucose forms true compounds with the bases. There is a *glucosate of calcium*, $C^6H^{10}Ca''O^6 + H^2O$. It is precipitated when alcohol is added to a solution of calcium hydroxide in an aqueous solution of glucose. The glucosates are not stable: carbonic acid decomposes them, regenerating glucose.

If potassium hydroxide be added to a solution of glucose and the liquid be heated, it first becomes yellow, and then rapidly assumes a deep-brown color. Ordinary or cane-sugar does not produce this reaction, and can thus be distinguished from glucose.

The action of lime on glucose gives rise to the formation of a substance which forms beautiful crystals of the orthorhombic type, and which Peligot called *saccharin*.* It is dextrorotatory, has a bitter taste, and melts at 160°. According to Scheibler, it contains $C^6H^{10}O^5$, and is the anhydride of a *saccharinic acid*, $C^6H^{12}O^6$.

Glucose reduces various metallic solutions. Gold and silver are precipitated by it from their solutions. If a solution of cupric sulphate be poured into a solution of glucose, and potassium hydroxide be added, no precipitate is formed, but the liquid acquires a dark-blue color. On heating it, a red precipitate of cuprous oxide is formed.

This reaction, which was discovered by Troemmer, is very sensitive, and can be used for the detection of the smallest quantities of glucose. In making the test an alkaline copper solution, known as *Fehling's solution*, is employed. It is best prepared by dissolving separately 34.6 grammes of crystallized copper sulphate, and 173 grammes of Rochelle salt and 60 grammes of caustic soda, each in half a litre of water, and mixing equal volumes of these solutions when the test is to be made. The quantity of glucose can be determined by titration with this solution, for one molecule of sugar reduces exactly five molecules of cupric oxide.

When a solution of glucose is heated with bismuth nitrate and an excess of potassium hydroxide, a black precipitate of reduced metallic bismuth is formed.

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* This substance must not be confounded with *saccharine*, or benzoic acid sulfinide, $C^6H^4 < {}^{SO^2}_{CO} > NH$, which is a derivative of benzene, and, owing to its intensely sweet taste, is sometimes used as a substitute for sugar.

Glucose is one of the *aldoses*, being at the same time a pentahydric alcohol and an aldehyde. Its constitution is represented by the formula

$$CH^2.OH\text{–}CH.OH\text{–}CH.OH\text{–}CH.OH\text{–}CH.OH\text{–}CHO$$

This is deduced from the following facts: acetic anhydride converts glucose into a pentacetyl derivative, showing it to contain five hydroxyl groups; its reducing properties are due to the presence of an aldehyde group, which is shown by its oxidation to gluconic acid, $CH^2OH\text{–}(CH.OH)^4\text{–}COOH$, and its reduction by nascent hydrogen to mannitol, a primary alcohol. It is confirmed by the behavior of glucose with hydroxylamine and with phenylhydrazine. With one molecule of the latter reagent, it yields the hydrazone $CH^2.OH(CH.OH)^4\text{–}CH{=}N^2H\text{–}C^6H^5$, but upon heating with an excess of phenylhydrazine, *phenylglucosazone*, $CH^2.OH(CH.OH)^3\text{–}C(N^2HC^6H^5)\text{–}CH{=}N^2C^6H^5$, is produced.

Galactose, $C^6H^{12}O^6$.—This is one of the products of the action of dilute acids and of certain ferments on lactose (page 644). Galactose crystallizes in little masses, formed by the agglomeration of small needles. It is less soluble in water than glucose, and deviates the plane of polarization to the right. It is fermentable, and readily reduces cupro-potassic solutions. Nascent hydrogen converts it into *dulcitol.* Nitric acid oxidizes it with formation of mucic acid.

FRUCTOSE, OR LEVULOSE.

$$C^6H^{12}O^6 = CH^2.OH\text{–}CH.OH\text{–}CH.OH\text{–}CH.OH\text{–}CO\text{–}CH^2OH$$

Besides the glucose which effloresces on their surface after desiccation, many fruits contain another sugar, which strongly deviates the plane of polarization to the left. It is fructose, formerly known as levulose.

Fructose exists in inverted sugar (page 643). Many sweet fruits contain inverted sugar; among them are grapes, cherries, figs, gooseberries, etc.

The extraction of fructose from inverted sugar—of which it constitutes one-half—is a laborious procedure. Dubrunfant recommends the conversion of the sugars into their calcium compounds: the fructosate of calcium is difficultly soluble in water, while the glucosate is readily dissolved. A better method of preparing fructose consists in warming inulin with dilute acids. For this purpose a few drops of sulphuric acid are added to a solution of inulin in water and the liquid heated gently for some time. The sulphuric acid is then precipitated with barium hydrate and the filtrate evaporated. Upon adding a crystal of fructose, the fruit sugar separates in colorless acicular crystals. It may be purified by recrystallization from alcohol.

Fructose thus obtained contains no water of crystallization; the crystals belong to the orthorhombic system. It melts at 95°, and is readily soluble in water and in alcohol. The fructose contained in inverted sugar rotates the plane of polarization to the left, and rather more strongly than the other component, glucose, turns it to the right; for this reason inverted sugar is slightly levorotatory.

A fructose which is optically inactive, but agrees in all other respects with the natural product, has been artificially obtained by E. Fischer. He has further succeeded in converting this into mannose and glucose, and in resolving it into its dextro- and levo-rotatory modifications. Thus the synthesis of the most important monosaccharides has been accomplished.

Fructose is directly fermentable. Its reactions closely resemble those of glucose, except that on oxidation it does not yield an acid with the same number of carbon atoms, but is resolved into tartaric and glycollic acids. This proves that fructose is a ketone.

Sorbinose, $C^6H^{12}O^6$, a substance which crystallizes in large, transparent rhomboidal octahedra, has been obtained from the berries of the mountain-ash by Pelouze. It appears to be stereoisomeric with the fructoses.

SACCHAROSE, OR CANE-SUGAR.

$C^{12}H^{22}O^{11}$

Extraction.—Ordinary sugar, which is widely distributed in the vegetable kingdom, is extracted principally from sugar-cane, sugar-maple, and beet-root. Fresh sugar-cane contains about 18 per cent. of sugar, and beet-roots from 12 to 16 per cent.

Certain sweet fruits contain cane-sugar, independently of inverted sugar. According to Buignet, such are apricots, peaches, pine-apples, lemons, plums, and raspberries.

We can only briefly indicate the processes which are employed for the extraction of sugar from beet-root.

The roots are washed, and reduced to pulp in a machine provided with a cylinder armed with teeth and having a rapid rotary motion. This pulp is then strongly pressed in woollen sacks by means of a hydraulic press, and the juice is immediately transferred to large boilers having double bottoms and heated by steam, and milk of lime is added.

This operation, which is called *clarification*, is intended not only to separate certain substances which form insoluble compounds with the lime, but to prevent the juice from becoming altered by reason of its acidity. As the sugar itself dissolves a large quantity of lime, the latter must be got rid of. A current of carbon dioxide is consequently passed into the solution, and decomposes the saccharate of calcium. Another process for removing the excess of lime depends on the employment of ammonium phosphate. Insoluble calcium phosphate is formed, and the ammonia is disengaged on account of the high temperature at which the operation is conducted. By this process the neutralization is more perfect.

The liquid is then heated to about 95°, and filtered through a layer of animal charcoal in grains; it is then concentrated in evaporating-pans heated by steam. When the syrup marks 25° Baumé, it is again filtered through animal charcoal, and the concentration is finished in pans heated by steam, and in which a vacuum is maintained during the evaporation. The cooking of the syrup is thus carried on at a temperature not above 75 or 80°, and these conditions assure a fine quality of product and a good yield by preventing as much as possible the transformation of the sugar into uncrystallizable sugar.

When the syrup marks 42 or 43°, it is run into cooling-pans, where it is continually stirred until the sugar is deposited in small crystals. These are distributed in moulds, which consist of terra-cotta cones having a hole in the summit, which for the time is closed. These cones are placed in an oven heated to 25°, where the crystallization takes place; when the syrup has solidified, the holes in the cones are opened and the thick and colored mother-liquor is allowed to drain out; it constitutes molasses. The loaves of sugar, drained and dried, are delivered to commerce as crude or brown sugar.

For some years an apparatus has been used for draining and bleaching of crude sugars, which consists of a cylindrical cage having perforated metallic walls. It is put into rapid motion on its axis, and the molasses is expelled through the perforated walls by centrifugal force. The apparatus is called the centrifugal drier.

Refining of Crude Sugar.—The crude sugar is crushed, sifted, and dissolved in about 30 per cent. its weight of water, the operation being conducted in a boiler heated by steam. 5 per cent. of animal charcoal is then thrown into the hot solution, and, after stirring, ½ per cent. of beef's blood is added. The latter coagulates in the liquid and envelops all of the suspended particles, uniting them in a scum which is easily removed. When the liquid becomes clear, it is drawn off and filtered. It is then passed through grained animal charcoal, which completely decolorizes it. It is concentrated in vacuum-pans, from which it is drawn into a large copper vessel having a double bottom. It is continually stirred until crystallization commences, after which it is run into moulds, which are then placed in rooms heated to 20°. After the crystallization is completed, the syrup remaining liquid is allowed to drain out.

At the termination of the draining, a creamy mixture of white clay and water is poured on the surface of the sugar in each mould, and the water of this broth slowly penetrates the mass of sugar, liquefies the syrup which remains between the crystals, and carries it to the lower part of the mass. The clay, having lost its water, contracts, dries up, and remains upon the decolorized sugar as a dry cake. It is removed, and a syrup of white sugar is run into the whitened and porous loaf and fills up all of the spaces when it solidifies in the oven.

This operation, the object of which is the decolorizing of the sugar-loaves, is called *claying.* The clay broth may be replaced by syrup of white sugar, an operation which is called *decoloring.*

The sugar solidified in the moulds is a compact, crystalline, white mass, composed of little grains. It may be obtained in voluminous crystals by concentrating the syrup until it marks 37° Baumé, and then exposing it for some days to a temperature of 30° in copper vessels, across which threads are stretched. The sugar is deposited on the threads in large crystals known as rock-candy.

Properties of Sugar.—Sugar crystallizes in large, oblique rhombic prisms, having hemihedral facettes. The crystals are hard, anhydrous, and unalterable in the air. Density, 1.606.

It dissolves in one-third its weight of cold water; the solution is thick, and is known as *simple syrup*. Sugar is insoluble in ether and in cold absolute alcohol. Boiling absolute alcohol dissolves a little more than one per cent.; ordinary alcohol will take up more. The aqueous solution of sugar deviates the plane of polarization to the right, ($[\alpha]_D = +66.5°$), at 20°.

At 160°, sugar melts to a thick, transparent liquid, which solidifies to an amorphous, vitreous mass on cooling.

When maintained for a long time at a temperature of 160 or 161°, it breaks up into glucose and levulosan (Gélis).

$$\underset{\text{Saccharose.}}{C^{12}H^{22}O^{11}} = \underset{\text{Glucose.}}{C^6H^{12}O^6} + \underset{\text{Levulosan.}}{C^6H^{10}O^5}$$

Between 190 and 200° it loses the elements of water and is converted into a bitter, brown, amorphous mass, which is designated as *caramel.*

Cane-sugar does not reduce alkaline copper solutions, and does not react with phenylhydrazine.

Inverted Sugar.—By the action of dilute acids, sugar is converted, slowly in the cold and rapidly on boiling, into a mixture, in equal proportions, of two isomeric sugars which have opposite rotatory powers: they are glucose and fructose. The mixture is called *inverted sugar.*

$$\underset{\text{Saccharose.}}{C^{12}H^{22}O^{11}} + H^2O = \underset{\text{Glucose.}}{C^6H^{12}O^6} + \underset{\text{Fructose.}}{C^6H^{12}O^6}$$

The same transformation is effected by the soluble matter of yeast (Berthelot), and also, according to Buignet, by the action of the peculiar ferments which exist in most fruits.

Sugar only ferments after having first undergone this transformation into inverted sugar by the action of the ferment.

Nitric acid converts sugar into *saccharic acid*, $C^6H^{10}O^8$, and oxalic acid.

Concentrated sulphuric acid carbonizes it.

Saccharose resists the action of alkalies better than glucose. It forms with them and with the bases in general, definite combinations known as saccharates.

If a mixture of sugar and slaked lime be triturated with water and the whole be thrown upon a filter, the liquid which passes through will be colorless and strongly alkaline. When it is heated to ebullition, it changes into a solid mass which again becomes liquid on cooling. It is a solution of saccharate of calcium, $(C^{12}H^{22}O^{11})^2.3CaO$. Alcohol precipitates from it the compound $C^{12}H^{22}O^{11}.CaO$.

An excess of strontium hydrate precipitates cane-sugar completely from a hot solution; the resulting disaccharate, $C^{12}H^{22}O^{11}.2SrO$, is readily decomposed by carbon dioxide into sugar and strontium carbonate. Scheibler has founded a process for extracting crystallizable sugar from molasses upon these reactions.

When sugar is fused with potassium hydrate, it disengages hydrogen, and carbonate, oxalate, formate, acetate, and propionate of potassium are formed.

When distilled with quick-lime, sugar is decomposed with formation of carbon dioxide, water, acetone, and *metacetone*, C^3H^6O, a liquid having a pleasant odor and boiling at 84°.

Sugar forms a crystalline compound with sodium chloride.

LACTOSE, OR MILK-SUGAR.

$C^{12}H^{22}O^{11} + H^2O$

This sugar exists in solution in the milk of mammals, and is extracted from the whey which remains after the manufacture of cheese. It is only necessary to evaporate this liquid to crystallization.

Milk-sugar occurs in commerce in cylindrical masses, formed of an agglomeration of crystals around a little stick which serves as a nucleus. The crystals are colorless, hard, and creak when crushed by the teeth. They are right rhombic prisms, terminated by octahedral points. They contain one molecule of water of crystallization which they lose at about 140°. They dissolve in 6 parts of cold, and in 2 parts of boiling water. The solution turns the plane of polarization to the right. The rotatory power of old solutions is $[\alpha]_D = +52.53°$.

When heated with nitric acid, lactose yields certain acids, among which is one which is but slightly soluble in water, and which is called *mucic acid*. It contains $C^6H^{10}O^8$, and is stereoisomeric with *saccharic acid*, which is also produced by the oxidation of lactose by nitric acid. Moderate oxidation with bromine water converts lactose into lactobionic acid, $C^{12}H^{22}O^{12}$, which upon warming with dilute acids yields galactose and gluconic acid.

When boiled with dilute sulphuric acid, milk-sugar is converted into glucose and galactose.

Milk-sugar reduces cupro-alkaline solutions, but more slowly than glucose.

With phenylhydrazine it yields phenyllactosazone, $C^{24}H^{32}N^{4}O^{9}$, yellow needles melting at 200°. When exposed to the air at summer heat, a solution of lactose in presence of calcium carbonate soon undergoes the lactic fermentation (page 647).

MALTOSE.

$C^{12}H^{22}O^{11} + H^{2}O$

This name is given to the crystallizable sugar produced, together with dextrin, by the action of diastase on starch. It may be prepared by digesting starch paste at 60° with a solution of diastase. The solution is precipitated by alcohol, which separates the dextrin, filtered, the alcoholic liquid evaporated to a syrupy consistence, more alcohol added, and the solution set aside to crystallize over sulphuric acid. Maltose is a product of the incomplete hydration of starch.

Maltose forms masses composed of hard, white needles. It loses its water at 100°. Its solution turns the plane of polarization to the right, $[\alpha]_D = +137°$. It reduces Fehling's solution, and when boiled with dilute acids is converted into glucose. Maltose is directly fermentable. Heated with acetic anhydride and sodium acetate, it yields an octoacetyl derivative, $C^{12}H^{14}O^{3}(O.CO.CH^{3})^{8}$, and with an excess of phenylhydrazine it gives phenylmaltosazone, $C^{24}H^{32}N^{4}O^{9}$.

Isomaltose, $C^{12}H^{22}O^{11}$, is formed by the action of hydrochloric acid upon glucose, and from starch in presence of diastase. It has an intensely sweet taste, and is dextrorotatory to about the same extent as maltose. It is decomposed upon gentle heating, but does not seem to be directly fermentable.

Mycose, or *trehalose*, $C^{12}H^{22}O^{11} + 2H^{2}O$, was extracted by Mitscherlich from the ergot of rye, and has been obtained by Berthelot from a Turkish manna (*trehala*). It crystallizes in hard, rectangular octahedra, gritty between the teeth, and having a sweet taste. It is strongly dextrogyrate, $[\alpha]_D = +199°$. It is distinguished from cane-sugar by its ready solubility in boiling alcohol.

Melitose, or *raffinose*, $C^{18}H^{32}O^{16} + 5H^{2}O$, was extracted by Berthelot from Australian manna, a sweet exudation of the eucalyptus, and is known to exist in sugar-beets. Being more soluble than ordinary sugar, it accumulates in the molasses. It crystallizes in fine needles which lose their water of crystallization at 100°, while the residue melts at 118°. Melitose is powerfully dextrorotatory, $[\alpha]_D = 104.4°$, a property which interferes with the estimation of ordinary sugar by polarimetry when both are present. It does not react with Fehling's solution, but is completely fermentable. On hydrolysis, it yields fructose, glucose, and galactose.

Melezitose, $C^{18}H^{32}O^{16} + 2H^2O$, was obtained by Berthelot from Briançon manna, exuded by the larch (*Pinus larix*). It crystallizes in monoclinic prisms, with two molecules of water, which it loses at 108°. It is dextrogyrate, $[a]_D = +94°$. It melts at 157°. Its complete hydrolysis yields only glucose.

FERMENTATION.

If yeast be introduced into a tolerably concentrated solution of glucose, and the liquid be exposed to a temperature between 20 and 30°, bubbles of an incombustible gas will soon be disengaged, and this gas will produce a cloud in lime-water. It is carbon dioxide.

After the disengagement of gas has ceased, a small quantity of alcohol may be obtained by distilling the liquid.

In this experiment, the glucose disappears; it is broken up into alcohol and carbon dioxide. The decomposition is effected by yeast, and is called *fermentation.* The sugar is the *fermentable* substance; the yeast is the *ferment.*

The ferment is an organized matter which develops and multiplies at the expense of the glucose. The latter, is directly attacked by this being which lives at its expense, and undergoes a complete decomposition, of which carbon dioxide and alcohol are the principal products. The ferment plays an active part, which was first suspected by Cagniard-Latour and Schwann, and demonstrated by Pasteur.

Alcoholic Fermentation.—The decomposition of glucose under the influence of yeast constitutes the alcoholic fermentation.

The principal reaction is expressed in the following equation:

$$\underset{\text{Glucose.}}{C^6H^{12}O^6} = \underset{\text{Alcohol.}}{2C^2H^6O} + 2CO^2$$

It is shown by the experiments of Pasteur, that only 94 per cent. of the quantity of glucose decomposed undergoes the change indicated by the above formula. The remaining 6 per cent. are employed: 1, in the formation of small quantities of higher alcohols, succinic acid, and glycerol; 2, in the development of new yeast cells.

Yeast is composed of a mass of cells or ovoid corpuscles, having a diameter of $\frac{1}{100}$ of a millimetre, and arranged in clusters (Fig. 129). Their walls are an elastic membrane, and their contents are liquid or granular. They contain cellulose, albuminoid matter, and mineral salts. When they are introduced into a substance which contains the materials necessary for their development, they multiply rapidly. Pasteur has made decisive experiments on this point. He planted some yeast cells in a solution of sugar to which he had added a small quantity of an ammoniacal salt and some phosphates. The solution of sugar fermented, and the ferment developed by budding, the new cells absorbing the ammonia and the phosphates. They obtained from the sugar the matter necessary to form cellulose, and from the ammonia the nitrogen required for the elaboration of the albuminoid matters. However, these artificial conditions are not those which are best adapted for the propagation of the cells. The latter increase with extreme energy in liquids which contain, besides the yeast, glucose, and a small quantity of albuminoid matter ready formed.

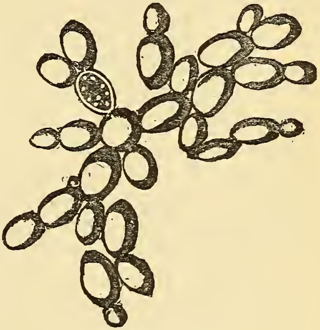


Fig. 129.

Lactic Fermentation.—This fermentation, of which the conditions have already been indicated (page 597), is accomplished by the action of a peculiar ferment of vegetable character. It is formed of small round or elongated cells, very short, and isolated, or in masses. They are much smaller than yeast cells, and constitute the lactic yeast of Pasteur. It only acts upon glucose or lactose in a neutral or alkaline liquid. Hence the necessity of adding sodium carbonate or chalk to the liquid. The reaction consists in a splitting of the glucose molecule.

$$\underset{\text{Glucose.}}{C^6H^{12}O^6} = \underset{\text{Lactic acid.}}{2C^3H^6O^3}$$

Butyric Fermentation.—This consists in the transformation of calcium lactate into butyrate,—a transformation that is accompanied by a disengagement of hydrogen. According to Pasteur, this fermentation is caused by a low organism which can live and thrive only in situations where its members cannot obtain free oxygen. Such is the energy of their respiratory functions that free oxygen kills them (Pasteur). They decompose oxidized bodies and assimilate the oxygen.

We have already considered the *acetic fermentation.* We may add that by the action of a certain ferment, glucose is converted into mannitol and a gummy matter, very soluble in water, and which gives a viscous consistence to the fermented liquid. This is called the *viscous fermentation.*

There are many other kinds of fermentation, an exceedingly large number of carbon compounds being capable of decomposition in this manner; the ferments are also very numerous, and the special fermentation undergone by a substance depends upon the peculiar ferment present.

FERMENTED BEVERAGES.—The foregoing summary indications regarding fermentation may be supplemented by some general notions upon the fermented beverages wine and beer.

Wine.—It is universally known that wine is the product of the fermentation of grape-juice. This juice contains in solution inverted sugar, small quantities of gummy matters, vegetable albumen, a trace of fatty matters, coloring matters, free tartaric and malic acids, and various tartrates, principally potassium acid-tartrate, or cream of tartar.

The clarified wine which results from the fermentation of this juice consists of an aqueous solution of various products, some of which existed in the juice, and others which are the result of the transformation through which it has passed. Among the first are the mineral and vegetable salts of the juice (in smaller proportion, because they are partly deposited with the lees), the gummy matter, a small quantity of fatty and albuminoid substances, the coloring matters, free tartaric and malic acids, and the tannin derived from the grape-stems and from the skins and seeds.

Among the substances which result from the fermentation are:

1. Alcohol, which is the principal product.

2. Carbonic acid gas; still wines retain but a small proportion, the fermentation taking place entirely in open vessels, but sparkling wines contain it abundantly under pressure, the final fermentation having taken place in the bottle after corking.

3. Small quantities of aldehyde and acetic acid produced by oxidation of the alcohol. The acetic acid reacts upon the alcohol contained in the wine, forming acetic ether.

4. Glycerol and succinic acid, in small quantities (Pasteur).

5. Traces of compound ethers, which contribute to the *bouquet* of the wine. Besides acetic ether, traces of a compound ether called *œnanthic ether* have been found in wine; it appears to be *pelargonic*

ether, $C^9H^{17}O^2(C^2H^5)$. Berthelot states the existence of but slightly volatile acid ethers (malic, tartaric) in wine.

The following table indicates the quantities by volume of pure alcohol contained in 100 volumes of various wines:

California Port	22.00
Madeira	20.48
Port	20.22
Sherry	18.00
Sauterne (white)	15.00
Catawba	13.00
Rhine Wines	11.11
California Riesling	11.20
Champagnes	11.00 to 18.00
Strong Clarets	8.00 to 12.00
Light Clarets	7.5 to 8.00
Red Burgundy	7.66
Red Mâcon	7.66
White Burgundy	7.83

Beer.—Beer is a fermented beverage, made from a *wort* of germinated barley, and ordinarily rendered aromatic by hops. Like all other cereals, barley contains a considerable proportion of starch. During the germination, this starch is partially converted into maltose by the action of a nitrogenized matter, which is formed in the sprouting grains, and which is called *diastase*. In order to saccharify the barley, it is then first necessary to cause it to germinate, and for this purpose it is moistened with water, and kept for some time at a temperature of 14 or 15° ; the object of this operation, called malting, is the development of the diastase necessary for the saccharification of the starchy matter. When the sprout has acquired about the same length as the grain (Fig. 130), the germination is arrested by exposing the malt to the action of a temperature of about 50°. The dry malt is then reduced to a coarse powder, placed in a large vat, and brewed for about three hours with water heated to 50 or 60°. In this operation, the diastase of the malt converts the starch into dextrin and maltose, which dissolve, together with the other soluble principles of the grain.

FIG. 130.

The sweet wort thus obtained is heated with hops, which yield to it their essential aromatic oil. It is then properly cooled and allowed to ferment in deep vats, into which a certain quantity of yeast produced in a previous operation is introduced at the same time. The alcoholic fermentation soon begins and goes on with great activity during a few days. As soon as it has ceased, the liquid can be delivered for consumption. The quality of beer is better when the fermentation takes place at a low temperature.

Beer contains much water, free carbonic acid gas, alcohol (2 to 5 per cent.), variable quantities of saccharine matters, dextrin, nitrogenized matters, extractive, bitter, and coloring matters, essential oil, and various salts. Ale and porter are in nature analogous to beer, but are relatively richer in alcohol and nitrogenous and extractive matters.

STARCH.

$(C^6H^{10}O^5)^n$

Starch is universally diffused throughout the vegetable kingdom. It is especially abundant in the seeds of leguminous plants and cereals, and in the potato.

Extraction.—To extract starch from potatoes, they are reduced to pulp by means of a rasp, and the pulp is placed in a sieve and washed by a stream of water. The water carries with it the fine granules of starch, while the torn cells of the potato remain in the sieve. The starch gradually deposits from the water, and collects in the bottom of the vessel, where it settles, forming a cake from which the supernatant water may be separated by decantation.

Starch may be extracted from wheat by making a paste of flour and kneeding it in a sieve under a jet of water: the starch granules are carried with the water, and a soft, gray, elastic mass remains in the sieve, constituting the nitrogenized matter of the flour, or *gluten.*

Another process, almost abandoned at present on account of its offensiveness, consists in allowing the coarsely-ground grain to putrefy. Putrefaction destroys the gluten, while the starch resists decomposition.

Physical Properties.—Starch is a white powder, formed of granules which present an organized structure. Their size and shape are variable (Fig. 131), their diameter being from 2 to 185 thousandths of a millimetre. Those of potato starch are larger than those of starch from grain. These granules are made up of concentric layers, which are more dense as they are nearer the surface. It is easy to make this structure apparent by causing the granules to undergo a partial disintegration by the action of hot water. They swell up, burst open, and separate into thin layers, as shown in Fig. 132.

Chemical Properties.—Starch is insoluble in water, alcohol, and ether. Contact with water heated to 60 or 70° causes it to swell up considerably, without dissolving. A semi-transparent, gelatinous mass results, which is known as starch paste. When starch is boiled with a large quantity of water and the whole is thrown on a filter, the liquid which passes is slightly turbid, and constitutes an emulsion of starch. It contains in suspension flakes of amylaceous matter small enough to pass through the filter. It also contains a small quantity of soluble starch (see farther on).

If a few drops of solution of iodine be added to the emulsion, a deep-blue color is at once produced. This blue color disappears when the liquid is heated to 90°, and reappears on cooling. The compound contains about 18 per cent. of iodine, and is known as "iodide of starch"; its constitution is unknown. The reaction serves as a delicate test both for starch and iodine.

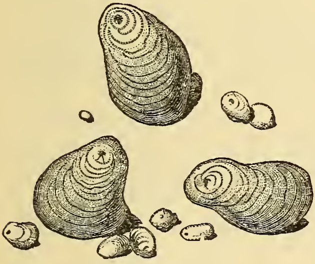


Fig. 131.

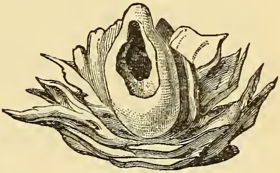


Fig. 132.

Metamorphoses of Starch—Dextrin.—When long heated to 100° starch is converted into soluble starch, which yields a blue color with iodine (Maschke).

Between 160 and 200° it is converted into a body which is very soluble in water, and the solution of which is not colored by iodine. This solution strongly turns the plane of polarization to the right; hence the name *dextrin* given to this body, which is regarded as isomeric with starch, $(C^6H^{10}O^5)^n$. A very concentrated solution of dextrin has the appearance of a solution of gum. It is used as a mucilage for labels and postage-stamps, and for the preparation of immovable surgical dressings.

Alcohol added to a solution of dextrin precipitates the latter substance in the form of flakes. Subacetate of lead does not precipitate dextrin, a character which permits the latter body to be distinguished from gum arabic.

When starch is boiled with water containing a few per cent. of sulphuric acid, it is first converted into dextrin, then into glucose. It is generally considered that the dextrin is formed by a simple molecular transformation of the elements of the starch, and that the glucose is then produced by the simple fixation of one molecule of water.

$$\underset{\text{Starch.}}{C^6H^{10}O^5} + H^2O = \underset{\text{Glucose.}}{C^6H^{12}O^6}$$

According to Musculus, this is not the case; but soluble starch is the result of a metameric transformation of starch, and subsequently is converted into dextrin and glucose by a true decomposition.

$$\underset{\text{Starch.}}{3C^6H^{10}O^5} + H^2O = \underset{\text{Dextrin.}}{C^{12}H^{20}O^{10}} + \underset{\text{Glucose.}}{C^6H^{12}O^6}$$

By the prolonged action of the acid, the dextrin itself is converted into glucose.

The transformation of starch into dextrin and saccharine matter (maltose) takes place easily under the influence of a peculiar ferment which is developed in grain during germination, and to which the name *diastase* has been given. It may be obtained by precipitating aqueous extract of malt by alcohol.

If starch be triturated with one and a half times its weight of concentrated sulphuric acid, avoiding an elevation of temperature, and the mixture be left to itself for half an hour and alcohol then added, a substance is precipitated which is soluble in water and assumes a rich blue tint by the action of iodine. It is *soluble starch* (Béchamp).

Starch dissolves abundantly in monohydrated nitric acid, and water precipitates from this solution a white substance, which, after washing and drying, constitutes *xyloidin.* It is *mononitrate of starch*, and is formed by the following reaction:

$$\underset{\text{Starch.}}{C^6H^{10}O^5} + HNO^3 = H^2O + \underset{\text{Xyloidin.}}{C^6H^9(NO^3)O^4}$$

Xyloidin burns with deflagration when heated to 180°.

A dinitrate has also been obtained.

INULIN.

$(C^6H^{10}O^5)^n + H^2O$

This body also is largely diffused throughout the vegetable kingdom. It exists in the roots of the elecampane (*Inula helenium*), chicory, and Spanish chamomile, in the bulbs of colchicum, the tubers of the dahlia, in the Jerusalem artichoke, etc. It may be extracted from the tubers of the dahlia by reducing them to a pulp and washing the latter in a sieve under a stream of water. The milky liquid which passes through deposits the inulin, which consists of granules analogous to those of starch. It swells in cold water, in which it is very slightly soluble. It is very soluble in boiling water, which again deposits it in a pulverulent form on cooling. The aqueous solution turns the plane of polarization to the left. It is not colored blue by iodine, which communicates to it a fugitive, yellow-brown tint.

By long boiling with water, or by the action of dilute acids, inulin is converted into fructose, and this reaction affords a convenient mode of preparing fruit-sugar.

GLYCOGEN.

$(C^6H^{10}O^5)^n$

This body, isomeric with cellulose and starch, exists in the animal economy. Claude Bernard discovered it in the liver, and afterwards in the placenta. It exists also in many organs during the fœtal life. Nearly pure glycogen may be obtained by adding a large quantity of crystallizable acetic acid to a cold and concentrated decoction of liver. It is also precipitated when alcohol is added to an aqueous decoction of liver. In a pure state, it is a white, amorphous powder. When dried in the air, it has the composition $C^6H^{12}O^6$ (E. Pelouze). At 100° it loses one molecule of water.

With water it forms an opalescent liquid. Alcohol and ether do not dissolve it. Boiling with dilute acids converts it into glucose. Iodine communicates to it a violet or brown-red color.

GUMS.

By the names *gums* and *mucilages* are understood certain substances existing everywhere in the vegetable kingdom, and which dissolve or swell up in water, giving a mucilaginous consistence to the liquid. The gums proper are distinguished from the mucilaginous substances, which are not really soluble. Both furnish mucic and oxalic acids when treated with nitric acid. Hydrolysis decomposes them into hexoses and pentoses (galactose, arabinose, xylose).

Gum Arabic.—Gum arabic is identical with Senegal gum. It flows naturally from different species of acacia. It dissolves abundantly in cold water and is precipitated from its solution by alcohol. Fremy considers that it is composed essentially of the calcium and potassium salts of an acid which he designates as *gummic acid* (*arabin*).

When dried at 100°, the latter body has the composition indicated by the formula $C^{12}H^{22}O^{11}$. It is very soluble in water, and its solution rotates the plane of polarization to the left.

When heated to 120–150°, it becomes insoluble in water and is converted into *metagummic acid.* According to Fremy, the gum of cherry- and plum-trees is a mixture of gummates, which are soluble in cold water, and insoluble metagummates. The metagummates are insoluble in water, but when boiled with that liquid are transformed into soluble gummates.

Subacetate of lead forms an abundant white precipitate in solutions of gum arabic.

When gum arabic is boiled with dilute sulphuric acid, it is converted into saccharine substances; some varieties of this gum yield considerable quantities of galactose when treated in this manner, while others are largely converted into arabinose. On oxidation with nitric acid, the former give mucic acid, and the latter oxalic acid.

Gum Tragacanth.—This gum flows from the Astragalus of the Levant and of Persia. *Bassora gum* is derived from a species of cactus. Both contain a mucilaginous matter insoluble in water, but which swells up in that liquid, forming a transparent jelly. This matter is *bassorin.* With nitric acid, it yields much mucic acid. When boiled with dilute sulphuric acid, it is readily converted into crystallizable glucose.

CELLULOSES.

$(C^6H^{10}O^5)^n$

The frame-work of plant tissues consists of a more or less delicate membrane which is a secretion of protoplasmic activity, and is known as the *cell-wall.* In the earlier stages of its growth and development this consists of *cellulose,* $(C^6H^{10}O^5)^n$, with a varying amount of water. Gradually, however, it is transformed into bodies of more complex constitution,—the *compound celluloses,*—and, at the same time, mineral matters are deposited in it.

The term cellulose does not denote a chemical individual, but a group of closely related isomers of similar properties. Cotton, hemp, flax, and the pith of certain trees consist essentially of cellulose. Wood, cork, and mucilage are chiefly made up of the compound celluloses produced by the metamorphosis of cellulose. All these bodies are permeated by foreign substances, such as nitrogenous, coloring, and mineral matters; the latter are found more or less modified in the ashes.

Old linen and cotton serve for the preparation of pure cellulose. Such materials are boiled with a weak solution of potassium hydrate, washed, and successively exhausted with a solution of chlorine, acetic acid, alcohol, ether, dilute hydrochloric acid, dilute hydrofluoric acid, and, finally, water, and dried at 100°. The undissolved residue is pure cellulose.

Properties.—Cellulose is a diaphanous, white solid, of a density of 1.5. It is insoluble in all simple solvents, but in presence of certain metallic compounds it forms gelatinous hydrates which are soluble in water. It dissolves completely upon warming with concentrated aqueous solution of zinc chloride, more rapidly and in the cold when a solution of the salt in strong hydrochloric acid is employed (Cross and Bevan). Another valuable solvent for cellulose is cuprammonium hydroxide dissolved in strong ammonia water (Schweitzer's reagent); this rapidly converts cellulose into a hydrate, which is gradually dissolved in the blue liquid. Salts of the alkali metals, acids, alcohol, etc., reprecipitate the hydrate.

When submitted to dry distillation, cellulose leaves a residue of carbon and yields numerous gaseous and liquid products. The gas obtained by the distillation of wood is used for illuminating purposes in some localities. The liquid product ordinarily separates into two layers, one of which is aqueous and contains acetic acid, wood-spirit, acetone, etc.; the other is insoluble in water and constitutes *wood-tar.*

Cellulose is readily attacked by concentrated sulphuric acid: the resulting viscous solution probably contains a compound of sulphuric acid and cellulose, and also various other products resulting from a rapid disintegration of this sulphate. When the solution is diluted with water and boiled, glucose is formed and sulphuric acid regenerated. Certain celluloses yield mannose instead of glucose.

$$\underset{\text{Cellulose.}}{C^6H^{10}O^5} + H^2O = \underset{\text{Glucose.}}{C^6H^{12}O^6}$$

When paper is dipped into a cold mixture of sulphuric acid with half its volume of water, and is then carefully washed and dried, a semi-transparent matter is obtained which has a certain rigidity, and is similar to parchment in aspect and toughness. This *parchment paper* is extensively used as a substitute for animal parchment.

Colloidal cellulose is formed by the action of sulphuric acid of density 1.53 on cellulose, and forms with water a milky liquid which can be filtered. The action of sulphuric acid or zinc chloride on cellulose produces a body analogous to starch and called *amyloid.* Cellulose moistened with iodine tincture and then treated with strong sulphuric acid becomes blue. By treatment with acetic anhydride, cellulose has been converted into the triacetate $C^6H^7O^2(C^2H^3O^2)^3$ and the tetracetate $C^6H^6O(C^2H^3O^2)^4$, and there are indications that higher acetates may exist.

Gun-Cotton.—When carded cotton is immersed for half a minute in monohydrated nitric acid, and then rapidly washed in a large quantity of water and allowed to dry in the air, a substance is obtained which possesses all the exterior appearances of cotton, but is very inflammable and burns suddenly without residue. It is gun-cotton, or *pyroxylin*, which was discovered by Schönbein in 1847.

In its preparation, the monohydrated nitric acid may be advantageously replaced by a mixture of one volume of nitric acid (sp. gr. 1.5) and three volumes of sulphuric acid. The duration of the action determines the composition of the product. When the acid is allowed to act upon the cotton for a short time only, the latter is converted into a mixture of the compounds, $C^{12}H^{16}(NO^3)^4O^6$ and $C^{12}H^{15}(NO^3)^5O^5$, but upon continued treatment with the acids a gun-cotton of the composition $C^{12}H^{14}(NO^3)^6O^4$ results.

These bodies, like nitroglycerin, are true nitric ethers. Alkalies decompose them into an alkaline nitrate and cellulose.

Gun-cotton looks like cotton, but is more harsh to the touch. It burns with a flash, leaving no residue, and produces a great volume of gaseous products consisting of carbon monoxide, carbon dioxide, nitric oxide, etc., and vapor of water. The hexanitrate is insoluble in water, alcohol, ether, and the cupro-ammoniacal solution. The lower nitrates, however, are soluble in a mixture of ether and alcohol, and *collodion* is essentially such a solution: it is used in surgery and photography.

Celluloid, a substitute for ivory, bone, and horn, is made by dissolving nitrocellulose in melted camphor, to which resinous substances and coloring matters are sometimes added.

Nitro-powders, largely used on account of their smokeless explosion, are prepared by gelatinizing finely divided gun-cotton by means of a solvent such as ethyl acetate or acetone. The solvent is removed by pressure and evaporation, and the gelatinous residue is cut into slices or pressed into suitable form. Other substances are usually added to modify the force of the explosion.

GLUCOSIDES.

The glucosides are complex compounds, which break up under various conditions, fixing the elements of water and yielding a sugar, generally glucose, and other bodies, just as the compound ethers, in fixing the elements of water, are decomposed into alcohols and acids.

Various immediate principles of vegetable origin can be classed as glucosides. We may mention particularly the following:

GLUCOSIDES.	FORMULAS.	ORIGIN.
Amygdalin	$C^{20}H^{27}NO^{11}$	bitter almonds.
Salicin	$C^{13}H^{18}O^{7}$	willow and poplar bark.
Populin	$C^{20}H^{22}O^{8}$	bark and leaves of the aspen.
Phloridzin	$C^{21}H^{24}O^{10}$	bark and roots of fruit-trees.
Arbutin	$C^{12}H^{16}O^{7}$	leaves of the *Arctostaphylos uva ursi.*
Esculin	$C^{21}H^{24}O^{13}$	bark of India chestnut.
Quercitrin	$C^{36}H^{38}O^{20}$	bark of Quercus tinctoria (quercitron).
Tannin	$C^{34}H^{28}O^{22}$	oak-bark, nut-gall, etc.
Coniferin	$C^{16}H^{22}O^{8}$	cambium of the *Coniferæ.*
Digitalin	$C^{29}H^{46}O^{12}$	leaves of *Digitalis purpurea.*

Amygdalin, $C^{20}H^{27}NO^{11}$.—This body is extracted from the cake of bitter almonds, and it deposits from its alcoholic solution in crystals containing two molecules of water. Its aqueous solution allows it to crystallize in quite large crystals containing three molecules of water

Amygdalin is very soluble in water and in boiling alcohol. Its aqueous solution rotates the plane of polarization to the left.

By the action of dilute acids amygdalin is decomposed into hydrocyanic acid, benzaldehyde (oil of bitter almonds), and glucose.

$$\underset{\text{Amygdalin.}}{C^{20}H^{27}NO^{11}} + 2H^2O = \underset{\text{Benzaldehyde.}}{C^7H^6O} + \underset{\text{Hydrocyanic acid.}}{CHN} + \underset{\text{Glucose.}}{2C^6H^{12}O^6}$$

The same decomposition takes place by the action of water and a peculiar ferment which is contained in both bitter and sweet almonds, and which is called *emulsin*, or *synaptase*. It is a nitrogenized matter, soluble in water, and only acts on amygdalin in presence of water. It is well known, indeed, that bitter almonds only develop the odor of prussic acid when moistened with water.

Salicin, $C^{13}H^{18}O^7$.—Salicin exists already formed in the bark of the willow and poplar. Wöhler discovered its existence in castoreum. It may be prepared by exhausting willow-bark with boiling water, concentrating the liquid and digesting it with litharge. The solution is then filtered and evaporated to a syrupy consistence; the salicin deposits in a few days.

It occurs in small scales, or brilliant needles, soluble in water and alcohol and insoluble in ether. Its taste is bitter.

By the action of a solution of emulsin (the nitrogenous matter of almonds), it breaks up into a neutral body called saligeninol, and glucose.

$$\underset{\text{Salicin.}}{C^{13}H^{18}O^7} + H^2O = \underset{\text{Saligeninol.}}{C^7H^8O^2} + \underset{\text{Glucose.}}{C^6H^{12}O^6}$$

Dilute sulphuric and hydrochloric acids decompose it by the aid of heat into *saliretin* and glucose.

By the action of a mixture of potassium dichromate and sulphuric acid, salicin yields carbon dioxide, formic acid, and an oxidized oil, which is salicylaldehyde, $C^7H^6O^2$ (Piria).

Salicin has been obtained synthetically (Michael).

Populin, $C^{20}H^{22}O^8+2H^2O$.—Braconnot discovered this substance in the bark and leaves of the aspen (*Populus tremula*). When properly purified, it occurs in very fine, silky, colorless needles. Its taste is sweet; it is but slightly soluble in water, more soluble in alcohol. By the action of dilute acids it is decomposed into benzoic acid, saliretin, and glucose; the latter two products result from the decomposition of salicin, so that populin is a combination of benzoic acid and salicin, from which substances it has also been obtained artificially.

$$\underset{\text{Populin.}}{C^{20}H^{22}O^{8}} + H^{2}O = \underset{\text{Benzoic acid.}}{C^{7}H^{6}O^{2}} + \underset{\text{Salicin.}}{C^{13}H^{18}O^{7}}$$

Phloridzin, $C^{21}H^{24}O^{10} + 2H^{2}O$.—This substance exists in the bark of apple, pear, plum, and cherry trees, and principally in the roots of fruit-trees.

When pure, it forms colorless, silky needles, having a bitter taste, and an after-taste which is sweet. It is scarcely soluble in cold water, but dissolves abundantly in boiling water and in alcohol. The alcoholic solution turns the plane of polarization to the left.

Dilute acids decompose it into phloretin and glucose.

$$\underset{\text{Phloridzin.}}{C^{21}H^{24}O^{10}} + H^{2}O = \underset{\text{Phloretin.}}{C^{15}H^{14}O^{5}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}}$$

Phloretin is a white substance which crystallizes in little scales, slightly soluble in water and very soluble in alcohol. When phloretin is heated with potassium hydroxide, it breaks up into *phloretic acid* and *phloroglucinol* (page 696).

$$\underset{\text{Phloretin.}}{C^{15}H^{14}O^{5}} + H^{2}O = \underset{\text{Phloretic acid.}}{C^{9}H^{10}O^{3}} + \underset{\text{Phloroglucinol.}}{C^{6}H^{6}O^{3}}$$

Coniferin, $C^{16}H^{22}O^{8}$, is a glucoside which occurs in the cambium of the *Coniferæ*. It is a crystalline body which melts at 185°, and effloresces in the air. On treatment with boiling dilute acids or with emulsin, it yields glucose and *coniferyl alcohol*, $C^{10}H^{12}O^{3}$, a substance from which *vanillin*, the essential principle of the vanilla bean, can be obtained by oxidation.

Digitalin, $C^{29}H^{46}O^{12}$.—This is an amorphous body which may be extracted from the leaves of *Digitalis purpurea* and *lutea*. When treated with concentrated hydrochloric acid, it yields glucose and various complex bodies. Owing to the peculiar effect it produces on the contractions of the heart, it is of great medicinal value.

Tannin, or Tannic Acid, $C^{14}H^{10}O^{9}$.—The names tannins and tannic acids are applied to certain slightly acid compounds which are largely diffused in the vegetable kingdom, and which have two important properties: they precipitate solutions of gelatin and albuminous matters, and produce a bluish or greenish-black color with the ferric salts. The most important of these compounds is the tannin of oak bark, or quercitannic acid. It was formerly considered a glucoside: according to Strecker, it has the composition $C^{34}H^{28}O^{22}$, and yields glucose upon treatment with dilute acids.

$$\underset{\text{Tannin.}}{C^{34}H^{28}O^{22}} + 4H^{2}O = \underset{\text{Gallic acid.}}{4C^{7}H^{6}O^{5}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}}$$

More recent researches of Schiff render it probable, however, that pure tannin is digallic acid, $C^{14}H^{10}O^{9}$, the anhydride of gallic acid (see page 713).

Tannin exists in oak bark, in sumac, and in large quantities in nut-galls, which are excrescences developed by the sting of an insect on the leaves and branches of the *Quercus infectoria*.

It is prepared by introducing coarsely-powdered nut-galls into a percolator, and exhausting them with ordinary commercial ether. The ethereal solution which passes through is collected in a flask, and in the course of a day separates into two or sometimes three layers. The lower layer is a very concentrated, aqueous solution of tannin. It is separated and dried in a hot-air oven. The tannin remains as a light, bulky mass, having a yellowish color.

Tannin is a colorless, amorphous solid, having a very astringent taste. It is very soluble in water, less soluble in alcohol, insoluble in pure ether.

On contact with the air, the aqueous solution of tannic acid absorbs oxygen, disengages carbon dioxide, and deposits gallic acid. This transformation takes place more rapidly when oak tannin is boiled with dilute sulphuric or hydrochloric acid.

A solution of tannic acid produces with ferric salts a bluish-black precipitate, which constitutes ink. Tannin does not color ferrous salts, but the mixture soon blackens on exposure to the air by absorbing oxygen.

Tannin is employed in medicine as an astringent. Nut-galls, which are very rich in tannin, are used for the manufacture of ink. A good ink may be prepared by the following receipt: One kilogramme of powdered nut-galls is exhausted with 14 litres of water; the solution is filtered, and a solution of 500 grammes of gum arabic is first added, then a solution of 500 grammes of ferrous sulphate (green vitriol). The mixture is well stirred up, and then exposed to the air until it has acquired a fine black color.

ACIDS DERIVED FROM THE SACCHARINE BODIES.

By moderate oxidation (careful treatment with bromine water) the sugars containing the aldehyde group are converted into the corresponding monobasic acids. The most important of these are mannonic acid, gluconic acid, and galactonic acid. They are derived from hexoses and have the composition $C^6H^{12}O^7$.

When subjected to a more energetic oxidizing action (nitric acid or excess of bromine water), the saccharoses and their corresponding monocarboxylic acids yield dibasic acids. Of these we may mention the four isomers represented by the formula $C^6H^{10}O^8$,—namely, mannosaccharic acid, saccharic acid, mucic acid, and isosaccharic acid.

The relations which exist between these acids and the sugars from which they are derived afford valuable indications regarding the constitution of the hydrates of carbon.

Mannonic Acid results from the oxidation of mannose. It forms a syrupy liquid which readily passes into a crystalline anhydride (*lactone*) by the loss of a molecule of water.

Gluconic Acid is obtained from glucose by oxidation with bromine water. It is stereoisomeric with the preceding. Upon evaporation of its solution it remains as a syrup, which gradually deposits crystals of its lactone.

Galactonic Acid corresponds to galactose, and may be prepared from milk-sugar. It has been obtained crystallized; its lactone is also known.

Mannosaccharic Acid is the dibasic acid resulting from the oxidation of mannose or mannonic acid. When its aqeous solution is evaporated, it loses two molecules of water and is converted into the corresponding lactone.

Saccharic Acid is produced together with oxalic acid when cane-sugar is oxidized by nitric acid. It is also formed by the oxidation of sorbitose, glucose, and gluconic acid. Free saccharic acid is a thick liquid, which solidifies upon standing owing to the formation of its lactone, $C^6H^8O^7$. The acid potassium salt is sparingly soluble in cold water.

Mucic Acid was discovered by Scheele in 1780. It is prepared by the oxidation of milk-sugar with nitric acid. It may also be obtained from dulcitol, galactose, and galactonic acid. It forms a white crystalline powder which melts at 213°, and is but sparingly soluble in cold water. By boiling with water it is converted into a lactonic acid. By dry distillation it is converted into pyromucic acid, $C^5H^4O^3$ (p. 746).

PECTIC MATTERS.

These bodies, of which the constitution is still obscure, are largely diffused in the vegetable world, notably in fleshy fruits and in many roots. They remain in a gelatinous condition on evaporation of their aqueous solutions, from which they can be precipitated by alcohol. They are probably related to the hydrates of carbon.

AROMATIC COMPOUNDS.

The compounds of carbon which we have thus far considered may be regarded as derived from methane, CH^4, and the great majority of them may be obtained from this hydrocarbon by substitution or by synthesis. They constitute what is known as the *aliphatic* or *fatty* series, and are sharply distinguished from another important and not less numerous class of organic compounds designated as the *aromatic* series. These latter are derived from benzene, C^6H^6, a hydrocarbon occurring in coal-tar, and they bear to this a relation similar to that which exists between methane and its derivatives.

The term *aromatic* is used because the first studied substances of this series were obtained from aromatic resins and oils. It is now recognized that an aromatic smell or taste is not essential to these compounds, but the old name is still retained: we even speak of their "aromatic character" with reference to their chemical behavior.

As a rule the aromatic compounds contain a larger proportion of carbon than the members of the fatty series; nevertheless, they generally behave like saturated compounds. They further differ from the aliphatic compounds in the facility with which they are modified by substitution, and the products of substitution exhibit many peculiarities which distinguish them from the marsh-gas derivatives.

Since the aromatic compounds are all derived from benzene, a clear conception of the constitution of this fundamental body is of the utmost importance. It is thirty-five years since (1865) this problem began to engage the attention of chemists, but in spite of the vast amount of work that has been done in this direction, it cannot be said that an entirely satisfactory and conclusive solution has been reached. We are chiefly indebted to Kekulé and Baeyer for the theories which are now generally accepted as accounting for the peculiar character of the aromatic compounds. However, before we can proceed to discuss these theories, it is necessary that we acquaint ourselves with the principal facts on which they are based.

1. The hydrogen of benzene may be readily replaced by chlorine, bromine, etc., by which monochlorobenzene, monobromobenzene, dichlorobenzene, etc., are obtained.

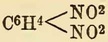
C^6H^6	C^6H^5Cl	C^6H^5Br
Benzene.	Monochlorobenzene.	Monobromobenzene.
	$C^6H^4Cl^2$	$C^6H^4Br^2$
	Dichlorobenzene.	Dibromobenzene.

These chlorides and bromides are analogous to the corresponding compounds of the fatty series, but the chlorine or bromine is much more strongly combined with the benzene nucleus, and cannot be exchanged by double decomposition, as is the case with ethyl bromide and ethylene bromide, etc.

2. By treatment with strong nitric acid, the hydrogen of benzene may be replaced by one or more groups (NO^2), forming the following compounds:

C^6H^6 Benzene.

$C^6H^5{-}NO^2$ Nitrobenzene.



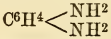
$C^6H^4 < \begin{matrix} NO^2 \\ NO^2 \end{matrix}$

Dinitrobenzene.

3. The substitution of the group (NH^2) for one atom of hydrogen produces phenylamine, or aniline; that of two groups NH^2 for two atoms of hydrogen yields phenylene-diamine.

C^6H^6 Benzene.

$C^6H^5{-}NH^2$ Phenylamine (aniline).

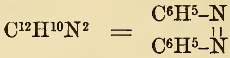


$C^6H^4 < \begin{matrix} NH^2 \\ NH^2 \end{matrix}$

Phenylene-diamine and its isomerides.

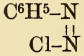
4. The amines of benzene result from the reduction of the nitrobenzenes, but there are other products of the reduction of nitrobenzene. They are the *azo*-derivatives, of which azobenzene, $C^{12}H^{10}N^2$, discovered by Mitscherlich, is the type. They

contain two nitrogen atoms (N=N), so united that each possesses one free atomicity which may be satisfied by a monatomic group such as C^6H^5.



$$C^{12}H^{10}N^2 = \begin{matrix} C^6H^5\text{–}N \\ \| \\ C^6H^5\text{–}N \end{matrix}$$

By the action of nitrous acid on aromatic compounds containing the group NH^2, peculiar explosive compounds are formed. They are the *diazo*-derivatives, and contain likewise the group N=N : one affinity, however, is satisfied by a monatomic aromatic group, while the other combines it with some other monatomic radical or element. Such is diazobenzene chloride.



$$\begin{matrix} C^6H^5\text{–}N \\ \| \\ Cl\text{–}N \end{matrix}$$

Only a few diazo-compounds have been obtained in the fatty series, and these are distinguished from the aromatic diazo-compounds by their inability to form salts with the mineral acids. Azo-compounds appear to exist only in the aromatic series.

5. Concentrated sulphuric acid effects the displacement of hydrogen in benzene by the group SO^3H, *sulphonic acids* being formed.

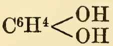
C^6H^6	$C^6H^5SO^3H$	$C^6H^4(SO^3H)^2$
Benzene.	**Benzene sulphonic acid.**	**Benzene disulphonic acid.**

Sulphonic acids exist also in the fatty series, but direct sulphonation is a reaction characteristic of the aromatic compounds.

6. The replacement of one or more atoms of hydrogen by the same number of hydroxyl groups converts benzene into compounds known as *phenols.* They correspond to the alcohols of the saturated hydrocarbons, but, while the alcohols are perfectly neutral, the phenols have acid characters, although they are neutral to litmus.

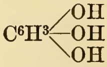
$C^6H^5.OH$

Phenol.



$$C^6H^4 < \begin{matrix} OH \\ OH \end{matrix}$$

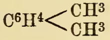
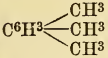
Oxyphenol
(resorcinol and isomerides).



$$C^6H^3 \begin{matrix} \diagup OH \\ \text{—}OH \\ \diagdown OH \end{matrix}$$

Dioxyphenol
(phloroglucinol and
isomerides.)

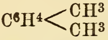
7. If one or more atoms of hydrogen in benzene be replaced by as many methyl groups, CH^3, the higher homologues of benzene are obtained.

$C^6H^6 = C^6H^6$ benzene.
$C^7H^8 = C^6H^5{-}CH^3$ toluene (methylbenzene).

$C^8H^{10} = C^6H^4<\begin{matrix}CH^3\\CH^3\end{matrix}$ xylene and isomerides (dimethylbenzenes).

$C^9H^{12} = C^6H^3\begin{matrix}\diagup CH^3\\ - CH^3\\ \diagdown CH^3\end{matrix}$ mesitylene and isomerides (trimethylbenzenes).
$C^{12}H^{18} = C(CH^3)^6$ hexamethylbenzene.

One ethyl group can replace one atom of hydrogen in benzene, and ethylbenzene, isomeric with dimethylbenzene, results.

$C^6H^5{-}C^2H^5$

Ethylbenzene.


$C^6H^4<\begin{matrix}CH^3\\CH^3\end{matrix}$

Dimethylbenzene.

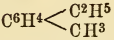
There are many instances of such isomerism, and they receive the same interpretation.

One atom of hydrogen in benzene may be replaced by a propyl group, C^3H^7, and propyl benzene, which is isomeric with trimethylbenzene, is the result.

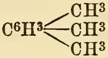
One atom of hydrogen may be replaced by an ethyl group and another by a methyl group, and the new compound would be ethyl-methylbenzene, isomeric with propylbenzene and with trimethylbenzene.

$C^6H^5{-}C^3H^7$

Propylbenzene (cumene).


$C^6H^4<\begin{matrix}C^2H^5\\CH^3\end{matrix}$

{Ethyl-meythelbenzene.

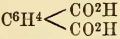

$C^6H^3\begin{matrix}\diagup CH^3\\ - CH^3\\ \diagdown CH^3\end{matrix}$

Trimethylbenzene.

The alcoholic radicals, which are thus substituted for the hydrogen of benzene, constitute, according to the expression of Kekulé, *lateral chains*, which are grafted, so to speak, on the benzene nucleus or principal chain.

8. The aromatic acids, properly speaking, result from the substitution of one or more carboxyl groups, $CO.OH = CO^2H$, for one or more hydrogen atoms in the benzene nucleus.

C^6H^6	$C^6H^5{-}CO^2H$	$C^6H^4<\begin{matrix}CO^2H\\CO^2H\end{matrix}$	$C^6H^3(CO^2H)^3$	$C^6(CO^2H)^6$
Benzene.	Benzoic acid.	Phthalic acid and isomerides.	Trimesic acid and isomerides.	Mellitic acid.


$C^6H^4<\begin{matrix}CO^2H\\CO^2H\end{matrix}$

9. **Isomerism of Constitution in Substituted Benzene Derivatives.**—In the homologues of benzene, the substitution of Cl, Br, OH, NH^2, CO^2H, etc., for hydrogen, may take place either in the benzene nucleus or in the lateral chain: isomeric compounds are thus formed.

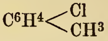
a. By substitution of one atom of chlorine for an atom of hydrogen in toluene, two isomeric compounds, C^7H^7Cl, may be obtained. In one, the chlorine will be attached to the lateral chain; in the other, it will be attached to the benzene nucleus, as is the group CH^3 itself.

$C^6H^5-CH^3$

Toluene.

$C^6H^5-CH^2Cl$

Benzyl chloride.



$C^6H^4<\begin{matrix}Cl\\CH^3\end{matrix}$

Chlorotoluene.

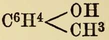
b. The *phenols* result from the substitution of OH for an atom of hydrogen in the nucleus. If this substitution take place in a lateral chain, an *aromatic alcohol*, isomeric with the corresponding phenol, is obtained.

$C^6H^5-CH^3$

Toluene.

$C^6H^5-CH^2(OH)$

Benzyl alcohol.



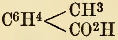
$C^6H^4<\begin{matrix}OH\\CH^3\end{matrix}$

Cresol.

c. The substitution of a carboxyl group, CO^2H, for an atom of hydrogen in the benzene nucleus of toluene, $C^6H^5-CH^3$, produces the aromatic acids, toluic acid, and its isomerides; if, however, the carboxyl replace a hydrogen atom in the lateral chain, CH^3, phenyl*acetic* (alpha-toluic) acid, isomeric with the preceding acids, results.

$C^6H^5-CH^3$

Toluene.



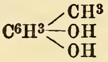
$C^6H^4<\begin{matrix}CH^3\\CO^2H\end{matrix}$

Toluic acids.

$C^6H^5-CH^2-CO^2H$

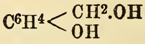
Phenylacetic acid.

d. When two groups OH are substituted for two atoms of hydrogen in the principal chain, oxyphenols are formed. If this substitution takes place in both the benzene group and in the lateral chain, phenol alcohols result.



$C^6H^3\begin{matrix}\diagup CH^3\\ -OH\\ \diagdown OH\end{matrix}$

Orcinol.



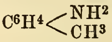
$C^6H^4<\begin{matrix}CH^2.OH\\OH\end{matrix}$

Saligeninol.

e. The substitution of the group NH^2 for one atom of hydrogen in the principal chain, on the one hand, and in the lateral chain, on the other, produces isomeric compounds.

$C^6H^5-CH(NH^2)$

Benzylamine.



$C^6H^4<\begin{matrix}NH^2\\CH^3\end{matrix}$

Toluidine.

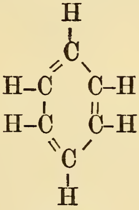
10. **Isomerism of Position in Substituted Benzene Derivatives.**—In addition to the preceding isomerisms, the lateral chains may be grafted at different points of the benzene nucleus by substitution for the different hydrogen atoms. Their positions and their relative distances from each other are the causes of numerous isomerisms, called isomerisms of position, to distinguish them from the isomerisms of constitution already explained.

It is important to understand the principle of this isomerism. Let us consider the most simple case, that in which two atoms of hydrogen are replaced by two other monatomic atoms or monatomic groups. Such compounds are the di-substituted derivatives of benzene, and experience has shown that there are three di-substituted derivatives of each kind.

Thus there are three hydrocarbons containing two groups CH^3, each substituted for one atom of hydrogen in benzene; three phenols, each containing two groups OH; three acids, each containing one group CO^2H, and one group OH, substituted each for one atom of hydrogen, and three acids, each containing two carboxyl groups substituted for two atoms of hydrogen.

Theory of the Constitution of Benzene.—How then shall we account for the tenacity with which the six carbon atoms of benzene and of the benzene nucleus of its derivatives are held together? What explanation can be offered for the isomerisms of the substitution products peculiar to the aromatic series?

According to a theory propounded by Kekulé in 1865, the 6 atoms of carbon in benzene form a closed chain, each being bound to its neighbors, on one side by one, and on the other by two bonds of saturation. One atom of hydrogen is attached to each of these carbon atoms.



Benzene.*

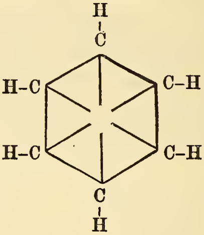
Innumerable experiments have shown that the chemical value of each of the six hydrogen atoms of benzene is absolutely the same. If by the action of reagents one of these hydrogen atoms be replaced by another atom or group of atoms, it is a matter of indifference which of the hydrogen atoms is so replaced, the product is always identical. This fact indicates that the

---

[*] In this formula, the connecting lines indicate the saturation of the atomicities; the double lines indicate the exchange of two atomicities between two neighboring atoms of carbon.

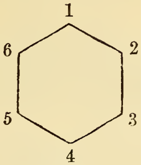
arrangement of the hydrogen atoms is perfectly symmetrical in relation to the carbon atoms around which they are grouped. In other words, the molecular constitution of benzene must be $(CH)^6$. In consequence, each atom of carbon must be united to one atom of hydrogen,—a requirement met by Kekulé's theory,—and each carbon atom must be symmetrically related to the other carbon atoms with which it is combined. The latter condition is not perfectly satisfied by Kekulé's theory, for a carbon atom would exchange a double affinity with its neighboring atom on one side, while with that on the other side it would exchange but a single atomicity. It would follow that the combination should be stronger on one side than on the other, and the molecule would not be symmetrical.

This difficulty disappears in the following formula proposed by Armstrong and by Baeyer, known as the *centric formula:*



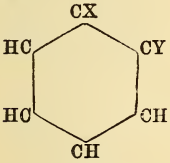
The 6 carbon atoms are arranged at the angles of a hexagon, as in the formula of Kekulé, but instead of assuming a double linking of alternate pairs of carbon atoms, we conceive the fourth affinity of each carbon atom to be directed towards the centre, but without actually connecting any two carbon atoms with each other. While thus augmenting the stability of the molecule, the fourth affinity of each carbon atom is rendered latent. Although this arrangement is the most satisfactory that has been proposed, it must be admitted that such a method of disposing of the valences is without analogy in the compounds we have thus far considered.

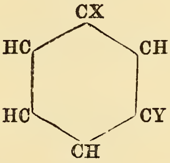
Isomerism of Position.—In the benzene molecule the position of each atom of hydrogen is of the same value. It will be convenient to represent the formula by a simple hexagon and to number these positions as in the following diagram:

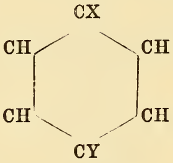


According to Kekulé and Baeyer.

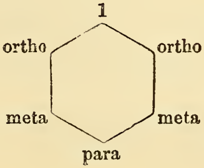
Experiment has shown that if but a single atom of hydrogen in benzene be replaced by another monatomic atom or group, the resulting compound does not vary, and is incapable of isomerism. This is not, however, the case if two hydrogen atoms be replaced, for theory then predicts, and experiment confirms, the existence of three isomeric compounds in each case. This isomerism results from the different positions of one of the substituted atoms or groups with relation to the other in their attachment to the benzene nucleus. Let X and Y be the two substituted monatomic atoms or groups, such as chlorine, hydroxyl, nitryl, etc., then the isomerism would be expressed as follows:



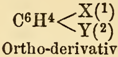




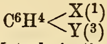
The position at 1 being always supposed to be occupied by one of the substituted groups, the compounds are named *ortho* if the other replacement be at 2 or 6, *meta* if it be at 3 or 5, and *para* if it be at 4. The relations of 2 and 6 to 1 are the same, as are also those of 3 and 5 to 1.



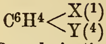
In the preceding compounds formed by X and Y, these positions would be marked as follows:


$C^6H^4<\begin{matrix}X(^1)\\Y(^2)\end{matrix}$

Ortho-derivative.


$C^6H^4<\begin{matrix}X(^1)\\Y(^3)\end{matrix}$

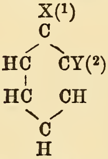
Meta-derivative.


$C^6H^4<\begin{matrix}X(^1)\\Y(^4)\end{matrix}$

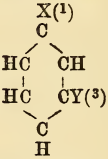
Para-derivative.

The following examples will further explain this isomerism of position, of which we must study numerous cases.

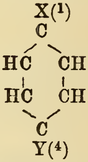
ORTHO-SERIES.

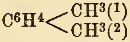


META-SERIES.

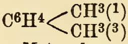


PARA-SERIES.

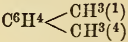



$C^6H^4<\begin{matrix}CH^3(^1)\\CH^3(^2)\end{matrix}$

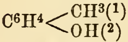
Orthoxylene.


$C^6H^4<\begin{matrix}CH^3(^1)\\CH^3(^3)\end{matrix}$

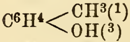
Metaxylene.


$C^6H^4<\begin{matrix}CH^3(^1)\\CH^3(^4)\end{matrix}$

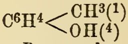
Paraxylene.


$C^6H^4<\begin{matrix}CH^3(^1)\\OH(^2)\end{matrix}$

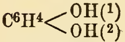
Orthocresol.


$C^6H^4<\begin{matrix}CH^3(^1)\\OH(^3)\end{matrix}$

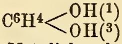
Metacresol.


$C^6H^4<\begin{matrix}CH^3(^1)\\OH(^4)\end{matrix}$

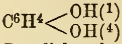
Paracresol.


$C^6H^4<\begin{matrix}OH(^1)\\OH(^2)\end{matrix}$

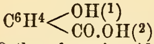
Orthodiphenol.
(pyrocatechin.)


$C^6H^4<\begin{matrix}OH(^1)\\OH(^3)\end{matrix}$

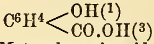
Metadiphenol.
(resorcinol.)


$C^6H^4<\begin{matrix}OH(^1)\\OH(^4)\end{matrix}$

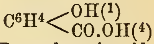
Paradiphenol.
(hydroquinone.)


$C^6H^4<\begin{matrix}OH(^1)\\CO.OH(^2)\end{matrix}$

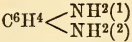
Orthoxybenzoic acid.
(salicylic.)


$C^6H^4<\begin{matrix}OH(^1)\\CO.OH(^3)\end{matrix}$

Metoxybenzoic acid.


$C^6H^4<\begin{matrix}OH(^1)\\CO.OH(^4)\end{matrix}$

Paroxybenzoic acid.


$C^6H^4<\begin{matrix}NH^2(^1)\\NH^2(^2)\end{matrix}$

Orthophenylene diamine.


$C^6H^4<\begin{matrix}NH^2(^1)\\NH^2(^3)\end{matrix}$

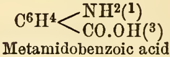
Metaphenylene diamine.


$C^6H^4<\begin{matrix}NH^2(^1)\\NH^2(^4)\end{matrix}$

Paraphenylene diamine.


$C^6H^4<\begin{matrix}NH^2(^1)\\CO.OH(^2)\end{matrix}$

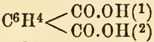
Orthoamidobenzoic acid.


$C^6H^4<\begin{matrix}NH^2(^1)\\CO.OH(^3)\end{matrix}$

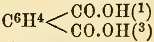
Metamidobenzoic acid.


$C^6H^4<\begin{matrix}NH^2(^1)\\CO.OH(^4)\end{matrix}$

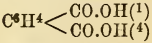
Paramidobenzoic acid.


$C^6H^4<\begin{matrix}CO.OH(^1)\\CO.OH(^2)\end{matrix}$

Phthalic acid.


$C^6H^4<\begin{matrix}CO.OH(^1)\\CO.OH(^3)\end{matrix}$

Isophthalic acid.


$C^6H^4<\begin{matrix}CO.OH(^1)\\CO.OH(^4)\end{matrix}$

Terephthalic acid.

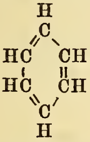
These indications will suffice to illustrate the class of isomerides under consideration. With the tri-substituted derivatives of benzene, theory foresees and experiment has demonstrated the existence of still more numerous isomerides, but we cannot dwell on them here.

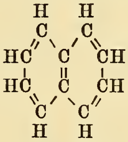
Two very important hydrocarbons are now considered as directly related to benzene. They are naphthalene, $C^{10}H^8$, and anthracene, $C^{14}H^{10}$.

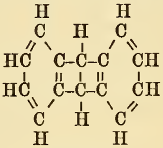
Naphthalene is formed by the union of two benzene nuclei, two atoms of carbon being common to each nucleus (Erlenmeyer).

Anthracene results from the union of two benzene nuclei by the intermediation of two carbon atoms, which are themselves combined together, each by one atomicity, and each of which is combined with one atom of hydrogen (Graebe).

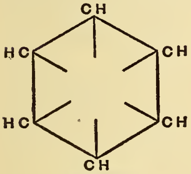
These ideas are indicated in the following graphic formulæ, which express the reciprocal relations between the atoms of carbon and hydrogen, but not their real positions in space:

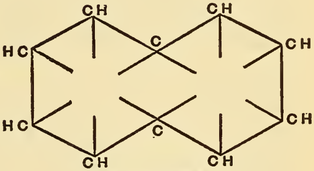

Benzene.


Naphthalene.


Anthracene.

or their "centric" equivalents:


Benzene


Naphthalene

BENZENE AND ITS DERIVATIVES.

BENZENE, OR BENZOL.

C^6H^6

This important body was discovered in 1825 by Faraday. Mitscherlich obtained it by heating benzoic acid with an excess of lime.

$$C^7H^6O^2 = CO^2 + C^6H^6$$

It is now obtained in large quantities from coal-tar by distilling the latter body. The more volatile products contain the benzene, which is purified by fractional distillation. That which passes below 85° is principally benzene, and the latter crystallizes out when the liquid which passes between 80 and

85° is cooled to —5°. The crystals are collected and separated by pressure from the adhering liquid. The product is benzene containing a very small proportion of a compound named thiophene (page 746), which may be removed by repeated agitation with strong sulphuric acid (V. Meyer). Berthelot has made the direct synthesis of benzene by exposing acetylene to a temperature near redness.

$$\underset{\text{Acetylene.}}{3C^2H^2} = \underset{\text{Benzene.}}{C^6H^6}$$

Benzene is a colorless, strongly refracting liquid. At 0° it solidifies to crystals which melt at 5.5°. It boils at 80.5°. It is insoluble in water, but dissolves in alcohol and ether. It is inflammable, and burns with a bright, smoky flame.

When benzene vapor is passed through a red-hot tube, *diphenyl*, $C^{12}H^{10}$, is formed.

$$2C^6H^6 = C^6H^5\text{–}C^6H^5 + H^2$$

When heated to 275 or 280° for twenty-four hours with 80 to 100 parts of concentrated hydriodic acid, benzene is converted into *hexahydrobenzene*, C^6H^{12} (hexamethylene), iodine being set free. The formation of small amounts of hexane, C^6H^{14}, has been observed in this reaction.

CHLORINE AND BROMINE DERIVATIVES OF BENZENE.

By the action of chlorine or bromine on benzene, two sorts of derivatives are obtained,—addition products and substitution compounds.

Addition Compounds.—Two, four, or six atoms of chlorine may combine directly with benzene, forming the compounds

Benzene dichloride,	$C^6H^6Cl^2$;
Benzene tetrachloride,	$C^6H^6Cl^4$;
Benzene hexachloride,	$C^6H^6Cl^6$.

The last is easily formed by the action of an excess of chlorine on benzene exposed to direct sunlight. It crystallizes in brilliant plates. There is a corresponding hexabromide, formed in the same manner. Boiling potassium hydrate removes the elements of three molecules of hydrochloric acid from benzene hexachloride, converting it into trichlorobenzene.

$$C^6H^6Cl^6 = 3HCl + C^6H^3Cl^3$$

Substitution Compounds.—These compounds are numerous, and present interesting examples of isomerism. Only the mono-, penta-, and hexa-derivatives have no isomerides.

Monochlorobenzene or phenyl chloride, C^6H^5Cl, is obtained by passing chlorine through benzene in the presence of a small quantity of iodine. It is also formed by the action of phosphorus pentachloride on phenol: hence the name phenyl chloride.

$$C^6H^5.OH + PCl^5 = HCl + POCl^3 + C^6H^5Cl$$

Chlorobenzene is a colorless, strongly refracting liquid, having a pleasant odor, and boiling at 132°. It is readily prepared by heating diazobenzene chloride (page 687) with cuprous chloride (Sandmeyer).

$$C^6H^5\text{–}N{=}N\text{–}Cl = C^6H^5Cl + N^2$$

Dichlorobenzene, $C^6H^4Cl^2$.—There are three isomerides:—

Ortho-dichlorobenzene, $C^6H^4{<}\begin{array}{l}Cl(^1)\\Cl(^2)\end{array}$, liquid, boiling at 179°.

Meta-dichlorobenzene, $C^6H^4{<}\begin{array}{l}Cl(^1)\\Cl(^3)\end{array}$, liquid, boiling at 172°.

Para-dichlorobenzene, $C^6H^4{<}\begin{array}{l}Cl(^1)\\Cl(^4)\end{array}$, fusible at 56°, and boiling at 173°.

Among the other chloro-derivatives we will mention only hexachlorobenzene, C^6Cl^6, which is formed not only by the complete chlorination of benzene, but also when vapor of chloroform or of carbon tetrachloride, CCl^4, is passed through a red-hot tube. It is a crystallizable solid, fusible at 222°, and boiling at 332°.

Monobromobenzene, C^6H^5Br, may be made by mixing benzene and bromine in the proportion of one molecule of the first to two atoms of the second, adding some thin iron wire, and heating for several hours over a small flame. The product is washed with caustic potash and distilled. A more convenient method is to warm diazobenzene bromide with cuprous bromide. Monobromobenzene boils at 157°. When heated with sodium, it yields to the latter its bromine, and a hydrocarbon $C^{12}H^{10} = \begin{array}{c}C^6H^5\\|\\C^6H^5\end{array}$, called *diphenyl*, is obtained.

Dibromo-benzenes, $C^6H^4Br^2$.—There are three isomerides. The para-derivative, $C^6H^4{<}\begin{array}{l}Br(^1)\\Br(^4)\end{array}$, is readily formed by the action of an excess of bromine on benzene. It crystallizes in beautiful prisms, fusible at 89°. It boils at 218°.

Iodine and fluorine derivatives of benzene are also known.

NITRO-DERIVATIVES OF BENZENE.

Nitrobenzene, $C^6H^5(NO^2)$.—If benzene be poured in small portions into a mixture of strong nitric and sulphuric acids, and water be added to the mixture, an oily, yellow liquid separates, constituting nitrobenzene.

$$C^6H^6 + HNO^3 = H^2O + C^6H^5(NO^2)$$

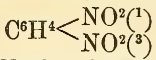
It is benzene in which one hydrogen atom is replaced by the group $(NO^2)'$.

Nitrobenzene is a yellowish liquid, having a strong odor of bitter almonds. It boils at 205°, and solidifies at 3°. It is employed in perfumery under the name *essence of Mirbane.*

By the action of reducing agents, such as hydrogen sulphide, ammonium sulphide, tin and hydrochloric acid, or iron-filings and acetic acid, nitrobenzene is converted into aniline or phenylamine.

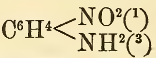
$$\underset{\text{Nitrobenzene.}}{C^6H^5(NO^2)} + 3H^2 = 2H^2O + \underset{\text{Aniline.}}{C^6H^5(NH^2)}$$

Dinitrobenzenes, $C^6H^4(NO^2)^2$.—The three isomerides are formed when benzene is treated with a large excess of a mixture of nitric and sulphuric acids. The nitro-compounds separate on the addition of water, and are purified by crystallization in alcohol. Metadinitrobenzene separates first, crystallizing in long colorless needles, fusible at 89.9°. Reducing agents convert it successively into nitrophenylamine and phenylene-diamine.



$$C^6H^4 < \begin{matrix} NO^2(^1) \\ NO^2(^3) \end{matrix}$$

Metadinitrobenzene.



$$C^6H^4 < \begin{matrix} NO^2(^1) \\ NH^2(^3) \end{matrix}$$

Metanitrophenylamine.

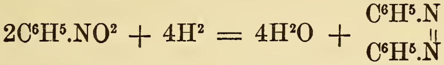
$$C^6H^4 < \begin{matrix} NH^2(^1) \\ NH^2(^3) \end{matrix}$$

Metaphenylenediamine.

AZO-DERIVATIVES OF BENZENE.

Besides aniline, there are other products of the reduction of nitrobenzene, and they are of great importance, for they have become types of numerous analogous compounds. The first was described in 1834, by Mitscherlich, under the name of azobenzide; it is now called azobenzene.

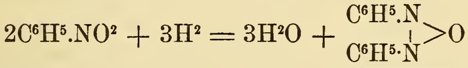
Azobenzene, $C^{12}H^{10}N^2$, is obtained by the action of sodium amalgam on an alcoholic solution of nitrobenzene.



$$2C^6H^5.NO^2 + 4H^2 = 4H^2O + \begin{matrix}C^6H^5.N\\ \|\\ C^6H^5.N\end{matrix}$$

Azobenzene forms large red crystals, fusible at 66.5°. It boils at 293°. It is only slightly soluble in water, but dissolves readily in alcohol and ether.

Azoxybenzene, $C^{12}H^{10}NO$.—This compound, which is a product of the incomplete reduction of nitrobenzene, was discovered by Zinin. It is formed by boiling an alcoholic solution of potassium hydrate with nitrobenzene. Under these conditions the alcohol is oxidized by the oxygen of the group NO^2.

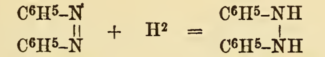


$$2C^6H^5.NO^2 + 3H^2 = 3H^2O + \left.\begin{matrix}C^6H^5.N\\ |\\ C^6H^5.N\end{matrix}\right>O$$

Azoxybenzene.

Azoxybenzene crystallizes in long needles, soluble in alcohol and ether, insoluble in water. It melts at 36°, and is decomposed when distilled. If heated with iron filings, it becomes converted into azobenzene.

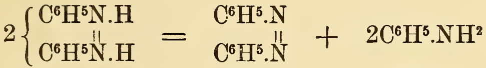
Hydrazobenzene, $C^{12}H^{12}N^2$.—Alkaline reducing agents, such as zinc dust and sodium hydroxide, and ammonium sulphide, in presence of alcohol, convert azobenzene into hydrazobenzene.



$$\begin{matrix}C^6H^5\text{–}N\\ \|\\ C^6H^5\text{–}N\end{matrix} + H^2 = \begin{matrix}C^6H^5\text{–}NH\\ |\\ C^6H^5\text{–}NH\end{matrix}$$

Azobenzene. Hydrazobenzene.

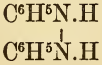
The latter body crystallizes in tables, fusible at 131°, almost insoluble in water but soluble in alcohol and ether. When submitted to dry distillation, it breaks up into azobenzene and aniline.



$$2\left\{\begin{matrix}C^6H^5N.H\\ \|\\ C^6H^5N.H\end{matrix}\right. = \begin{matrix}C^6H^5.N\\ \|\\ C^6H^5.N\end{matrix} + 2C^6H^5.NH^2$$

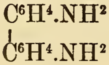
Hydrazobenzene. Azobenzene. Aniline.

Acids convert hydrazobenzene into a basic isomeride, *benzidine*, from which a number of valuable dye-stuffs (azo-dyes) are derived.



$$\begin{matrix}C^6H^5N.H\\ |\\ C^6H^5N.H\end{matrix}$$

Hydrazobenzene.



$$\begin{matrix}C^6H^4.NH^2\\ |\\ C^6H^4.NH^2\end{matrix}$$

Benzidine.

Hydrazobenzene may be considered as derived from diamide, $\begin{array}{c}NH^2\\|\\NH^2\end{array}$, by replacement of two hydrogen atoms by phenyl groups. The *aromatic hydrazines* proper are the unsymmetrical derivatives resulting from the substitution of one or two aromatic radicals for hydrogen in one NH^2 group.

$C^6H^5.HN.NH^2$ — Phenylhydrazine.

$(C^6H^5)^2N.NH^2$ — Di-phenylhydrazine.

Phenylhydrazine is obtained by reducing diazobenzene chloride with sodium sulphite or stannous chloride.

$$C^6H^5N{=}NCl + 2H^2 = C^6H^5{-}NH.NH^2.HCl$$

It is a colorless oil, solidifying upon cooling in tabular crystals which melt at 17.5°. It boils at 241° with partial decomposition. The density at 23° is 1.097. Phenylhydrazine is sparingly soluble in water, but readily in alcohol and ether.

It acts as a powerful base, forming salts with the acids. Its property to react with aldehydes and ketones to form hydrazones has made it a most important reagent for the detection and isolation of those bodies, especially the sugars. *Antipyrine* and a number of dye-stuffs are derived from it.

BENZENESULPHONIC ACID.

$C^6H^5{-}SO^2.OH$

Aromatic compounds are readily acted upon by concentrated or fuming sulphuric acid, the *sulphonic* group $(SO^2.OH)'$ replacing one or several atoms of hydrogen.

Thus, *benzenesulphonic* acid is formed in the following reaction:

$$C^6H^6 + SO^2{<}\begin{smallmatrix}OH\\OH\end{smallmatrix} = H^2O + C^6H^5.SO^2.OH$$

It is prepared by heating for a long time a mixture of equal parts of benzene and concentrated sulphuric acid. The liquid is then diluted with a large quantity of water, and neutralized with barium carbonate. The concentrated solution then yields a barium salt, $Ba(C^6H^5.SO^3)^2 + H^2O$, which crystallizes in pearly plates. From this salt the acid can be liberated by the careful addition of sulphuric acid. It crystallizes in small plates, soluble in water and alcohol. When fused with an excess of potassium hydroxide, it yields phenol.

Benzene Sulphone, or Sulphobenzide, $(C^6H^5)^2SO^2$.—The hydroxyl group in benzenesulphonic acid may be replaced by a phenyl group, and the compound so formed is called sulphobenzide. It may be obtained by heating phenylsulphuric acid with phosphoric anhydride to 150° in sealed tubes, treating the product of the reaction with a dilute alkaline hydrate, and crystallizing the residue in alcohol. It crystallizes from water in silky needles, and from benzene in large rhombic prisms. It melts at 128°.

CYANOBENZENE.

(PHENYL CYANIDE, BENZONITRILE.)

$C^6H^5.CN$

This body is formed in various reactions, particularly in the destructive distillation of hippuric acid, and by the dehydration of benzamide by phosphoric anhydride.

$$\underset{\text{Benzamide.}}{C^6H^5\text{–}CO.NH^2} \quad - \quad H^2O \quad = \quad \underset{\text{Benzonitrile.}}{C^6H^5\text{–}CN}$$

It is a colorless oil, which boils at 191°. When heated with the alkalies, it yields benzoic acid and ammonia.

$$\underset{\text{Benzonitrile.}}{C^6H^5\text{–}CN} \quad + \quad 2H^2O \quad = \quad \underset{\text{Benzoic acid.}}{C^6H^5\text{–}CO^2H} \quad + \quad NH^3$$

PHENOL, OR CARBOLIC ACID.

$C^6H^5.OH$

This body bears the same relation to benzene that wood-spirit does to marsh gas: it is hydroxy-benzene.

$$\underset{\text{Methane.}}{CH^4} \qquad \underset{\text{Methyl hydroxide.}}{CH^3.OH}$$

$$\underset{\text{Benzene.}}{C^6H^6} \qquad \underset{\text{Phenol.}}{C^6H^5.OH}$$

It was discovered in coal-tar by Runge, who named it *carbolic acid*. Laurent demonstrated that it plays the part of an alcohol. Indeed, it presents points of resemblance with the monohydric alcohols, but it differs from them by its acid character, on account of which it is sometimes called *phenic acid*.

Preparation.—Large quantities of phenol are obtained from coal-tar, from which it is separated by distillation. That part which passes between 150° and 200° is collected apart and mixed with a saturated solution of potassium or sodium hydroxide to which solid caustic alkali is added. A crystalline phenate of potassium or sodium is formed; it is dissolved in boiling water, the insoluble oil which floats is separated, and the alkaline solution is neutralized with hydrochloric acid. The phenol separates; it is washed with a small quantity of water, dehydrated with calcium chloride, and rectified. The distilled product is cooled to —10°, and the crystals which are deposited are allowed to drain out of contact with the air.

Phenol may be made artificially from benzene by a process which is applicable to the preparation of all the phenols. It consists in treating benzene with fuming or even ordinary sulphuric acid. Benzenesulphonic acid is formed; this is diluted with water to separate the excess of hydrocarbon, and the solution is neutralized with chalk; calcium phenylsulphonate, which is soluble, and sulphate, which is insoluble, are formed. The calcium benzenesulphonate is converted into sodium salt by double decomposition with sodium carbonate, and after evaporation and desiccation the product is fused in a silver crucible with an excess of potassium hydroxide. The mass is exhausted with water, and the alkaline solution is decomposed by hydrochloric acid. The phenol separates and is dried and purified by distillation (Dusart, Wurtz, Kekulé).

The decomposition of sodium or potassium benzenesulphonate is expressed in the following equation:

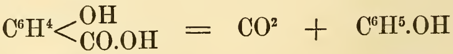
$$\underset{\text{Potassium benzenesulphonate.}}{C^6H^5.SO^3K} + KOH = \underset{\text{Phenol.}}{C^6H^5.OH} + \underset{\text{Potassium sulphite.}}{K^2SO^3}$$

There is another very simple synthesis of phenol. In presence of aluminium chloride, benzene absorbs oxygen directly and phenol is formed.

$$C^6H^6 + O = C^6H^6O$$

This reaction is one of the most unexpected and most interesting applications of a general method of synthesis discovered by Friedel and Crafts (see page 698).

Phenol is also formed by the dry distillation of the oxybenzoic acids (page 709).



$$\underset{\text{Oxybenzoic acid.}}{C^6H^4<\begin{matrix}OH\\CO.OH\end{matrix}} = CO^2 + \underset{\text{Phenol.}}{C^6H^5.OH}$$

Properties of Phenol.—Phenol is a solid, crystallizing in long, colorless needles, having at 0° a density of 1.084. It fuses at 42°, and boils at 183°. Its odor is peculiar and characteristic, its taste acrid and burning. It is poisonous and antiseptic. It is very soluble in alcohol, ether, and acetic acid, and dissolves in 15 parts of water at 20°. Its solution is colored dark violet by ferric salts, and bromine water forms, even in very dilute solutions, a yellow precipitate of tribromophenol. A pine shaving moistened with hydrochloric acid assumes a blue color when dipped in phenol and exposed to the air.

Although phenol is neutral to litmus-paper, it forms definite combinations with the alkalies. When it is mixed with a very concentrated solution of potassium hydrate, a crystalline mass is obtained which constitutes potassium phenate, $C^6H^5.OK$.

The same compound is formed, with disengagement of hydrogen, by the action of potassium on phenol.

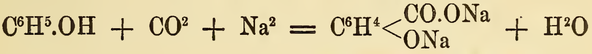
The solubility of phenol in the alkaline hydrates is applied in the separation of this body from the neutral oils which accompany it. The property is common to the phenols, and indicates the slightly acid character of the class.

Phosphorus perchloride converts phenol into phenyl chloride, identical with monochlorobenzene.

$$\underset{\text{Phenol.}}{C^6H^5.OH} + PCl^5 = \underset{\text{Phenyl chloride.}}{C^6H^5Cl} + POCl^3 + HCl$$

The hydrogen of the radical C^6H^5 in phenol can be readily replaced by chlorine, bromine, or groups such as NO^2, NO, NH^2, etc. The compounds so formed may sometimes be obtained directly, as the nitro-phenols,—sometimes by indirect processes.

In the presence of sodium, phenol directly combines with carbon dioxide, forming salicylic acid (page 709).



$$C^6H^5.OH + CO^2 + Na^2 = C^6H^4\!<\!\begin{matrix}CO.ONa\\ ONa\end{matrix} + H^2O$$

Sodium-salicylate of sodium.

The following remarkable reaction of phenol was first noticed by Reimer and Tiemann. When it is heated with chloroform and an excess of sodium hydrate, in the proportion of one molecule each of phenol and chloroform and four molecules of alkali, it is converted into salicylaldehyde.

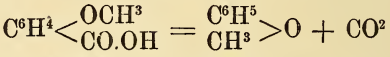
$$\underset{\text{Sodium phenate.}}{C^6H^5.ONa} + 3NaOH + CHCl^3 = \underset{\text{Sodium salicylite.}}{C^7H^5O^2Na} + 3NaCl + 2H^2O$$

The compound $C^7H^5O^2Na$ is the sodium compound of salicylaldehyde, into which it is converted by hydrochloric acid.

ETHERS OF PHENOL.

Phenyl Oxide, $(C^6H^5)^2O$.—This body is formed, together with other products, by the dry distillation of copper benzoate. It crystallizes in long needles, fusible at 28°. It boils at 246°. It is very soluble in alcohol and in water. It cannot be reduced by either zinc or hydriodic acid.

Methylphenyl Oxide, or Anisol, $\begin{matrix}C^6H^5\\CH^3\end{matrix}>O$. — Anisol was first obtained by distilling anisic acid (page 712) with barium oxide or lime.



$$C^6H^4<\begin{matrix}OCH^3\\CO.OH\end{matrix} = \begin{matrix}C^6H^5\\CH^3\end{matrix}>O + CO^2$$

Anisic acid. Anisol.

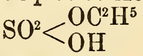
It may be prepared more readily by synthesis in the reaction of methyl iodide on potassium phenate.

$$C^6H^5.OK + CH^3I = KI + C^6H^5.OCH^3$$

It is a colorless liquid, having an ethereal odor. Its density at 15° is 0.991; it is insoluble in water, and boils at 152°.

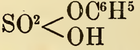
Ethylphenyl Oxide, or Phenetol, $\begin{matrix}C^6H^5\\C^2H^5\end{matrix}>O$, may be obtained by a process analogous to the last method indicated for preparing anisol. It is an aromatic liquid, boiling at 172°.

Phenylsulphuric Acid is analogous to ethylsulphuric acid.



$$SO^2<\begin{matrix}OC^2H^5\\OH\end{matrix}$$

Ethylsulphuric acid.



$$SO^2<\begin{matrix}OC^6H^5\\OH\end{matrix}$$

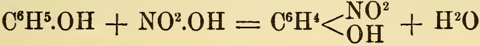
Phenylsulphuric acid.

The acid is not known in the free state. Its potassium salt is formed when potassium phenate is heated with an aqueous solution of potassium pyrosulphate, $K^2S^2O^7$. It exists in the urine of herbivorous animals. If phenol be ingested, it appears in the urine as potassium phenylsulphate (Baumann).

SUBSTITUTED DERIVATIVES OF PHENOL.

Among the numerous compounds derived from phenol by the substitution of various elements or groups for the hydrogen of the group C^6H^5, we can only describe a few of the nitro- and sulphonic compounds.

Mononitrophenols, $C^6H^4<\begin{matrix}NO^2\\OH\end{matrix}$.—There are three isomeric mononitrophenols. Two of them, the ortho- and the para-, are formed by the action of dilute nitric acid on phenol. The meta-derivative is obtained by indirect processes.



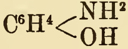
$$C^6H^5.OH + NO^2.OH = C^6H^4\left<\begin{array}{l}NO^2\\ OH\end{array}\right. + H^2O$$

Orthonitrophenol crystallizes in large yellow prisms, slightly soluble in water, fusible at 45°, and boiling at 214°. It is readily carried over with vapor of water, and may so be separated from the para-isomeride.

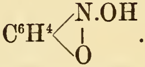
Metanitrophenol is in yellow crystals, fusible at 96°, and quite soluble in water. It does not distil with vapor of water.

Paranitrophenol deposits from its boiling aqueous solution in long colorless needles, fusible at 114°. They redden on exposure to the air.

Nascent hydrogen (tin and hydrochloric acid) converts the mononitrophenols into amido-phenols.

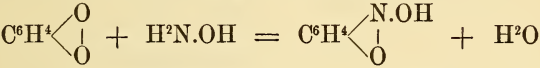


$$C^6H^4\left<\begin{array}{l}NH^2\\ OH\end{array}\right.$$



Nitrosophenol, or Quinonemonoxime, $C^6H^4\left<\begin{array}{l}N.OH\\ \mid\\ O\end{array}\right.$.—By the action of potassium nitrite and acetic acid, phenol is converted into nitrosophenol.

This compound is also formed by the action of hydroxylamine upon quinone (see page 696), thus:



$$C^6H^4\left<\begin{array}{l}O\\ \mid\\ O\end{array}\right. + H^2N.OH = C^6H^4\left<\begin{array}{l}N.OH\\ \mid\\ O\end{array}\right. + H^2O$$

Nitrosophenol crystallizes from hot aqueous solutions in fine, colorless needles. It dissolves in water, alcohol, and ether, forming pale-green solutions. It becomes brown on exposure to the air, and explodes when heated to 110–120°.

Trinitrophenol, or Picric Acid, $C^6H^2(NO^2)^3.OH$.—When phenol is boiled with concentrated nitric acid, it is converted into trinitrophenol.

$$C^6H^5.OH + 3HNO^3 = 3H^2O + C^6H^2(NO^2)^3.OH$$

This body has long been known, and is generally called *picric acid.* It deposits from boiling water in lemon-yellow, crystalline plates, only slightly soluble in cold water. Its taste is very bitter. It has acid properties, the three groups NO^2 seeming to increase the basic nature of the hydrogen atom of the group OH. With bases it forms crystallizable salts which detonate with violence when heated.

Potassium picrate, $C^6H^2(NO^2)^3.OK$, crystallizes in long, yellow needles, soluble in 14 parts of boiling water and in 250 parts at 15°. It explodes violently when heated or struck.

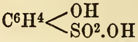
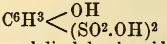
Picramic Acid.—When a current of hydrogen sulphide is passed through an alcoholic solution of picric acid saturated with ammonia, sulphur separates and the picric acid is converted into *picramic acid* (A. Girard).

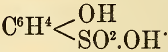
$$\underset{\text{Picric acid.}}{C^6H^2(NO^2)^3.OH} + 3H^2S = 2H^2O + S^3 + \underset{\text{Picramic acid.}}{C^6H^2(NO^2)^2(NH^2)OH}$$

The hydrogen sulphide partially reduces the picric acid, and one of the three groups (NO^2) is thus converted into a group (NH^2). Picramic acid is dinitro-amido-phenol, that is, phenol in which two atoms of hydrogen are replaced by two groups (NO^2), and a third atom of hydrogen by the group NH^2.

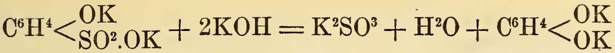
When acetic acid is added to a hot aqueous solution of the ammonium salt of picramic acid, the picramic acid is deposited in fine red needles, which melt at 170°.

Phenol-sulphonic Acids.—These bodies bear the same relation to phenol that benzenesulphonic acid bears to benzene.

C^6H^6 Benzene.	$C^6H^5.OH$ Phenol.
$C^6H^5\text{–}SO^2.OH$ Benzenesulphonic acid.	 $C^6H^4<\begin{matrix}OH\\SO^2.OH\end{matrix}$ Phenol-sulphonic acids.
	 $C^6H^3<\begin{matrix}OH\\(SO^2.OH)^2\end{matrix}$ Phenol-disulphonic acids.



Phenol-sulphonic Acids, $C^6H^4<\begin{matrix}OH\\SO^2.OH\end{matrix}$.—The three isomeric phenol-sulphonic acids are known. The ortho- and para-compounds are formed when phenol is dissolved in concentrated sulphuric acid. The first is formed in large quantity in the cold, and is readily converted into the para-derivative by heat. The excess of sulphuric acid is separated by neutralizing with chalk, removing the calcium sulphate by filtration, and decomposing the solution of the calcium salts with potassium carbonate. When evaporated, the solution first deposits potassium para-phenolsulphonate in hexagonal plates, and the ortho-phenolsulphonate afterwards crystallizes out in needles, containing two molecules of water. The latter salt is very soluble in water; if heated with an excess of potassium hydrate it is converted into pyrocatechin (page 693).



$$C^6H^4{<}\begin{matrix}OK\\SO^2.OK\end{matrix} + 2KOH = K^2SO^3 + H^2O + C^6H^4{<}\begin{matrix}OK\\OK\end{matrix}$$

Potassium phenolsulphonate of potassium.

Potassium compound of pyrocatechin.

The ortho acid is used as an antiseptic (*aseptol*).

Metaphenolsulphonic acid has also been isolated. It crystallizes in fine needles, containing two molecules of water. When heated with an excess of potassium hydrate it yields resorcinol (page 693).

ANILINE, AMIDOBENZENE, OR PHENYLAMINE.

$$C^6H^7N = C^6H^5.NH^2$$

Aniline was discovered by Unverdorben among the products of the distillation of indigo, and was extracted from coal-tar by Runge. It is now prepared artificially by a process discovered by Zinin. This process consists in converting benzene into nitrobenzene, and subjecting the latter to the action of reducing agents (see nitrobenzene).

Iron and hydrochloric acid are advantageously used to accomplish this reduction on a large scale; in the laboratory tin is generally substituted for the iron.

Aniline is a colorless, mobile, highly-refracting liquid, having a peculiar, unpleasant smell, and an acrid, burning taste. Its density at 0° is 1.036. It boils at 184.8°. When exposed to the air, it becomes brown and is eventually resinified. When pure, it may be solidified by cold, and then fuses at —8°.

Aniline is almost insoluble in water, but mixes in all proportions with alcohol, ether, and the fatty and volatile oils.

It does not restore the blue color to reddened litmus-paper, but nevertheless possesses the character of a base, for it forms well-defined salts with the acids.

Reactions.—1. If a nitrate and sulphuric acid be added to aniline, a red color is produced.

2. If a few drops of aniline be poured into an excess of sulphuric acid, and a small quantity of potassium dichromate be added, a magnificent blue color is developed, which changes to violet on the addition of water.

3. A solution of calcium hypochlorite (chloride of lime) added to aniline produces a beautiful violet tint.

4. When a solution of an aniline salt is heated with cupric chlorate, an intense black color is developed (Ch. Lauth).

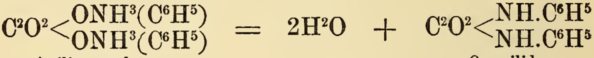
These reactions are applied in the arts in the preparation of coloring matters of wonderful brilliancy. Among the more important of these are *rosaniline* or *magenta*, and *pararosaniline*, which will be described farther on.

5. When aniline is added to a mixture of chloroform and alcoholic potash, and heat is applied, the penetrating and characteristic smell of phenylcarbylamine is noticed.

Salts of Aniline.—These are obtained by saturating aniline by the acids.

Aniline hydrochloride, $C^6H^7N.HCl$, forms colorless needles, which are fusible, and can be distilled without alteration; they are very soluble in water and in alcohol. Platinic chloride precipitates from the solution fine yellow needles of a chloro-platinate, $(C^6H^7N.HCl)^2PtCl^4$.

Aniline oxalate, $(C^6H^7N)^2C^2H^2O^4$, crystallizes from water in hard, thick prisms. When heated, it loses the elements of water, and is converted into oxanilide.

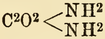


$$C^2O^2{<}\begin{matrix}ONH^3(C^6H^5)\\ONH^3(C^6H^5)\end{matrix} = 2H^2O + C^2O^2{<}\begin{matrix}NH.C^6H^5\\NH.C^6H^5\end{matrix}$$

Aniline oxalate. Oxanilide.

ANILIDES.

By the action of heat, the aniline salts lose the elements of water, and form compounds which are analogous to the acid amides, and which Gerhardt named *anilides*. When aniline acetate is heated, it is converted into acetanilide, which is no other than acetamide in which an atom of hydrogen is replaced by a phenyl group, (C^6H^5).



$$C^2O^2{<}\begin{matrix}NH^2\\NH^2\end{matrix}$$

Oxamide.

$$C^2O^2{<}\begin{matrix}NH.C^6H^5\\NH.C^6H^5\end{matrix}$$

Phenyl oxamide (oxanilide).

$C^2H^3O.NH^2$

Acetamide.

$C^2H^3O.NH(C^6H^5)$

Phenylacetamide (acetanilide).

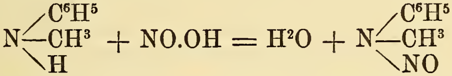
Acetanilide is readily obtained by boiling equi-molecular quantities of aniline and glacial acetic acid. It may be purified by crystallization in boiling water.

It melts at 114°, is readily soluble in hot water and in alcohol. Under the name of *antifebrin*, it is used in medicine as an antipyretic.

ALKYL DERIVATIVES OF ANILINE.

The alcoholic radicals may be substituted for one or both of the hydrogen atoms related to the nitrogen in aniline, thus forming secondary and tertiary amines. Among these we will only consider methyl-aniline and dimethyl-aniline, which are obtained in the arts by heating to 220° a mixture of aniline, aniline hydrochloride, and wood-spirit. The product contains the hydrochlorides of the methyl-anilines.

Methyl-Aniline, $C^6H^5{-}NH(CH^3)$, is a colorless liquid, which gradually becomes brown. Its density at 15° is 0.976, and it boils at 190–191°. By the action of nitrous acid on methyl-aniline, or, better, by the addition of methyl-aniline hydrochloride to a solution of potassium nitrite, a thick oil, *nitrosomethylaniline*, is obtained.

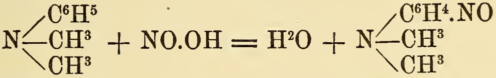


$$N\begin{array}{l}\diagup C^6H^5\\ {-}CH^3\\ \diagdown H\end{array} + NO.OH = H^2O + N\begin{array}{l}\diagup C^6H^5\\ {-}CH^3\\ \diagdown NO\end{array}$$

It is methylaniline in which the hydrogen atom of the group NH is replaced by the nitrosyl group, NO.

All of the secondary aromatic amines undergo analogous reactions.

Dimethyl-aniline, $C^6H^5{-}N(CH^3)^2$, is an oily liquid, boiling at 192°, and solidifying at 5°. Its density is 0.945. When it is submitted to the action of nitrous acid, the phenyl group is attacked.



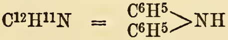
$$N\begin{array}{l}\diagup C^6H^5\\ {-}CH^3\\ \diagdown CH^3\end{array} + NO.OH = H^2O + N\begin{array}{l}\diagup C^6H^4.NO\\ {-}CH^3\\ \diagdown CH^3\end{array}$$

Dimethyl-aniline. Nitrosodimethylaniline.

Nitrosodimethylaniline, produced by this reaction, crystallizes in green plates. It may be obtained by treating dimethyl-aniline hydrochloride with ethyl nitrite or amyl nitrite.

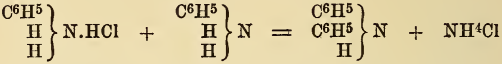
A number of valuable dyes, *malachite green*, for example, are derived from dimethyl-aniline.

DIPHENYLAMINE.



$$C^{12}H^{11}N = \begin{array}{l}C^6H^5\\C^6H^5\end{array}\!\!>NH$$

This body is derived from ammonia by the substitution of two phenyl groups for two atoms of hydrogen. It is formed in various reactions, of which the most interesting was discovered by Girard and de Laire. It consists in heating aniline hydrochloride to 256° with aniline. Ammonia is disengaged, and diphenylamine hydrochloride is formed.



$$\left.\begin{matrix}C^6H^5\\H\\H\end{matrix}\right\}N.HCl + \left.\begin{matrix}C^6H^5\\H\\H\end{matrix}\right\}N = \left.\begin{matrix}C^6H^5\\C^6H^5\\H\end{matrix}\right\}N + NH^4Cl$$

Free diphenylamine forms crystals fusible at 54°. It boils at 310°. It is insoluble in water, but dissolves in alcohol, ether, benzene, and petroleum. Its odor recalls that of oil of rose. Its basic character is not very pronounced, for its salts are readily decomposed by water.

When heated with a mixture of oxalic and sulphuric acids, it yields a splendid blue color, soluble in water, and known as *diphenylamine blue* (Girard and de Laire).

When a trace of nitric acid is added to diphenylamine dissolved in strong sulphuric acid, an intense blue color is developed. This is a delicate test for nitric acid.

DIAZOBENZENE COMPOUNDS.

Nitrous acid exerts an energetic action upon aniline and the analogous bases; it is indicated here because it presents a great generality and gives rise to remarkable bodies, discovered by P. Griess, and known as *diazo-compounds.*

When a current of nitrous vapors—generated by the action of nitric acid upon arsenic trioxide—is passed into a saturated solution of an aniline salt, such as the nitrate, crystals of *diazobenzene nitrate* are deposited.

$$\underset{\text{Aniline nitrate.}}{C^6H^7N.HNO^3} + HNO^2 = 2H^2O + \underset{\text{Diazobenzene nitrate.}}{C^6H^5N^2.NO^3}$$

This body is formed by the substitution of one atom of nitrogen for three atoms of hydrogen in aniline nitrate.

$C^6H^5\text{–}NH^2.HNO^3$ aniline nitrate.
$C^6H^5\text{–}N{=}N\text{–}(NO^3)$ diazobenzene nitrate.

It forms long, colorless prisms, very soluble in water, slightly soluble in alcohol, and insoluble in ether. It explodes violently by heat or by percussion.

Besides this nitrate, there are other compounds of diazobenzene. They all contain the diatomic group $N{=}N$, combined on one hand with phenyl, and on the other with chlorine, bromine, or an oxidized group. The following formulæ will explain their constitutions:

$C^6H^5\text{–}N{=}N.Cl$	diazobenzene chloride.
$C^6H^5\text{–}N{=}N.Br$	diazobenzene bromide.
$C^6H^5\text{–}N{=}N.NO^3$	diazobenzene nitrate.
$C^6H^5\text{–}N{=}N.SO^4H$	diazobenzene sulphate.

These compounds present several interesting reactions.

1. When heated with water, they disengage nitrogen, and are converted into phenols.

$$C^6H^5N^2.NO^3 + H^2O = C^6H^5.OH + N^2 + HNO^3$$

2. When they are boiled with absolute alcohol, they are reduced to hydrocarbons, nitrogen being disengaged and the alcohol being transformed into aldehyde.

$$\underset{\text{Diazobenzene sulphate.}}{C^6H^5N^2.HSO^4} + C^2H^6O = \underset{\text{Aldehyde.}}{C^2H^4O} + \underset{\text{Benzene.}}{C^6H^6} + N^2 + H^2SO^4$$

3. When warmed with cuprous salts, diazo-compounds give off nitrogen gas and are converted into substitution products of benzene.

$$C^6H^5\text{–}N{=}N.Br = C^6H^5.Br + N^2$$

It is thus possible to replace the NH^2 group in aromatic compounds by the halogens or cyanogen. This is known as *Sandmeyer's reaction.*

4. With auric and platinic chlorides, diazobenzene chloride forms double salts. When the platino-chloride is submitted to dry distillation, it yields chlorobenzene.

$$(C^6H^5.N^2.Cl)^2PtCl^4 = 2C^6H^5Cl + N^2 + 2Cl^2 + Pt$$

5. Diazobenzene bromide can fix two atoms of bromine, and the bromide so formed yields, on dry distillation, nitrogen, bromine, and bromobenzene.

$$C^6H^5.N^2Br^3 = C^6H^5Br + Br^2 + N^2$$

A very convenient method of *diazotizing* aromatic amines consists in acidifying a mixture of their salts and sodium nitrite (V. Meyer and Ambuhl). It is unnecessary to isolate the compounds from the resulting solution in order to bring about the above reactions, which support the view already presented of the constitution of diazo-compounds.

Diazoamidobenzene.—When aniline is added to an aqueous solution of diazobenzene nitrate or chloride, a diazo-compound is obtained which is more complex than the preceding and is called *diazoamidobenzene.*

$$\mathrm{C^6H^5N^2(NO^3) + NH^2.C^6H^5 = C^6H^5{-}N^2{-}NH.C^6H^5 + HNO^3}$$

Diazobenzene nitrate. Aniline. Diazoamidobenzene.

The same body is formed when a current of nitrogen trioxide is passed into a *cooled alcoholic solution* of aniline. It forms brilliant, golden-yellow scales, fusible at 91°. It explodes at a higher temperature.

If an alcoholic solution of diazoamidobenzene be left to itself, or, better, if it be warmed with a small proportion of aniline hydrochloride, it undergoes a curious transformation, first noticed by Kekulé. The diazo-compound is converted into an azo-derivative, amidazobenzene.

$$\mathrm{C^6H^5{-}N^2{-}NH.C^6H^5} \qquad \mathrm{C^6H^5{-}N^2{-}C^6H^4.NH^2}$$

Diazoamidobenzene. Amidazobenzene.

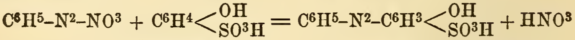
This change shows the difference existing between the azo-derivatives described on page 675, and the diazo-compounds. Both contain the diatomic group $\mathrm{N{=}N}$, but in the former compounds it is related to two aromatic groups, while in the latter it links together an aromatic group, and a monatomic atom or group. This may be understood from the following formulæ:

Azo-derivatives.	Diazo-derivatives.
$\mathrm{C^6H^5{-}N^2{-}C^6H^5}$ Azobenzene.	$\mathrm{C^6H^5{-}N^2.Cl}$ Diazobenzenechloride.
$\mathrm{C^6H^5{-}N^2{-}C^6H^4(NH^2)}$ Amidazobenzene.	$\mathrm{C^6H^5{-}N^2{-}NH(C^6H^5)}$ Diazoamidobenzene.

The salts of diazobenzene react not only with aniline and the other primary and secondary aromatic amines, yielding diazoamidobenzene and its analogues; they undergo analogous reactions with other aromatic compounds, such as the phenols, naphthols, tertiary aromatic amines, metaphenylene-diamine, etc. These reactions invariably form azo-compounds, of which a large number are manufactured and used as dyestuffs. An example is the action of diazobenzene nitrate on phenol, and on its sulpho-derivative, metaphenolsulphonic acid (page 683).

$$\mathrm{C^6H^5{-}N^2{-}NO^3 + C^6H^5.OH = C^6H^5{-}N^2{-}C^6H^4.OH + HNO^3}$$

Diazobenzenenitrate. Phenol. Azobenzene-phenol.



$$\mathrm{C^6H^5{-}N^2{-}NO^3 + C^6H^4{<}\begin{matrix}OH\\SO^3H\end{matrix} = C^6H^5{-}N^2{-}C^6H^3{<}\begin{matrix}OH\\SO^3H\end{matrix} + HNO^3}$$

Metaphenolsulphonic acid. Azobenzene-phenolsulphonic acid.

The last compound is the sulphonic acid of azobenzenephenol, and is one of that class of dye-stuffs known as tropæolines.

These compounds have acquired great importance from their applications in dyeing. That they are numerous may be understood if it be considered that all aromatic compounds containing the group NH^2 may be converted into diazo- and azo-compounds by the methods which have just been indicated.

ROSANILINE AND ITS DERIVATIVES.

$C^{20}H^{21}N^3O$

The magnificent red coloring matter known as magenta is the chloride of rosaniline: it is obtained by oxidizing a mixture of aniline and ortho- and para-toluidine by means of nitrobenzene or arsenic acid. A mixture of equal molecular proportions of the three bases, with enough hydrochloric acid to saturate two-thirds, and nitrobenzene, is heated to 190°, while small quantities of iron are introduced. With the aid of a current of steam the excess of nitrobenzene, as well as the unchanged part of the bases, is expelled from the product, and the residue is dissolved in water. Upon addition of salt and hydrochloric acid, rosaniline chloride separates out; by recrystallization it is obtained in magnificent crystals which present a green reflection, like the scales of cantharides, and dissolve in alcohol with a rich purple color.

The formation of rosaniline is represented by the following equation:

$$\underset{\text{Aniline.}}{C^6H^7N} + \underset{\text{Toluidine.}}{2C^7H^9N} + O^3 = \underset{\text{Rosaniline.}}{C^{20}H^{21}N^3O} + 2H^2O$$

More recently rosaniline has been manufactured synthetically by heating paranitrobenzoic aldehyde, $(CHO)C^6H^4\text{–}NO^2$, with aniline and sulphuric acid.

Properties of Rosaniline.—The methods of preparation just indicated furnish the salts of rosaniline, such as the chloride, which is the rich red coloring matter known as *magenta* or *fuchsine.* The free base is obtained by treating a hot, saturated solution of the chloride with an excess of soda. The rosaniline separates as an almost colorless, crystalline precipitate. It is a triacid base which requires three molecules of hydrochloric acid for its saturation.

The monochloride of rosaniline, $C^{20}H^{20}N^3Cl$ (magenta), forms dark-colored, rhombic tables, having a splendid green reflection. It is but slightly soluble in water, but dissolves readily in alcohol, forming an intense purple solution.

The trihydrochloride, $C^{20}H^{19}N^3.3HCl$, forms yellow-brown needles which lose hydrochloric acid when heated or when dissolved in water.

Rosaniline and its salts present two important reactions:

1. When a salt of rosaniline is treated with reducing agents, such as nascent hydrogen (zinc and hydrochloric acid), the base fixes two atoms of hydrogen and is converted into *leuco-rosaniline*, $C^{20}H^{21}N^3$, a white powder slightly soluble in water.

2. By the action of nitrogen trioxide, rosaniline is converted into a diazo-derivative which yields rosolic acid when boiled with water (pages 687 and 692) and diphenyltolyl methane,

$CH\begin{cases}(C^6H^5)^2\\ C^6H^4\text{–}CH^3\end{cases}$, when heated with alcohol.

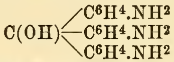
Commercial magenta is not a pure salt of rosaniline. Besides certain isomerides of this base, it contains considerable quantities of pararosaniline, $C^{19}H^{19}N^3O$, of which rosaniline is the next higher homologue. Our knowledge of these bases and their chemical composition is chiefly due to Hofmann, but it is to the researches of E. and O. Fischer that we are indebted for the true explanation of their constitution.

These chemists have shown that pararosaniline and rosaniline must be regarded as derivatives of triphenylmethane, $CH(C^6H^5)^3$, and diphenyl-tolylmethane,

$CH\begin{cases}(C^6H^5)^2\\ C^6H^4.CH^3\end{cases}$.

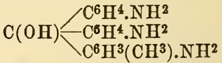
Upon treatment with strong nitric acid, these hydrocarbons yield substitution products in which the three hydrogen atoms occupying the para-positions to the CH group are replaced by the nitro-group, and the nitro-compounds are converted by reduction into the corresponding amido-derivatives. The latter are *leuco-pararosaniline* and *leuco-rosaniline;* upon oxidation, they give para-rosaniline and rosaniline.

The constitution of these bases is expressed by the formulæ



$$C(OH)\begin{cases}C^6H^4.NH^2\\ C^6H^4.NH^2\\ C^6H^4.NH^2\end{cases}$$

Pararosaniline or triamido-triphenylcarbinol.



$$C(OH)\begin{cases}C^6H^4.NH^2\\ C^6H^4.NH^2\\ C^6H^3(CH^3).NH^2\end{cases}$$

Rosaniline or triamido-diphenyl-tolylcarbinol.

By subjecting the corresponding leucanilines to the action of nitrous anhydride, and reducing the diazo-compounds thus formed by alcohol, the same chemists also obtained the hydrocarbons $C^{20}H^{18}$ and $C^{19}H^{16}$.

Coloring Matters derived from Rosaniline.—When rosaniline is heated with ethyl iodide, three atoms of hydrogen are replaced by three ethyl groups, and this *triethyl-rosaniline* yields with the acids a magnificent violet color, known as Hofmann's violet.

Triphenyl-rosaniline, in which three atoms of hydrogen are replaced by three phenyl groups, C^6H^5, is formed when rosaniline is heated with an excess of aniline. This reaction, in which ammonia is disengaged, was discovered by Girard and de Laire.

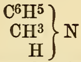
$$\underset{\text{Rosaniline.}}{C^{20}H^{21}N^3O} + \underset{\text{Aniline.}}{3C^6H^5.NH^2} = \underset{\text{Triphenyl-rosaniline.}}{C^{20}H^{18}(C^6H^5)^3N^3O} + 3NH^3$$

The hydrochloride of triphenyl-rosaniline is of a magnificent blue color, and is known as *aniline blue* or *Lyons blue* (Ch. Girard and de Laire). The following formulæ show the interesting relations which exist between rosaniline and its ethyl and phenyl derivatives:

$$\underset{\text{Rosaniline.}}{C^{20}H^{21}N^3O} \qquad \underset{\substack{\text{Triethyl-rosaniline.}\\ \text{(Base of Hofmann's violet.)}}}{C^{20}H^{18}(C^2H^5)^3N^3O} \qquad \underset{\substack{\text{Triphenyl-rosaniline.}\\ \text{(Base of Lyons blue.)}}}{C^{20}H^{18}(C^6H^5)^3N^3O}$$

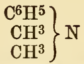
We may mention among the derivatives of rosaniline *Paris violet* and the aniline greens, particularly the beautiful coloring matter known as *night-green*, because it retains its rich green tint in artificial light.

Paris violet, first manufactured by Poirrier, is a splendid color, produced by the oxidation of methylaniline or dimethylaniline.



$$\left.\begin{matrix}C^6H^5\\ CH^3\\ H\end{matrix}\right\}N$$

Methylaniline.



$$\left.\begin{matrix}C^6H^5\\ CH^3\\ CH^3\end{matrix}\right\}N$$

Dimethylaniline.

Ch. Lauth realizes this oxidation, or rather dehydrogenation, by heating methylaniline with cupric chloride. The reaction is complex, and, according to Hofmann and Martius, gives rise to trimethyl-rosaniline.

When heated with methyl chloride, the base of Paris violet fixes two molecules of that compound, forming a combination of trimethyl-rosaniline and methyl chloride. This combination constitutes night-green.

$$C^{20}H^{16}(CH^3)^3N^3.(CH^3Cl)^2$$

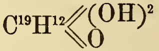
Dichloromethylate of trimethyl-rosaniline (night-green).

ROSOLIC ACIDS.

To the rosanilines which have been described correspond derivatives containing hydroxyl, and which have been named rosolic acids. They contain two hydroxyl groups, substituted for two groups NH^2 of the rosanilines, and an atom of oxygen which replaces the remaining NH^2 group and the group OH.

$C^{19}H^{12}(NH^2)^3.OH$

Pararosaniline.

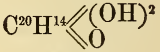


$C^{19}H^{12}\begin{cases}(OH)^2\\ O\end{cases}$

Aurin.

$C^{20}H^{14}(NH^2)^3.OH$

Rosaniline.



$C^{20}H^{14}\begin{cases}(OH)^2\\ O\end{cases}$

Rosolic acid.

AURIN AND ROSOLIC ACID.

$C^{19}H^{14}O^3$ $C^{20}H^{16}O^3$

When 1½ part of phenol is heated with 1 part of oxalic acid and 2 parts of sulphuric acid, it is converted into a coloring-matter, which was first described under the name rosolic acid, or coralline-yellow. The same body or analogous bodies may be obtained by means of the rosanilines (see farther on). Indeed, it has been recognized that there are several homologous bodies having the properties and the constitution of rosolic acid.

Rosolic acid made from pure phenol contains $C^{19}H^{14}O^3$, and is called *aurin* (Dale and Schorlemmer). It occurs in very brilliant, red, triclinic prisms having a blue or green reflection. Rosolic acid proper is a methyl derivative of aurin.

Aurin was formerly used in dyeing. When it is heated to 180° with an alcoholic solution of ammonia, it is converted into a bright-red coloring matter, noticed by Persoz, and employed in dyeing under the name *coralline-red.*

DIOXYBENZENES.

$C^6H^4(OH)^2$

Three isomeric bodies having the composition $C^6H^6O^2 = C^6H^4<\begin{matrix}OH\\ OH\end{matrix}$ are known; they are derived from benzene by the substitution of two hydroxyl groups for two atoms of hydrogen. These three bodies are pyrocatechin, resorcinol, and hydroquinone.

Pyrocatechin, or Catechol, $C^6H^4<\begin{smallmatrix}OH(^1)\\OH(^2)\end{smallmatrix}$, is so named because it was first obtained by the destructive distillation of catechu. It is also produced by the distillation of gum kino and various tannins which produce a green color with ferric salts. It is generally prepared by conducting hydriodic acid gas into *guaiacol*, $C^6H^4(OH)(OCH^3)$, heated to 195°. Pyrocatechin is a solid body, very soluble in water and alcohol, very slightly soluble in ether; it crystallizes from its aqueous solution in rectangular prisms, belonging to the orthorhombic system. It melts at 104°, and sublimes below that temperature in brilliant, colorless plates. It boils between 240 and 245°. Its odor is strong and excites sneezing. It has the character of an acid, like phenol itself. It dissolves in the alkalies and in the alkaline carbonates. When exposed to the air, these solutions become colored, first green, then brown and black. An aqueous solution of pyrocatechin produces a deep-green color with ferric chloride, which changes to dark-red on the addition of an alkali. This reaction characterizes the ortho-dihydric phenols.

Resorcinol, $C^6H^4<\begin{smallmatrix}OH(^1)\\OH(^3)\end{smallmatrix}$, which is the homologue of orcinol, $C^7H^8O^2$, is formed when certain gums, such as galbanum, asafœtida, gum ammoniac, sagapenum, etc., are fused with potassium hydrate (Hlasiwetz and Barth). It is manufactured on a large scale by fusing benzene meta-disulphonic acid with caustic potash.

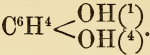
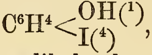
$$C^6H^4<\begin{smallmatrix}SO^3K\\SO^3K\end{smallmatrix} + 2KOH = C^6H^4<\begin{smallmatrix}OH\\OH\end{smallmatrix} + 2K^2SO^3$$

The fused mass is dissolved in water, supersaturated with sulphuric acid, filtered, and the filtered solution shaken with ether, which dissolves the resorcinol. After having driven off the ether on a water-bath, a residue is obtained which is distilled: the resorcinol sublimes and condenses in radiated crystals.

Resorcinol is also obtained from many other di-substituted benzenes—ortho- and para- as well as meta-derivatives—by fusion with alkaline hydroxides.

Resorcinol forms colorless, prismatic or tabular crystals. It melts at 110°, and boils at 276°. It is very soluble in water, alcohol, and ether, but insoluble in chloroform. With ferric chloride its aqueous solution gives a violet color.

Like other meta-dihydric phenols it yields a *fluoresceïn* with phthalic anhydride. When a mixture of resorcinol and the anhydride is strongly heated, and the residual mass is dissolved in dilute alkali, a brownish solution exhibiting green fluorescence results.

Hydroquinone,  $C^6H^4 < {OH(^1) \atop OH(^4)}$.—This body is formed when para-iodophenol,  $C^6H^4 < {OH(^1) \atop I(^4)}$, is fused with potassium hydroxide, or more readily by the action of reducing agents, such as sulphur dioxide, on quinone.

$$C^6H^4O^2 + H^2 = C^6H^6O^2$$

Wöhler, who discovered it, found it also among the products of the dry distillation of quinic acid.

Hydroquinone crystallizes in beautiful, transparent, and colorless, hexagonal prisms. It has no odor; its taste is sweetish. It dissolves in 17 parts of water at 15°, and is very soluble in alcohol and ether. It melts at 169°, and solidifies at 165°. When gently heated, it sublimes in brilliant plates, like those of sublimed benzoic acid. It partially decomposes when abruptly heated. When its vapor is passed through a tube heated to dull redness, it breaks up into quinone and hydrogen. Various oxidizing agents, such as chlorine, ferric chloride, nitric acid, and potassium dichromate, transform it into a substance which deposits in magnificent green needles having a metallic reflection. It is *quinhydrone*, $C^{12}H^{10}O^4$, a combination of quinone and hydroquinone.

Hydroquinone is used as a developer in photography.

QUINONE.

$C^6H^4O^2$

This remarkable body, discovered by Woskresensky, is a product of the oxidation of quinic acid, which exists in cinchona bark. It may be obtained by distilling that acid with a mixture of manganese dioxide and sulphuric acid. The mass swells up and disengages vapors of quinone, which condense in the receiver in brilliant, golden-yellow needles. They are pressed between folds of filter-paper and purified by resublimation.

It is also formed when various para disubstituted benzenes, such as phenylene-diamine, amidophenol, phenolsulphonic acid, etc., are treated with oxidizing agents. The best method of preparation consists in adding a concentrated solution of sodium dichromate (3 parts) to a well-cooled mixture of aniline (1 part), water (25 parts), and sulphuric acid (8 parts). The dark-colored liquid is extracted with ether, the latter evaporated, and the product crystallized from petroleum ether.

Quinone crystallizes in long, brilliant, transparent needles of a golden-yellow color. It is very soluble in cold water, and more soluble in alcohol and ether. It melts at 115.7° to a yellow liquid. Quinone sublimes at ordinary temperatures, emitting pungent vapors which excite tears.

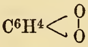
Chlorine converts it into a trichloro-derivative, $C^6HCl^3O^2$, crystallizable in small, yellow prisms, fusible at 164–166°.

When treated with a mixture of potassium chlorate and hydrochloric acid, quinone is converted into tetrachloroquinone, $C^6Cl^4O^2$, better known as *chloranile*. This name was given by Erdmann, who first obtained this body by the action of chlorine on indigo, of which the Portuguese name is *anil*. The same body is formed by the action of a mixture of potassium chlorate and hydrochloric acid on a great number of aromatic compounds, such as phenol, picric acid, salicylic acid, salicin, isatine, etc. Tetrachloroquinone forms pale-yellow scales, having a pearly, metallic lustre. When gently heated, it sublimes without fusing, and leaves no residue. It is insoluble in water and almost insoluble in cold alcohol, but dissolves in boiling alcohol and separates on cooling in golden-yellow scales.

Constitution of Quinone and Hydroquinone.—According to Graebe, these bodies are allied to benzene, from which the first is derived by the substitution of two atoms of oxygen for two atoms of hydrogen; but as the two atoms of oxygen represent four atomicities, of which two only are employed in replacing H^2 in benzene, the other two serve to bind together the two atoms of oxygen. The couple $(O''-O'')''$ can indeed play the part of a diatomic group. In the formation of hydroquinone, these atoms of oxygen separate from each other and each fixes one atom of hydrogen, so that two hydroxyl groups are formed and substituted each for one atom of hydrogen in benzene. The following formulæ express these relations:

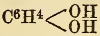
C^6H^6

Benzene.



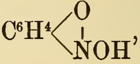
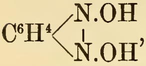
$$C^6H^4 < \begin{matrix} O \\ | \\ O \end{matrix}$$

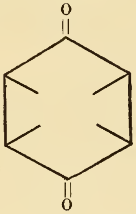
Quinone.

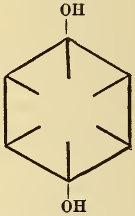


$$C^6H^4 < \begin{matrix} OH \\ OH \end{matrix}$$

Hydroquinone.

In certain respects, however, quinone resembles the diketones. The observation that upon treatment with hydroxylamine both a monoxime,  $C^6H^4\left\langle\begin{matrix}O\\ |\\ NOH\end{matrix}\right.$, and a dioxime,  $C^6H^4\left\langle\begin{matrix}N.OH\\ |\\ N.OH\end{matrix}\right.$, are produced, is perhaps best explained by the following centric formula, which also satisfactorily exposes the relation between quinone and hydroquinone.





PHLOROGLUCINOL.

$$C^6H^6O^3 = C^6H^3(OH)^3$$

Phloroglucinol and its isomeride pyrogallol are trioxybenzenes; they represent benzene in which three atoms of hydrogen are replaced by three hydroxyl groups. The relations between phloroglucinol, dioxybenzene, and phenol are the same as those between glycerol, propylene glycol, and propyl alcohol.

$C^3H^7.OH$	$C^3H^6\left\{\begin{matrix}OH\\ OH\end{matrix}\right.$	$C^3H^5\left\{\begin{matrix}OH\\ OH\\ OH\end{matrix}\right.$
Propyl alcohol.	Propylglycol.	Glycerol.
$C^6H^5.OH$	$C^6H^4\left\{\begin{matrix}OH\\ OH\end{matrix}\right.$	$C^6H^3\left\{\begin{matrix}OH\\ OH\\ OH\end{matrix}\right.$
Phenol.	Dioxybenzene.	Phloroglucinol.

Phloroglucinol was discovered by Hlasiwetz, who obtained it by heating phloretin (page 659) with a very concentrated solution of potash. It is also formed in many other reactions, especially when resorcinol, gum-kino, gamboge, and dragon's-blood are fused with potassium hydroxide.

Phloroglucinol crystallizes in hard, rhombic prisms, having a very sweet taste. It is quite soluble in water, alcohol, and ether. Its aqueous solution is neutral, and produces a deep-violet color with ferric chloride. Its ethereal solution, evaporated upon a microscope-slide, deposits prisms in tangled, tree-like forms which are very characteristic.

The crystals deposited from ether are anhydrous, while those formed in water contain two molecules of water of crystallization, which they lose at 100°. The dry crystals melt at 220°.

The chemical character of phloroglucinol is very curious. While in many respects it behaves like a trihydric phenol,—it forms salts with the alkalies and a triacetate with acetyl chloride,—it is also capable of reacting like a triketone: with hydroxylamine, for example, it yields the trioxime $C^6H^6(N\text{–}OH)^3$. Bodies which react as if they belonged to two distinct chemical classes are said to be *tautomeric.*

Phenols containing more than three hydroxyl groups have been obtained. The potassium compound of hexoxybenzene, $C^6(OK)^6$, constitutes the explosive potassium carbonyl (page 297).

TOLUENE AND ITS DERIVATIVES.

TOLUENE.

$$C^7H^8 = C^6H^5\text{–}CH^3$$

Toluene is a homologue of benzene. It was discovered in 1837 by Pelletier and Walter; H. Deville obtained it by distilling balsam of Tolu; hence its name. It exists in coal-tar, and is separated from that body, like benzene, by fractional distillation. It is *methyl-benzene*, or *phenylmethane*, and has been obtained by synthesis by heating a mixture of methyl iodide and monobromobenzene with sodium (Fittig and Tollens).

$$\underbrace{C^6H^5Br}_{\text{Monobromobenzene.}} + CH^3I + 2Na = NaI + NaBr + \underbrace{C^6H^5\text{–}CH^3}_{\text{Methyl-phenyl.}}$$

A method of synthesis of toluene, which by the generality of its applications is one of the most fecund in chemistry, is due to Friedel and Crafts. It consists in the reaction of methyl chloride on benzene in presence of aluminium chloride. Toluene is formed, and hydrochloric acid is disengaged.

It is probable that the aluminium chloride first acts on the benzene, disengaging hydrochloric acid and forming a phenyl derivative of aluminium chloride, which derivative is continually formed and continually decomposed by the methyl chloride. The cycle of reactions would then be represented by the following two equations:

$$C^6H^6 + Al^2Cl^6 = Al^2Cl^5(C^6H^5) + HCl$$
$$Al^2Cl^5(C^6H^5) + CH^3Cl = C^6H^5(CH^3) + Al^2Cl^6$$

We may add that the toluene thus formed may react with an excess of methyl chloride, forming hydrochloric acid and dimethyl benzene (xylene), which in its turn may react upon an excess of methyl chloride. It is thus seen that the methylation of benzene does not stop with the first substitution compound, and that the nature of the products formed depends upon the proportions of the bodies which react. Friedel and Crafts thus succeeded in introducing six methyl groups into benzene, and made the synthesis of hexamethylbenzene.

$$C^6H^6 + 6CH^3Cl = 6HCl + \underset{\text{Hexamethylbenzene.}}{C^6(CH^3)^6}$$

Properties of Toluene.—Toluene is a colorless liquid, insoluble in water. Its density at 0° is 0.882, and it boils at 111°.

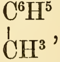
When it is boiled with dilute nitric acid or a solution of chromic acid, it is transformed into benzoic acid.

$$\underset{\text{Toluene.}}{C^6H^5\text{–}CH^3} + O^3 = \underset{\text{Benzoic acid.}}{C^6H^5\text{–}CO.OH} + H^2O$$

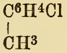
As is indicated, the methyl group is attacked and converted into carboxyl, CO.OH.

SUBSTITUTION PRODUCTS OF TOLUENE.

These compounds are numerous, and present various isomerisms, of which we will consider the principles.

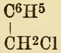
When chlorine acts upon toluene,  $\begin{matrix}C^6H^5\\|\\CH^3\end{matrix}$, one or more atoms of hydrogen may be removed and replaced by as many atoms of chlorine. The most simple of the products thus formed is the compound C^7H^7Cl, which results from the substitution of one atom of chlorine for one atom of hydrogen in toluene, C^7H^8. But this substitution may take place in the benzene nucleus

C^6H^5, or in the group CH^3, and two isomeric bodies are thus formed, monochlorotoluene and benzyl chloride.



$$\begin{array}{l} C^6H^4Cl \\ | \\ CH^3 \end{array}$$

Monochlorotoluene.



$$\begin{array}{l} C^6H^5 \\ | \\ CH^2Cl \end{array}$$

Benzyl chloride.

Monochlorotoluene, $C^2H^4 < \begin{matrix} CH^3 \\ Cl \end{matrix}$, is a di-substituted derivative of benzene; it may consequently exist in three isomeric modifications, as has already been explained (page 670).

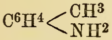
It is thus seen that there are four different bodies derived from toluene by the substitution of one atom of chlorine for one of hydrogen, namely, benzyl chloride and three monochlorotoluenes.

The following table includes a number of toluene derivatives:

$\begin{array}{l} C^6H^4Cl \\ \vert \\ CH^3 \end{array}$ Monochlorotoluene.	$\begin{array}{l} C^6H^4(NH^2) \\ \vert \\ CH^3 \end{array}$ Toluidine.	$\begin{array}{l} C^6H^4(OH) \\ \vert \\ CH^3 \end{array}$ Cresol.		$\begin{array}{l} C^6H^4(OH) \\ \vert \\ CHO \end{array}$ Salicyl aldehyde.	$\begin{array}{l} C^6H^4(OH) \\ \vert \\ CO.OH \end{array}$ Salicylic acid.
$\begin{array}{l} C^6H^5 \\ \vert \\ CH^2Cl \end{array}$ Benzyl chloride.	$\begin{array}{l} C^6H^5 \\ \vert \\ CH^2(NH^2) \end{array}$ Benzylamine.	$\begin{array}{l} C^6H^5 \\ \vert \\ CH^2.OH \end{array}$ Benzyl alcohol.	$\begin{array}{l} C^6H^5 \\ \vert \\ CHO \end{array}$ Benzaldehyde.	$\begin{array}{l} C^6H^5 \\ \vert \\ CO.OH \end{array}$ Benzoic acid.	

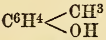
Among these compounds, those placed in the same vertical line present isomerisms easily understood from the formulæ, which express their constitutions and show the atomic groupings.

The bodies in the first horizontal series constitute di-substituted compounds of benzene.



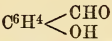
$$C^6H^4 < \begin{matrix} CH^3 \\ NH^2 \end{matrix}$$

Toluidines.



$$C^6H^4 < \begin{matrix} CH^3 \\ OH \end{matrix}$$

Cresols.



$$C^6H^4 < \begin{matrix} CHO \\ OH \end{matrix}$$

Salicyl aldehyde.

$$C^6H^4 < \begin{matrix} CO.OH \\ OH \end{matrix}$$

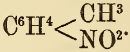
Salicylic acid.

Hence they may exist in three different isomeric modifications, and consequently there are four isomerides of each of these derivatives of toluene, excepting salicylic acid, just as for monochlorotoluene.

Chloro-Derivatives of Toluene.—The *monochlorotoluenes* are formed by the action of chlorine on cold toluene. Ortho- and metachlorotoluene are liquids boiling between 156 and 157°. Parachlorotoluene boils at 160.5°, and below 0° solidifies to a mass which melts at 6.5°.

Benzyl chloride, $C^6H^5\text{–}CH^2Cl$, is formed when chlorine is passed into boiling toluene.

Benzalchloride, $C^6H^5.CHCl^2$, and **Benzotrichloride,** $C^6H^5.CCl^3$, are also formed by the direct action of chlorine on boiling toluene. The former boils at 206° and the latter at 213°. The beautiful green dyestuff, malachite- or aldehyde-green, is formed by the action of zinc chloride on a heated mixture of benzotrichloride and dimethylaniline.

Nitrotoluenes.—Monohydrated nitric acid attacks toluene and converts it into nitrotoluenes, $C^7H^7(NO^2)$, and dinitrotoluenes, according to the duration of the reaction. There are three nitrotoluenes,  $C^6H^4<^{CH^3}_{NO^2}$.

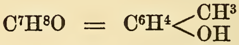
Orthonitrotoluene, fusible at 10.5° to a yellow liquid, which boils at 218°.

Metanitrotoluene, crystals, fusible at 16°. Boils at 230–231°.

Paranitrotoluene, almost colorless prisms, fusible at 54°, and boiling at 230°.

Dinitrotoluene, $C^6H^3(NO^2)^2CH^3$, is formed when toluene is treated with a mixture of nitric and sulphuric acids. Long needles, almost colorless, fusible at 70.5°. An isomeride is known, fusible at 48°.

CRESOLS.



$$C^7H^8O = C^6H^4<^{CH^3}_{OH}$$

There are three cresols, two solid and one liquid. They may be formed artificially by treating toluene with sulphuric acid, according to the process indicated on page 678, but in this reaction several isomeric sulphonic acids are formed, and when decomposed by caustic potash they yield different cresols. The different isomers are best obtained from the corresponding toluidines by means of the diazo-reaction (p. 687).

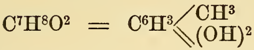
The cresol discovered by Fairlie, and extracted from wood-tar by Duclos, is a colorless liquid, having an odor like that of phenol. It boils at 190°, and appears to be a mixture.

Orthocresol is a crystalline mass, fusible at 31°, and boiling at 185–186°.

Metacresol is a liquid, boiling at 201°.

Paracresol forms colorless prisms, fusible at 36°. It boils at 198° (A. Wurtz).

ORCINOL.



$$C^7H^8O^2 = C^6H^3 \begin{matrix} \diagup CH^3 \\ \diagdown (OH)^2 \end{matrix}$$

This body is an oxycresol. It was discovered by Robiquet in 1829, and is obtained, at the same time as erythritol, by decomposing erythrin by slaked lime at 150°.

The orcinol is deposited first in beautiful crystals from the solution which contains both substances, and it is purified by recrystallization. It forms colorless, hexagonal prisms, containing one molecule of water of crystallization. It melts at 58°, losing its water, and the anhydrous orcinol boils at 290°.

The crystals of orcinol become rose-colored in the air. When ammonia is added to their aqueous solution and the liquid is exposed to the air, it absorbs oxygen and assumes first a violet color and afterwards a brown. A nitrogenized body is formed which is known as *orcein*, and constitutes the coloring principle of the archil of commerce.

The synthesis of orcinol has been made by the action of fused potassium hydroxide on the sulphonic acid of monochlorotoluene (cresyl chloride, $C^6H^4Cl.CH^3$). The chlorine and the group SO^3H of this compound are thus replaced by two groups OH (Vogt and Henninger).

$$\underset{\text{Potassium chlorocresyl-sulphonate.}}{C^6H^3\left\{\begin{matrix} Cl \\ SO^3K \\ CH^3 \end{matrix}\right.} + 2KOH = SO^3K^2 + KCl + \underset{\text{Orcinol.}}{C^6H^3\left\{\begin{matrix} OH \\ OH \\ CH^3 \end{matrix}\right.}$$

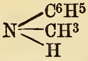
TOLUIDINES.

$$C^7H^9N = C^6H^4(NH^2)\text{-}CH^3$$

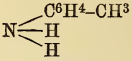
Paratoluidine.—Solid toluidine, which is paratoluidine, was discovered by Hofmann and Muspratt in 1848. They obtained it by the reduction of paranitrotoluene by ammonium hydrosulphide. This reduction may also be accomplished by iron and acetic acid, or by tin and hydrochloric acid.

$$\underset{\text{Nitrotoluene.}}{C^7H^7(NO^2)} + 3H^2 = \underset{\text{Toluidine.}}{C^7H^7(NH^2)} + 2H^2O$$

An interesting method of formation of paratoluidine was discovered by Hofmann and Martius. When methylaniline hydrochloride is heated to 350° under pressure, paratoluidine hydrochloride is formed. The methyl group which is united to the nitrogen of the former base is then transposed and exchanged for an atom of hydrogen of the phenyl group.



Methylaniline.



Toluidine.

Paratoluidine is a solid heavier than water. It crystallizes from its dilute alcoholic solution in large plates. It melts at 45°, and boils at 198°. It is almost insoluble in water, but very soluble in alcohol and in ether.

Toluidine exists nearly always in commercial aniline. It is important and necessary for the preparation of certain aniline colors.

Orthotoluidine was discovered by Rosenstiehl in commercial toluidine, which is a mixture of para- and orthotoluidine. It is formed by the reduction of orthonitrotoluene by nascent hydrogen. It is liquid and does not solidify at —20°. It boils at 199.5°.

Metatoluidine.—A colorless liquid, boiling at 197°. Density at 25°, 0.998.

BENZYL ALCOHOL.

$$C^7H^8O \quad = \quad C^6H^5\text{–}CH^2.OH$$

Benzyl alcohol is readily prepared by the action of potassium hydroxide upon benzaldehyde; one molecule of the aldehyde is oxidized to benzoic acid, while another is reduced to benzyl alcohol.

$$\underset{\text{Benzaldehyde.}}{2C^6H^5.CHO} + KOH = \underset{\text{Potassium benzoate.}}{C^6H^5.COOK} + \underset{\text{Benzyl alcohol.}}{C^6H^5.CH^2.OH}$$

It is also formed by boiling benzyl chloride with soda solution,

$$C^6H^5.CH^2.Cl + H^2O = C^6H^5.CH^2.OH + HCl,$$

and by the action of nascent hydrogen upon benzaldehyde,

$$C^6H^5.CHO + H^2 = C^6H^5.CH^2.OH$$

Benzyl alcohol is a colorless, oily liquid, having a faint but agreeable odor. It boils at 207°. Density at 0°, 1.0628.

When heated with nitric acid, it is converted into benzaldehyde (oil of bitter almonds).

$$C^7H^8O + O = H^2O + C^7H^6O$$

Chromic acid oxidizes it to benzoic acid.

$$C^7H^8O + O^2 = H^2O + C^7H^6O^2$$

The relations between benzyl alcohol, benzaldehyde, and benzoic acid are the same as those between alcohol, aldehyde, and acetic acid.

$CH^3\text{–}CH^2.OH$	alcohol.	$C^6H^5\text{–}CH^2.OH$	benzyl alcohol.
$CH^3\text{–}CHO$	aldehyde.	$C^6H^5\text{–}CHO$	benzaldehyde.
$CH^3\text{–}CO^2H$	acetic acid.	$C^6H^5\text{–}CO^2H$	benzoic acid.

Benzyl Compounds.—*Benzyl chloride*, $C^7H^7Cl = C^6H^5\text{–}CH^2Cl$, is formed, as has already been remarked, when chlorine is passed into boiling toluene. It is also formed by the action of hydrochloric acid on benzyl alcohol by the aid of heat. It is a colorless liquid having an irritating odor. It boils at 176°.

Benzylamine, $C^6H^5\text{–}CH^2.NH^2$.—This body is formed by the action of nascent hydrogen on benzonitrile (phenyl cyanide), which thus fixes four atoms of hydrogen. It is also formed in small quantity, together with dibenzylamine and tribenzylamine, when benzyl chloride is heated with alcoholic ammonia. It is a limpid liquid, boiling at 185°, and miscible with water, alcohol, and ether. Density, 0.99 at 14°.

Tribenzylamine, $(C^6H^5.CH^2)^3N$.—This is formed in abundance by the action of a hot alcoholic solution of ammonia on benzyl chloride. It crystallizes in beautiful, colorless needles or plates, fusible at 91°. It is insoluble in water, slightly soluble in cold alcohol, very soluble in hot alcohol and in ether.

BENZALDEHYDE.

$$C^7H^6O = C^6H^5\text{–}CHO$$

This body, formerly called benzoyl hydride, exists in the essential oil of bitter almonds, mixed with hydrocyanic acid, both substances being formed by the action of emulsin and water on amygdalin (page 658).

Grimaux and Lauth have obtained it by oxidizing benzyl chloride by boiling with nitrate of lead or of copper.

$$C^6H^5\text{–}CH^2Cl + O = HCl + C^6H^5\text{–}CHO$$

Benzaldehyde is a colorless, strongly-refracting liquid, having a pleasant odor and a pungent, aromatic taste. It boils at 179.5°.

When its vapor is passed through a porcelain tube filled with pumice-stone and heated to redness, benzaldehyde breaks up into benzene and carbon monoxide.

$$C^7H^6O = CO + C^6H^6$$

When exposed to air and light, it absorbs oxygen, and is converted into benzoic acid.

$$C^7H^6O + O = \underset{\text{Benzoic acid.}}{C^7H^6O^2}$$

Like the aldehydes of the fatty series, benzaldehyde reduces ammoniacal solutions of silver; it combines with sodium-acid sulphite, and yields characteristic compounds with hydroxylamine and phenylhydrazine.

Benzaldehyde reacts with diamide (hydrazine) readily with elimination of water (Curtius).

$$N^2H^4 + 2C^6H^5.CHO = N^2(C^6H^5.CH)^2 + 2H^2O$$

The resulting *benzalazine* melts at 93°.

Nascent hydrogen, produced by the action of water on sodium amalgam, transforms benzaldehyde into benzyl alcohol (Friedel).

$$C^7H^6O + H^2 = C^7H^7.OH$$

Chlorine converts it into benzoyl chloride.

$$\underset{\text{Benzaldehyde.}}{C^7H^5O.H} + Cl^2 = HCl + \underset{\text{Benzoyl chloride.}}{C^7H^5O.Cl}$$

Benzaldehyde readily undergoes condensation with other carbon compounds, and is therefore much used for synthetical purposes.

Benzoin, $C^6H^5\text{–}CH(OH)\text{–}CO\text{–}C^6H^5$.—When crude oil of bitter almonds containing hydrocyanic acid is mixed with alcoholic caustic potash, or when the pure oil is mixed with an alcoholic solution of potassium cyanide, the benzaldehyde is polymerized and converted into a solid body, which is *benzoin*, $C^{14}H^{12}O^2$. The latter crystallizes in brilliant, colorless prisms, fusible at 133–134°. It is but slightly soluble in water and cold alcohol, very soluble in boiling alcohol. Oxidation converts it into benzil.

Benzil, or Dibenzoyl, $C^6H^5–CO–CO–C^6H^5$, is the aromatic diketone which corresponds to diacetyl. It forms yellow hexagonal prisms, melting at 95°, and soluble in alcohol and ether. Benzil combines directly with hydrocyanic acid and with hydroxylamine. Both the monoxime and the dioxime exist in several stereoisomeric forms.

Benzoyl Chloride, $C^6H^5–COCl$.—This body is formed by the action of phosphorus pentachloride on benzoic acid or a dry benzoate. It is a colorless, highly-refractive liquid, having a peculiar, irritating odor. It boils at 199°. Water decomposes it into benzoic and hydrochloric acids.

$$C^7H^5O.Cl + H^2O = C^7H^5O.OH + HCl$$

Ammonia converts it into benzamide.

$$C^7H^5.OCl + NH^3 = \underset{\text{Benzamide.}}{C^7H^5O.NH^2} + HCl$$

Benzoyl chloride may exchange its chlorine for other elements. When it is distilled with potassium iodide, potassium chloride and benzoyl iodide are formed. Liebig and Wöhler, who discovered these important reactions, prepared in the same manner, by double decomposition, benzoyl sulphide and benzoyl cyanide. These experiments are celebrated; they were the starting-point of the *benzoyl theory*, which marked an important progress in the development of the theory of radicals. The following formulæ indicate the principal benzoyl combinations:

$(C^7H^5O)^2$	dibenzoyl (benzil).
$C^7H^5O.H$	benzoyl hydride (oil of bitter almonds).
$C^7H^5O.Cl$	benzoyl chloride.
$C^7H^5O.I$	benzoyl iodide.
$(C^7H^5O)^2S$	benzoyl sulphide.
$(C^7H^5O)^2O$	benzoyl oxide (benzoic anhydride).
$C^7H^5O.OH$	benzoyl hydroxide (benzoic acid).
$C^7H^5O.NH^2$	benzamide.

BENZOIC ACID.

$$C^7H^6O^2 = C^6H^5–CO^2H$$

Preparation.—This acid may be obtained from gum benzoin. That resin is placed in a flat dish over the top of which a sheet of tissue-paper, or light filter-paper is glued (Fig. 133). This diaphragm forms the base of a paper cone which is then placed over the dish, which is moderately heated on a sand-bath for several hours. At the end of that time, the whole is allowed to cool, and the benzoic acid is found in light, brilliant, crystalline flakes on the sides of the cone, and on the diaphragm.

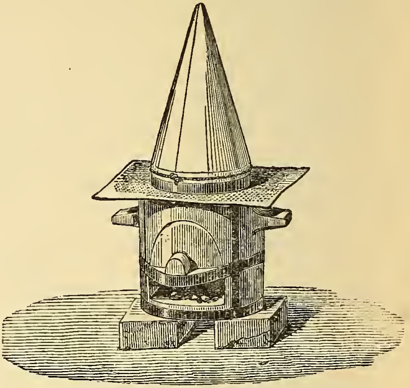


FIG. 133.

The benzoin resin may also be powdered and digested with milk of lime for twenty-four hours; it is then heated to ebullition and filtered. Hydrochloric acid precipitates benzoic acid from the filtered liquid, which contains calcium benzoate.

Benzoic acid is also prepared by boiling the urine of horses and cows with hydrochloric acid. The hippuric acid which these urines contain is thus decomposed into benzoic acid and glycocoll. The benzoic acid crystallizes on cooling, and is purified by sublimation.

On a large scale benzoic acid is now generally obtained by oxidizing toluene or benzyl chloride with nitric acid.

Properties.—Benzoic acid crystallizes in needles, or in thin, brilliant plates. It has an aromatic odor, and a slightly acid taste. It melts at 121°, and boils at 250°.

It dissolves in 607 parts of water at 0°, and in about 12 parts of boiling water. When boiled with a quantity of water insufficient to dissolve it, it melts. It volatilizes with the vapor of water. It dissolves readily in alcohol and in ether. When its vapor is passed over red-hot pumice-stone, contained in a porcelain tube, it is decomposed into carbonic anhydride and benzene.

$$C^7H^6O^2 = CO^2 + C^6H^6$$

When heated with phosphorus pentachloride, it yields benzoyl chloride.

$$C^7H^5O.OH + PCl^5 = POCl^3 + HCl + C^7H^5O.Cl$$

The metallic and ethereal salts of benzoic acid are analogous to those of acetic acid.

Benzamide, $C^6H^5{-}CO.NH^2$.—This body is formed by the action of ammonia gas on benzoyl chloride.

$$C^6H^5CO.Cl + 2NH^3 = NH^4Cl + C^6H^5{-}CO.NH^2$$

It is also formed by the action of ammonia on ethyl benzoate.

$$\underset{\text{Ethyl benzoate.}}{C^6H^5{-}CO.OC^2H^5} + NH^3 = \underset{\text{Alcohol.}}{C^2H^5.OH} + \underset{\text{Benzamide.}}{C^6H^5{-}CO.NH^2}$$

It occurs in brilliant, colorless, oblique rhombic crystals, fusible at 128°, and can be sublimed without decomposition. It is soluble in hot water and in alcohol.

Benzophenone, or Diphenyl-ketone, $C^{13}H^{10}O = C^6H^5{-}CO{-}C^6H^5$.—This body is formed, together with benzene, in the destructive distillation of calcium benzoate (Chancel).

$$\underset{\text{Calcium benzoate.}}{Ca(C^6H^5{-}CO^2)^2} = CaCO^3 + \underset{\text{Diphenyl-ketone.}}{(C^6H^5)^2CO}$$

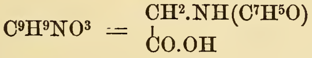
It is also obtained by the action of carbonyl chloride upon benzene in the presence of aluminium chloride (Friedel and Crafts).

$$2C^6H^6 + COCl^2 = 2HCl + (C^6H^5)^2CO$$

It forms large, colorless, or slightly yellow, right rhombic prisms, fusible at 48–49°, and boils at 295°. It is insoluble in water, but very soluble in alcohol.

Acetophenone, or **Methylphenyl-ketone,** $CH^3{-}CO{-}C^6H^5$, melts at 20°, and boils at 202°. It is used in medicine as a soporific under the name *hypnone.*

HIPPURIC ACID.



$$C^9H^9NO^3 = \begin{array}{l} CH^2.NH(C^7H^5O) \\ | \\ CO.OH \end{array}$$

Hippuric acid is an important benzoic derivative. Hydrochloric acid decomposes it into benzoic acid and glycocoll.

$$\underset{\text{Hippuric acid.}}{C^9H^9NO^3} + H^2O = \underset{\text{Glycocoll.}}{C^2H^2NO^5} + \underset{\text{Benzoic acid.}}{C^7H^6O^2}$$

Rouelle, Fourcroy, and Vauquelin discovered this acid in the urine of the horse, but confounded it with benzoic acid. Its true nature was recognized by Liebig in 1830. Dessaignes has made its synthesis by the reaction of benzoyl chloride on the zinc compound of glycocoll.

$$\underset{\text{Glycocoll.}}{C^2H^5NO^2} + \underset{\text{Benzoyl chloride.}}{C^7H^5O.Cl} = \underset{\text{Hippuric acid.}}{C^2H^4(C^7H^5O)NO^2} + HCl$$

Hippuric acid is obtained from the urine of horses and cows by mixing the urine with 2 or 3 times its volume of concentrated hydrochloric acid. The hippuric acid separates in colored crystals.

When properly purified, it crystallizes in long, colorless prisms, but slightly soluble in cold water, very soluble in boiling water and in alcohol. When heated in a retort, it decomposes and yields a sublimate of benzoic acid. At the same time a certain quantity of an oily body having a disagreeable odor distils: it is phenyl cyanide, or benzonitrile, $CN.C^6H^5$.

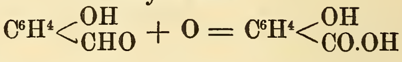
SALICYLALDEHYDE (ORTHOXYBENZALDEHYDE.

$$C^7H^6O^2 = C^6H^4(OH).CHO$$

This compound, which is isomeric with benzoic acid, exists naturally in the essential oil of the meadow-sweet (*Spiræa ulmaria*). Piria obtained it by oxidizing salicin by potassium dichromate and sulphuric acid (page 658).

It is also formed by the action of chloroform on phenol in presence of caustic soda (page 679).

It is a colorless, highly refracting liquid, and boils at 196.5°. Its density at 13.5° is 1.173. Its odor is pleasant and its taste burning. It is quite soluble in water, and dissolves in alcohol and ether in all proportions. It has an acid reaction. It produces a violet color with ferric chloride. Oxidizing agents convert it into salicylic acid.



$$C^6H^4<\begin{matrix}OH\\CHO\end{matrix} + O = C^6H^4<\begin{matrix}OH\\CO.OH\end{matrix}$$

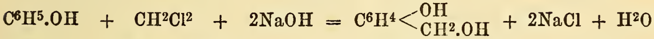
By the action of fused potassium hydroxide, it is likewise transformed into salicylic acid, with disengagement of hydrogen.

$$\underset{\text{Salicyl aldehyde.}}{C^7H^6O^2} + KOH = \underset{\text{Potassium salicylate.}}{KC^7H^5O^3} + H^2$$

Saligeninol.—In presence of sodium amalgam and water, salicyl aldehyde fixes H^2 and is converted into *saligeninol* (Reincke and Beilstein).

$$\underset{\text{Salicyl aldehyde.}}{C^7H^6O^2} + H^2 = \underset{\text{Saligeninol.}}{C^7H^8O^2}$$

The latter body is also formed, according to Piria, by the decomposition of salicin by ferments and acids (page 658). It crystallizes in tables having a pearly lustre, or in small, brilliant needles. It may be made synthetically by the action of methylene chloride on sodium phenate (Greene).



$$C^6H^5.OH + CH^2Cl^2 + 2NaOH = C^6H^4<^{OH}_{CH^2.OH} + 2NaCl + H^2O$$

Phenol. Methylene chloride. Saligeninol.

SALICYLIC (ORTHOXYBENZOIC) ACID.

$$C^7H^6O^3 = C^6H^4(OH).CO^2H$$

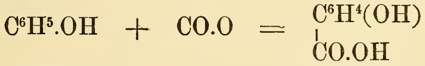
Formation and Preparation.—This body was discovered by Piria, who obtained it, in 1839, by fusing salicyl aldehyde with potassium hydrate.

$$C^7H^6O^2 + KOH = KC^7H^5O^3 + H^2$$

Oil of meadow-sweet contains it naturally, together with salicyl aldehyde. The essential oil of *Gaultheria procumbens* (winter-green) is methyl salicylate (Cahours), that is, salicylic acid, in which the atom of basic hydrogen is replaced by methyl.

Salicylic acid was formerly prepared by boiling oil of winter-green with caustic potassa as long as methyl alcohol is disengaged. Potassium salicylate is formed, and is afterwards decomposed by an excess of hydrochloric acid. The salicylic acid separates, and is purified by recrystallization from boiling water.

Kolbe and Lautemann formed salicylic acid by synthesis by passing carbon dioxide into phenol in which sodium was dissolved. Sodium salicylate is thus formed.



$$C^6H^5.OH + CO.O = \begin{array}{l} C^6H^4(OH) \\ | \\ CO.OH \end{array}$$

Phenol. Salicylic acid.

Kolbe and Schmitt have improved this process, and large quantities of salicylic acid are now manufactured by treating dry sodium phenate with carbon dioxide under pressure, and heating the product to 130°. According to Schmitt, *sodium phenylcarbonate*, $C^6H^5O.COONa$, is first formed, and upon heating under pressure this is converted into sodium salicylate.

$$2C^6H^5.ONa + CO^2 = C^6H^5.OH + C^6H^4\left\{\begin{matrix}CO^2Na\\ONa\end{matrix}\right.$$

Sodium phenate. Phenol. Sodium-salicylate of sodium.

After removing the excess of phenol by distillation, the mass is exhausted with water, and the solution is treated with hydrochloric acid, which sets free the salicylic acid.

Properties.—Salicylic acid crystallizes from its alcoholic solution in large, monoclinic prisms, and from its aqueous solution in long needles. It melts at 156°. When mixed with pumice-stone and rapidly distilled, it breaks up into carbon dioxide and phenol.

$$C^7H^6O^3 = CO^2 + C^6H^6O$$

It is very soluble in alcohol and ether, and in boiling water, but cold water scarcely dissolves it. Its aqueous solution produces a deep violet color with the ferric salts.

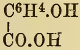
When salicylic acid is treated with nitric acid, it is converted into two isomeric nitrogenized acids; both are *nitrosalicylic acids*, $C^7H^5(NO^2)O^3$.

α–nitrosalicylic acid crystallizes in long, colorless needles, which are anhydrous and melt at 228°; they are very slightly soluble in cold water. It produces a blood-red color with ferric chloride.

β–nitrosalicylic acid crystallizes in long, colorless needles, containing one molecule of water of crystallization. When heated, it loses this water and melts at 144–145°. It is slightly soluble in cold water. Its solution also produces a blood-red color with ferric chloride. This acid is also formed when indigo is long boiled with nitric acid. It was formerly called *indigotic acid.*

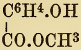
Salicylic acid possesses antiseptic properties like phenol, without presenting the same inconveniences as the latter as regards odor and causticity.

Methyl Salicylate, $C^7H^5(CH^3)O^3$.—Cahours first recognized the oil of *Gaultheria*, known as essence of winter-green, to be methyl salicylate. When purified, this body forms a colorless oil, having a pleasant odor. It boils at 223.7°. Its density at 0° is 1.1969. Like the phenols, it has the characters of a weak acid. When a concentrated solution of potassium hydrate is added to methyl salicylate, a precipitate of potassium gaultherate is formed. Cahours discovered the existence of an isomeride of methyl salicylate. It is methylsalicylic acid. The following formulæ indicate the constitutions of these bodies:



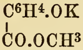
$$\begin{matrix}\mathrm{C^6H^4.OH} \\ | \\ \mathrm{CO.OH}\end{matrix}$$

Salicylic acid.



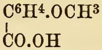
$$\begin{matrix}\mathrm{C^6H^4.OH} \\ | \\ \mathrm{CO.OCH^3}\end{matrix}$$

Methyl salicylate.



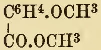
$$\begin{matrix}\mathrm{C^6H^4.OK} \\ | \\ \mathrm{CO.OCH^3}\end{matrix}$$

Potassium gaultherate



$$\begin{matrix}\mathrm{C^6H^4.OCH^3} \\ | \\ \mathrm{CO.OH}\end{matrix}$$

Methylsalicylic acid.



$$\begin{matrix}\mathrm{C^6H^4.OCH^3} \\ | \\ \mathrm{CO.OCH^3}\end{matrix}$$

Methyl methylsalicylate.

METOXYBENZOIC AND PAROXYBENZOIC ACIDS.

These two acids are isomeric with salicylic acid.

Metoxybenzoic acid is formed under various circumstances; especially when metachloro-benzoic acid, a chloro-derivative of benzoic acid, is heated with potassium hydrate.

$$\mathrm{C^7H^5ClO^2 + 2KOH = C^7H^5(OK)O^2 + KCl + H^2O}$$

It is an anhydrous, crystalline powder, consisting of small, square tables. Sometimes it is in mammillated crystals. It melts at 200°, and can be distilled without alteration. It is only slightly soluble in cold water, but dissolves more readily in boiling water.

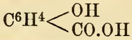
Paroxybenzoic Acid is formed under rather remarkable circumstances. We have already seen that in presence of sodium, phenol fixes carbon dioxide, forming sodium salicylate. If the sodium be replaced by potassium, the same reaction produces potassium paroxybenzoate. The same salt is formed when potassium phenate is heated to 210 or 220° in a current of carbon dioxide; below 150°, only potassium salicylate is formed.

Paroxybenzoic acid crystallizes in transparent, oblique rhombic prisms, containing one molecule of water of crystallization. When anhydrous, it melts at 210°, and is partially decomposed into phenol and carbon dioxide. It is much more soluble in water and alcohol than salicylic acid. Its aqueous solution does not produce a violet color with ferric chloride.

ANISIC ALDEHYDE AND ACID.

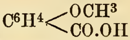
Anisic Compounds.—When the oils of anise, of fennel, or of tarragon are heated with nitric acid, they are converted into a colorless oil, having a spicy odor, and boiling at 248°. This is *anisic aldehyde*, $\mathrm{C^8H^8O^2}$. By a more complete oxidation, this aldehyde is converted into *anisic acid*, $\mathrm{C^8H^8O^3}$. The latter crystallizes from hot water in long needles, and from alcohol in rhomboidal prisms. It melts at 185°, and distils without decomposition at about 280°. When heated with barium oxide, it is decomposed into carbon dioxide and anisol (page 680). Anisic aldehyde and acid present very simple relations of composition with paroxybenzoic acid.

Anisic aldehyde is *methylparoxybenzoic* aldehyde, and anisic acid is *methylparoxybenzoic* acid.



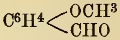
$$\mathrm{C^6H^4}<\begin{matrix}\mathrm{OH}\\ \mathrm{CO.OH}\end{matrix}$$

Paroxybenzoic acid.



$$\mathrm{C^6H^4}<\begin{matrix}\mathrm{OCH^3}\\ \mathrm{CO.OH}\end{matrix}$$

Methylparoxybenzoic, or anisic acid.



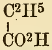
$$\mathrm{C^6H^4}<\begin{matrix}\mathrm{OCH^3}\\ \mathrm{CHO}\end{matrix}$$

Methylparoxybenzoic, or anisic aldehyde.

TYROSINE.

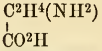
$C^9H^{11}NO^3$

This body seems to be related to the preceding compounds. It may be regarded as amidopropionic acid in which one atom of hydrogen is replaced by the group $C^6H^4.OH$ (paroxyphenyl) as it exists in paroxybenzoic acid.



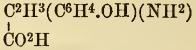
$$\begin{array}{l}\mathrm{C^2H^5}\\ |\\ \mathrm{CO^2H}\end{array}$$

Propionic acid.



$$\begin{array}{l}\mathrm{C^2H^4(NH^2)}\\ |\\ \mathrm{CO^2H}\end{array}$$

Amidopropionic acid.



$$\begin{array}{l}\mathrm{C^2H^3(C^6H^4.OH)(NH^2)}\\ |\\ \mathrm{CO^2H}\end{array}$$

Oxyphenyl-amidopropionic acid (tyrosine).

Tyrosine is the product of the decomposition of many nitrogenized matters in the animal economy. It may be prepared by boiling for sixteen hours 1 part of horn shavings with 2 parts of sulphuric acid diluted with 4 times its volume of water. The liquid is then neutralized with milk of lime, filtered, the filtrate evaporated to half its volume, acidified with sulphuric acid, and treated with an excess of lead carbonate.

The solution, which contains the tyrosine as lead salt, is decomposed by hydrogen sulphide, filtered, and evaporated. The tyrosine crystallizes out, and may be purified by several crystallizations. The mother-liquors contain leucine.

Tyrosine crystallizes in long, colorless needles, often united in tufts. It is but slightly soluble in water and in cold alcohol, more soluble in hot alcohol, and insoluble in ether. It forms definite compounds with both acids and bases. When fused with potassium hydrate, it breaks up into paroxybenzoic and acetic acids, and ammonia.

Tyrosine may be recognized by the following reaction. When its aqueous solution is boiled with a solution of mercuric nitrate, as neutral as possible, a voluminous yellow precipitate is formed, which assumes a deep copper-red color by boiling with nitric acid containing a small quantity of nitrous acid.

GALLIC ACID.

$C^7H^6O^5 = C^6H^2(OH)^3 - CO.OH$

This acid is closely related to salicylic acid. It is dioxysalicylic acid, and Lautemann obtained it by treating di-iodosalicylic acid with alkalies.

$$\underset{\text{Di-iodosalicylic acid.}}{C^7H^4I^2O^3} + 2KOH = 2KI + \underset{\text{Gallic acid.}}{C^7H^4(OH)^2O^3}$$

We have already seen that gallic acid is a product of the decomposition of tannic acid. It is prepared by exposing coarsely-powdered and moistened nut-galls to the air, renewing the water as it evaporates. At the end of two or three months a black liquid is separated from the mass by strong pressure, and the solid residue is exhausted with boiling water. Gallic acid crystallizes out on the cooling of the filtered liquid. It is purified by several crystallizations in boiling water.

Gallic acid forms long, silky needles, which contain one molecule of water of crystallization. It has no odor; its taste is astringent and slightly acid. When heated to 220° it melts, and losing carbon dioxide is converted into *pyrogallol*, or pyrogallic acid.

$$\underset{\text{Gallic acid.}}{C^7H^6O^5} = CO^2 + \underset{\text{Pyrogallol.}}{C^6H^3(OH)^3}$$

Gallic acid dissolves in 100 parts of cold water, and in 3 parts of boiling water. It is very soluble in alcohol, less soluble in ether. Its solution gradually absorbs oxygen when exposed to the air, and at the same time becomes colored and disengages carbon dioxide.

If a recently boiled solution of gallic acid be passed up into a tube filled with mercury and containing no air, and some recently boiled baryta-water be then added, a white precipitate is formed which at once changes to blue, if a few bubbles of oxygen be introduced. The change of color is the indication of an oxidation of the gallic acid, favored in this case by the presence of the alkali.

Pyrogallol, or Pyrogallic Acid, $C^6H^3(OH)^3$, occurs in brilliant white laminæ which melt at 115°. It is soluble in water, sparingly soluble in alcohol and ether. It is a powerful reducing agent: gold, silver, and mercury are precipitated by it from their solutions. Dissolved in an excess of potash lye, pyrogallol energetically absorbs oxygen. This solution is employed for the rapid estimation of oxygen in air and other gaseous mixtures.

The peculiar reducing properties of pyrogallic acid render it one of the best photographic developers.

XYLENES AND DERIVATIVES.

$C^8H^{10} = C^6H^4(CH^3)^2$

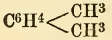
That portion of coal-tar which boils between 136 and 139° contains a mixture of isomeric hydrocarbons, which is designated as xylene. It is dimethylbenzene, $C^6H^4<\begin{matrix}CH^3\\CH^3\end{matrix}$, and can exist in three different isomeric modifications, like all of the di-substituted derivatives of benzene.

Metaxylene, which boils at 137°, predominates in the mixture of xylenes which is obtained from coal-tar. When oxidized by chomic acid, it is converted into isophthalic acid, $C^6H^4(CO^2H)^2$.

Orthoxylene is a colorless liquid, boiling at 140–141°. Nitric acid oxidizes it to orthotoluic acid and further to phthalic acid.

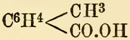
Paraxylene is solid, and crystallizes in oblique rhombic prisms, fusible at 15°. It boils at 136–137°. Dilute nitric acid converts it into paratoluic acid. Chromic acid oxidizes it to terephthalic acid.

There are very many derivatives allied to these isomeric xylenes. One or more atoms of hydrogen may be replaced, either in the benzene nucleus or in the methyl chains, by chlorine, bromine, or by groups such as OH, NO^2, NH^2, etc. The methyl chains may be oxidized by boiling the xylenes with nitric or chromic acid, as indicated above. In this case the group CH^3 is replaced by the carboxyl group CO.OH, and the hydrocarbons, $C^6H^4(CH^3)^2$, are converted into either toluic acids or phthalic acids, of each of which there are three isomerides.



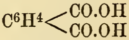
$C^6H^4<\begin{matrix}CH^3\\CH^3\end{matrix}$

Xylenes.



$C^6H^4<\begin{matrix}CH^3\\CO.OH\end{matrix}$

Toluic acids.



$C^6H^4<\begin{matrix}CO.OH\\CO.OH\end{matrix}$

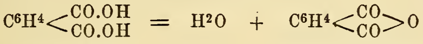
Phthalic acids.

We cannot describe all of these bodies here, but must limit ourselves to a brief description of phthalic acid and its isomerides.

PHTHALIC ACIDS.

$C^8H^6O^4 = C^6H^4(CO.OH)^2$

Ordinary, or Orthophthalic Acid.—Laurent obtained this acid by boiling naphthalene for a long time with nitric acid. It crystallizes in brilliant scales, or in short, thick prisms, which are but slightly soluble in cold water, very soluble in hot water, alcohol, and ether. It melts at 213°, and loses the elements of water, being converted into phthalic anhydride.

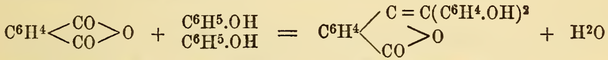


$$C^6H^4\left\langle\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. = H^2O + C^6H^4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$$

Phthalic acid. Phthalic anhydride.

Phthalic anhydride crystallizes in long, brilliant prisms, fusible at 127°–128°. It boils at 284°. It possesses a remarkable property, which was discovered by A. Baeyer, and which is now applied practically in the arts. When heated with the phenols, it combines with them directly with elimination of the elements of water, and compounds are obtained which are designated as *phthaleins.*

Thus, when phthalic anhydride is heated with ordinary phenol, two molecules of phenol combine with one molecule of phthalic anhydride, with elimination of one molecule of water, and the phthalein of phenol is obtained.

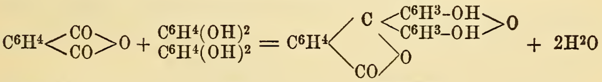


$$C^6H^4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + \begin{matrix}C^6H^5.OH\\C^6H^5.OH\end{matrix} = C^6H^4\left\langle\begin{matrix}C = C(C^6H^4.OH)^2\\ \quad\quad >O\\ CO\end{matrix}\right. + H^2O$$

Phthalic anhydride. 2 mol. phenol. Phenolphthalein.

Phenolphthalein occurs as a yellowish crystalline powder. It melts at 250° and dissolves readily in alcohol. Its solution turns pink with the slightest trace of free alkali; hence it is used as an *indicator* in alkalimetry.

When resorcinol is heated with phthalic anhydride, two molecules of water are eliminated, and a body is obtained to which Baeyer has given the name *fluorescein.*



$$C^6H^4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + \begin{matrix}C^6H^4(OH)^2\\C^6H^4(OH)^2\end{matrix} = C^6H^4\left\langle\begin{matrix}C\left\langle\begin{matrix}C^6H^3\text{–}OH\\C^6H^3\text{–}OH\end{matrix}\right\rangle O\\ \quad\quad >O\\ CO\end{matrix}\right. + 2H^2O$$

Phthalic anhydride. 2 mol. resorcinol. Fluorescein.

Fluorescein forms orange-red, crystalline grains, insoluble in cold water, and but slightly soluble in boiling water. It dissolves readily in solutions of the alkalies and alkaline carbonates. Its dilute solutions are yellow, and have a magnificent green fluorescence. Hence the name fluorescein.

Tetrabromo-fluorescein, $C^{20}H^{8}Br^{4}O^{5}$, is employed in dyeing under the name *eosin*. It communicates to silk a beautiful rose-red tint.

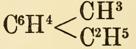
Terephthalic Acid.—Cailliot obtained this body by submitting oil of turpentine to a long ebullition with dilute nitric acid. The same acid is formed by the oxidation of paraxylene and its derivatives by potassium dichromate and sulphuric acid. It is a white powder, almost insoluble in water, alcohol, and ether. It sublimes without melting and without decomposition.

Isophthalic Acid is formed by the oxidation of metaxylene or metatoluic acid. Long, thin, colorless crystals, slightly soluble in water, soluble in alcohol, and fusible above 300°. It may be sublimed without decomposition.

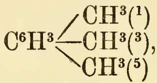
TRIMETHYL-BENZENES AND ISOMERIDES.

The hydrocarbons $C^{9}H^{12}$ may be derived from benzene by the substitution: 1, of three methyl groups for three atoms of hydrogen; 2, of a methyl and ethyl group for two atoms of hydrogen; 3, of a propyl or isopropyl group for one atom of hydrogen.

Their constitutions are then thus expressed:

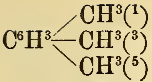
$C^{6}H^{3}(CH^{3})^{3}$	 $C^{6}H^{4}<\begin{matrix}CH^{3}\\C^{2}H^{5}\end{matrix}$	$C^{6}H^{5}-C^{3}H^{7}$
Trimethylbenzenes.	Methyl-ethyl benzenes.	Propyl and isopropyl benzenes.

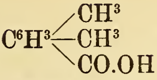
Trimethylbenzenes.—The methyl groups may be arranged in three different ways, and three isomers of position are actually known.

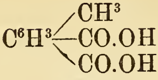


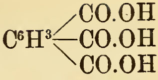
Mesitylene, $C^{6}H^{3}\begin{matrix}/CH^{3}(^{1})\\-CH^{3}(^{3})\\ \backslash CH^{3}(^{5})\end{matrix}$, the *symmetrical* trimethylbenzene, is obtained by distilling acetone with an equal measure of sulphuric acid diluted with half its volume of water: the reaction is moderated by adding sand to the mixture.

Mesitylene is a liquid having a pleasant odor, and boiling at 163°. When boiled with dilute nitric acid it is oxidized, and forms successively three acids, in which one, two, or all of the methyl groups are converted into carboxyl.

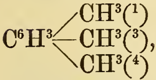

Mesitylene.

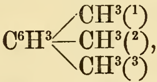

Mesitylenic acid.


Mesidic or uvitic acid.

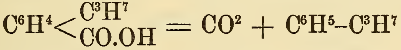

Trimesic acid.

With concentrated nitric acid it yields nitro-derivatives.

Pseudocumene, or *asymmetrical* trimethylbenzene, , exists, together with mesitylene, in coal-tar, but cannot be separated by fractional distillation. It is obtained synthetically by treating a mixture of bromoparaxylene and methyl iodide with sodium. It boils at 169°.

Hemimellithene, , has the methyl groups in *adjacent* positions, and is produced when bromometaxylene, $C^6H^3\overset{(1)}{C}H^3\overset{(2)}{B}r\overset{(3)}{C}H^3$, is made to react with methyl iodide and sodium (Jacobsen). It boils at 175°.

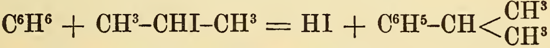
Cumene, or Isopropylbenzene, $C^6H^5\text{–}C^3H^{7i}$, was obtained by Gerhardt and Cahours by distilling cuminic acid with lime.



$$C^6H^4<^{C^3H^7}_{CO.OH} = CO^2 + C^6H^5\text{–}C^3H^7$$

Cuminic acid. Cumene.

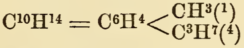
Its synthesis has been made by the action of isopropyl iodide on benzene, in presence of aluminium chloride.



$$C^6H^6 + CH^3\text{–}CHI\text{–}CH^3 = HI + C^6H^5\text{–}CH<^{CH^3}_{CH^3}$$

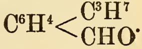
It is a colorless liquid, boiling at 151°.

CYMENE AND ITS DERIVATIVES.



$$C^{10}H^{14} = C^6H^4<^{CH^3(^1)}_{C^3H^7(^4)}$$

Cymene, which is a product of the dehydration of camphor, is methylisopropylbenzene. Its synthesis is made by the action of sodium on a mixture of parabromisopropyl benzene and methyl iodide (Widman).

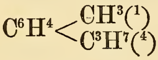
It exists naturally in the essential oil of *Cuminum Cyminum*, which contains also cuminol, or cuminic aldehyde,  $C^6H^4<^{C^3H^7}_{CHO}$. Together with thymol, it exists in oil of thyme. It may be best prepared by distilling laurel camphor with phosphorus pentachloride.

Cymene is a liquid of an agreeable odor; density at 0°, 0.872. It boils at 175–176°.

Upon oxidation with nitric acid it yields paratoluic acid; chromic acid converts it into terephthalic acid.

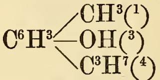
THYMOL, OR THYME-CAMPHOR.

This compound, which is a phenol, presents certain analogies to the camphors (page 727). Thymol and its isomeride, *carvacrol*, are related to cymene, being oxycymenes.



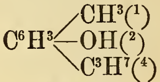
$$C^6H^4 < \begin{array}{l} CH^3({}^1) \\ C^3H^7({}^4) \end{array}$$

Cymene.



$$C^6H^3 \begin{array}{l} / CH^3({}^1) \\ - OH({}^3) \\ \backslash C^3H^7({}^4) \end{array}$$

Thymol.



$$C^6H^3 \begin{array}{l} / CH^3({}^1) \\ - OH({}^2) \\ \backslash C^3H^7({}^4) \end{array}$$

Carvacrol.

Thymol exists, with cymene and thymene ($C^{10}H^{16}$), in oil of thyme (*Thymus serpyllum*), and in the essential oils of *Ptychotis ajowan* and *Monarda punctata*. It is prepared by treating these oils with potassium hydrate solution, separating the insoluble hydrocarbons, and precipitating the alkaline solution with hydrochloric acid.

Thymol crystallizes in large colorless plates, fusible at 44°, and boiling at 230°. It possesses antiseptic properties.

TERPENES AND CAMPHORS.

Closely related to cymene are a number of hydrocarbons of the composition $(C^5H^8)^n$, known as the *terpenes*, and their oxygenized derivatives, the *camphors*. Both groups of compounds are widely distributed in nature.

The terpenes proper are represented by the formula $C^{10}H^{16}$. They form the basis of many *essential oils*, such as the oils of turpentine, lemon, orange-peel, bergamot, juniper, savin, elemi, eucalyptus, etc.

At low temperatures some of these deposit oxygenized solid bodies that were formerly designated as *stearoptenes*, but are now classed with the camphors.

Essential Oils.—These volatile liquids are generally obtained by distilling the vegetable products which contain them with water, for, although their boiling-points are between 150 and 200°, they distil readily with aqueous vapor, and collect in the form of a layer on the surface of the condensed water.

The more ordinary process consists in passing a current of steam through the plants or aromatic vegetables. For this purpose they are placed on a diaphragm, M (Fig. 134), which is fixed above the bottom of an ordinary still. The head of the still is then adjusted, connection is made with a condenser, and a current of steam is passed in by the tube TT′T″, which penetrates into the still. The steam carries with it the essential oil, which diffuses in it by virtue of the high tension of the vapor of these oils at 100°. The mixed vapors rise into the head of the still and condense in the condensing worm. The condensed water, generally clouded by little drops of the essential oil, is received in a vessel of peculiar form, which is called a *Florentine receiver*. It is shaped like an ordinary flask (Fig. 135), having at its bottom a tube which curves upwards, in the form of a swan's neck, and the upper part of which is but little below the mouth of the flask. As the condensed water and oil collect in this ingenious apparatus, the oil separates and floats on the water; as the distillation continues, the liquid rises not only in the flask, but in the lateral tube, until the water, which is always in large excess, reaches the level of the curved neck and flows off alone, the lighter oil accumulating in the flask.

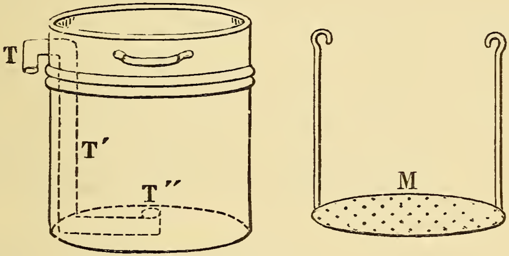


FIG. 134.

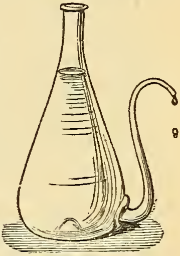


FIG. 135.

OIL OF TURPENTINE.

The most important of the essential oils is oil of turpentine, which is obtained by distilling the turpentine of commerce with water. Turpentine is a mixture of resin and essential oil, and flows from incisions cut in the trunks of trees of the genera *Pinus*, *Abies*, *Picea*, *Larix*.

When this resinous substance is distilled with water, the oil passes over and the resin remains; the latter is called *colophony*, or rosin.

Oil of turpentine is a colorless, mobile liquid, having a peculiar odor, and boiling at 158°. Its density at 16° is 0.870. It is insoluble in water, but miscible in all proportions with alcohol and ether. According to their origin, the turpentines exhibit certain peculiarities, especially in their action upon polarized light. The following are the most important varieties:

1. *American oil of turpentine* is obtained from the turpentine of *Pinus palustris*. It rotates the plane of polarization to the right.
2. *English oil of turpentine* (australene) is derived from *Pinus australis*, and is likewise dextro-rotatory.
3. *French turpentine* comes from the *Pinus maritima*; it yields an oil which turns the plane of polarization to the left.
4. *German oil of turpentine* is distilled from the turpentine of *Pinus sylvestris*. It is levo-rotatory.
5. *Venetian oil of turpentine* comes from the exudation of *Larix europæa*, and is levo-rotatory.

Metamorphoses of Oil of Turpentine.—1. When exposed to the air, oil of turpentine gradually absorbs oxygen, becomes yellow and partly resinified. This slow oxidation is due to the production of ozone, with which the oil becomes charged; it then possesses oxidizing properties (page 71).

2. If vapor of oil of turpentine be passed through a red-hot porcelain tube, it is decomposed, yielding *isoprene*, C^5H^8, cymene, benzene, toluene, xylene, and higher hydrocarbons.

3. Concentrated nitric acid oxidizes oil of turpentine with such energy that the mixture sometimes takes fire. When boiled with dilute nitric acid, it forms paratoluic, terephthalic, and oxalic acids.

4. When a mixture of alcohol, nitric acid, and oil of turpentine is left to itself for some time, the latter substance

fixes the elements of three molecules of water and is converted into a crystallized solid body, $C^{10}H^{20}O^2 + H^2O$, called *terpin hydrate.* If this hydrate be heated to 100°, it loses water and is converted into a crystalline mass, fusible at 117°: this is *terpin.*

5. When oil of turpentine is mixed with $\frac{1}{20}$ its weight of concentrated sulphuric acid, and the mixture is agitated, it is converted into *terebene*, an optically inactive mixture of terpenes, which boils at 156°, and a polymeric hydrocarbon, $C^{20}H^{32}$, which boils between 310 and 313° (H. Deville). By reason of the reducing action which the oil of turpentine exerts on the sulphuric acid, and which produces sulphurous oxide and water, two atoms of hydrogen are removed from the molecule $C^{10}H^{16}$, and, independently of terebene, a certain quantity of *cymene*, $C^{10}H^{14}$, is formed (Riban).

$$C^{10}H^{16} + SO^4H^2 = C^{10}H^{14} + SO^2 + 2H^2O$$

6. The halogens act energetically upon oil of turpentine. At low temperatures it combines with chlorine and bromine, forming di-halogen addition products, and these upon warming give off two molecules of hydrochloric or hydrobromic acid, and are converted into cymene.

$$C^{10}H^{16} + Cl^2 = C^{10}H^{16}Cl^2$$
$$C^{10}H^{16}Cl^2 = C^{10}H^{14} + 2HCl$$

This conversion of turpentine into cymene is most readily effected by heating it with iodine.

7. Oil of turpentine combines with the halogen acids. Some of the terpenes occurring in turpentine combine with only one molecule of hydrochloric acid, whilst others form addition products with two molecules (see below).

TERPENES.

Of the hydrocarbons having the composition $C^{10}H^{16}$, the following have been isolated:

Pinene.—This is the chief constituent of the common varieties of oil of turpentine; it is also met with in a large number of other essential oils. It exists in two optically active modifications: American oil of turpentine contains dextro-pinene, while the pinene of French turpentine is levorotatory.

Pinene combines with only one molecule of hydrochloric acid, forming the hydrochloride $C^{10}H^{16}.HCl$. This is a solid, melting at 125° and boiling at 208°. It smells like camphor, and was formerly called *artificial camphor.*

Addition products of pinene with two atoms of chlorine and bromine are also known.

Camphene.—Camphene is an artificial product, and is the only terpene which is solid at ordinary temperatures. It results from the elimination of hydrochloric acid from pinene hydrochloride, and is readily prepared by heating *bornyl chloride*, $C^{10}H^{17}Cl$, with aniline. The melting-point of camphene is 50°. Two optically active modifications of opposite rotatory power and an inactive camphene are known.

Camphene forms a monohydrochloride, but does not appear to be capable of combining with the free halogens.

Fenchene resembles camphene in many respects. It was obtained by Wallach by heating *fenchyl chloride*, an isomeride of bornyl chloride, with aniline. Its odor recalls that of camphene. Unlike the latter it does not solidify at low temperatures. It combines readily with one molecule of hydrochloric acid and with two atoms of bromine.

Limonene is present in many essential oils, especially in the oils of orange-peel, lemon, and bergamot. Two active varieties—dextro- and levo-limonene—have been obtained. This terpene boils at 175°. Its density at 20° is 0.846. It combines with only one molecule of *dry* hydrochloric acid, but the resulting compound, $C^{10}H^{16}.HCl$, forms addition products when treated with moist hydrochloric acid or with bromine. Limonene tetrabromide melts at 105°.

Dipentene is an optically inactive limonene, resulting from the combination of the dextro- and levo-varieties. It is formed when either of these varieties, or when pinene or camphene is heated to 250°–300°. It is also produced in the distillation of caoutchouc, and occurs naturally in oil of elemi. Its chemical properties are identical with those of the active limonenes.

Dipentene, as well as the limonenes, form characteristic combinations, $C^{10}H^{16}.NOCl$, with nitrosyl chloride: these *nitrosochlorides* upon boiling with alcohol are converted into the corresponding *carvoximes*, $C^{10}H^{16}.NOH$.

Sylvestrene occurs in Swedish and Russian oils of turpentine. Its characters are very like those of the limonenes.

It is dextro-rotatory, as is also its dihydrochloride, which melts at 72°.

Phellandrene.—This terpene is found in oil of fennel and in certain eucalyptus oils. It boils at 170° and rotates the plane of polarization to the right.

When a solution of phellandrene in petroleum ether is agitated with a solution of sodium nitrite, and acetic acid is gradually added, a voluminous crystalline mass of phellandrene *nitrosite*, $C^{10}H^{16}.N^2O^3$, separates. This rather unstable body is highly characteristic; its melting-point is 102° (Cahours, Wallach).

Terpinene is formed by an intramolecular rearrangement of other terpenes, and occurs in oil of cardamom: it boils about 180°, and forms a characteristic nitrosite fusible at 155°.

Terpinolene is obtained by heating pinene with sulphuric acid. It boils about 185°. The tetrabromide melts at 116°.

Dihydrocymene, which has been made synthetically by Baeyer, boils at 174°, and closely resembles some of the natural terpenes.

Of the other hydrocarbons which are included in the terpene group, only a few can be mentioned here.

Isoprene, C^5H^8, belongs to the *hemiterpenes*. It is produced in the destructive distillation of caoutchouc, and readily polymerizes to dipentene. Isoprene boils at 37°.

Cedrene and **Cubebene,** $C^{15}H^{24}$, represent the *sesquiterpenes*. They boil between 250 and 260°.

Caoutchouc $(C^5H^8)^x$.—This *polyterpene* is contained in the sap of many plants. It is obtained in an impure condition by allowing the "milk" of certain tropical trees (*Syphonia*, *Ficus elastica*) to become solid. When fresh it is colorless and extremely elastic, but upon exposure to air and light it becomes dark and brittle.

Pure caoutchouc cannot be melted without decomposition. It is insoluble in water and in alcohol, but soluble in ether, carbon disulphide, chloroform, and benzene. Its exact constitution is not known; it is free from oxygen, and on dry distillation yields hydrocarbons (isoprene, dipentene, etc.).

Caoutchouc acquires valuable properties when treated with sulphur. It is then said to be vulcanized.

Gutta-Percha is obtained from the Isonandra-tree, and resembles caoutchouc in many respects, but is hard at ordinary temperatures, and contains oxygen.

ORDINARY CAMPHOR, OR LAUREL CAMPHOR.

$C^{10}H^{16}O$

Camphor exists in all the parts of *Laurus camphora*, a tree occurring in Japan and China, and especially abundant in the Island of Formosa. When the wood is chipped and distilled with water, the camphor volatilizes and condenses in rice-straw, with which the heads of the stills in which the operation is conducted are filled. The product thus obtained in the form of small crystals, is refined by sublimation in glass vessels heated on a sand-bath.

Artificially, camphor has been obtained by the oxidation of camphene and borneol.

Camphor forms a semi-transparent, crystalline mass. Its odor is strong and aromatic; its taste, bitter and burning. It melts at 175°, and boils and distils without alteration at 204°. Its density at 0° is 1.0. At ordinary temperatures, the tension of its vapor is so great that it sublimes spontaneously in the vessels in which it is kept.

Camphor is almost insoluble in water; when thrown in small fragments on the surface of that liquid, it executes gyratory movements. It dissolves in alcohol and ether, and the alcoholic solution rotates the plane of polarization to the right.

A levo-rotatory modification of camphor results from the oxidation of levo-camphene, and occurs naturally in the oil of *Matricaria parthenium*.

Camphor is inflammable, and burns with a smoky flame. The following are its principal reactions:

1. When heated with phosphoric anhydride, or with chloride of zinc, it loses the elements of water and is converted into cymene.

$$\underset{\text{Camphor.}}{C^{10}H^{16}O} = H^{2}O + \underset{\text{Cymene.}}{C^{10}H^{14}}$$

2. The chemical behavior of camphor is that of a ketone. Although it does not fix hydrogen directly, it can nevertheless be converted into a compound, $C^{10}H^{18}O$, which is borneol, or Borneo camphor. This is accomplished by the action of sodium, which replaces the hydrogen of a portion of the camphor, forming a sodium-camphor, while the displaced hydrogen is fixed upon another portion of camphor (Baubigny).

According to this reaction, corroborated by the inverse reaction, which will be indicated farther on, the same relations exist between borneol and camphor as between isopropyl alcohol and acetone.

$C^{10}H^{16}O$	$C^{10}H^{18}O$
Camphor.	Borneol.

3. Like other ketones, camphor reacts with phenylhydrazine and with hydroxylamine, forming the hydrazone $C^{10}H^{16}(N^2HC^6H^5)$ and the oxime $C^{10}H^{16}(N.OH)$, respectively. *Camphoroxime* is readily prepared by heating camphor with hydroxylamine hydrochloride and sodium hydroxide in alcoholic solution (Auwers). It forms needle-like crystals which melt at 118°.

4. When camphor is heated for a long time with a alcoholic solution of potassium hydroxide, it is decomposed into an acid and an alcohol, which is borneol (Berthelot).

$$\underset{\text{Camphor.}}{2C^{10}H^{16}O} + KOH = \underset{\text{Potassium camphinate.}}{C^{10}H^{15}KO^2} + \underset{\text{Borneol.}}{C^{10}H^{18}O}$$

5. When vapor of camphor is passed over soda-lime, heated to about 300°, the sodium salt of *campholic acid* is obtained (Delalande).

$$\underset{\text{Camphor.}}{C^{10}H^{16}O} + NaOH = \underset{\text{Sodium campholate.}}{C^{10}H^{17}NaO^2}$$

6. When camphor is subjected to the action of aqueous hypochlorous acid, it is converted into *monochloro-camphor*, $C^{10}H^{15}ClO$, which constitutes a colorless, crystalline mass, slightly soluble in water, freely soluble in alcohol and ether, and fusible at 95°.

7. By the action of bromine on camphor at 100 or 120°, *monobromo-camphor*, $C^{10}H^{15}BrO$, and *dibromo-camphor*, $C^{10}H^{14}Br^2O$, are formed. These bodies crystallize in colorless prisms. The first fuses at 76°, the second, at 57°.

A bromide of camphor, $C^{10}H^{16}OBr^2$, is also known; it is formed by the action of bromine on a solution of camphor in chloroform. It is a crystalline body which decomposes spontaneously, especially by the action of light, losing hydrobromic acid and being converted into monobromo-camphor.

8. Heating with iodine converts camphor into carvacrol or oxycymene (page 718).

$$C^{10}H^{16}O + I^2 = C^{10}H^{14}O + 2HI$$

9. When camphor is boiled with nitric acid, it is oxidized and converted into *camphoric acid.*

$$\underset{\text{Camphor.}}{C^{10}H^{16}O} + 3O = \underset{\text{Camphoric acid.}}{C^{10}H^{16}O^{4}}$$

By further oxidation this acid, which contains two carboxyl groups, is converted into the tribasic *camphoronic acid.*

$$\underset{\text{Camphoric acid.}}{C^{10}H^{16}O^{4}} + 5O = \underset{\text{Camphoronic acid.}}{C^{9}H^{14}O^{6}} + CO^{2} + H^{2}O$$

Fenchone is the name given by Wallach to an isomeride of camphor which occurs in oil of fennel. It melts at 5° and boils at 192°. At 19° its specific gravity is 0.946. It is dextro-rotatory.

Although soluble in concentrated nitric acid, it is but slowly oxidized even when boiled with a large excess of this acid.

Fenchoneoxime forms beautiful crystals, melting at 161°.

BORNEOL, OR BORNEO CAMPHOR.

$C^{10}H^{18}O$

This camphor is extracted from the *Dryobalanops aromatica*, a tree which grows in the Sunda Islands. Berthelot has obtained it by the action of an alcoholic solution of potash on ordinary camphor. It occurs in small, colorless, transparent, and friable crystals. Its odor recalls at the same time that of camphor and that of pepper. Its taste is burning. It melts at 206°, and boils at 212°. It turns the plane of polarization to the right. It is insoluble in water, but dissolves readily in alcohol and in ether. When treated with cold, fuming nitric acid, it loses H^2, and is converted into ordinary camphor, $C^{10}H^{16}O$.

Cineol is isomeric with borneol. It is the chief constituent of the oils of cajeput and wormseed. It is a colorless liquid which boils at 176°. Its character is that of an oxide.

MENTHOL, OR MINT CAMPHOR.

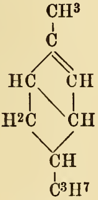
$C^{10}H^{20}O$

Menthol is the solid part of the essential oil of mint (*Mentha piperita*), in which it exists mixed with liquid terpenes. It is deposited in crystals when oil of mint is cooled.

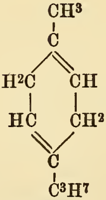
It forms colorless crystals, fusible at 42°; it boils at 213°. It rotates the plane of polarized light to the left. Dehydrating agents, such as phosphoric anhydride and zinc chloride, convert it into *menthene*, $C^{10}H^{18}$, boiling at 165°.

Constitution of the Terpenes and Camphors.—We have seen that, under certain conditions, the benzene nucleus is capable of forming *addition compounds* (page 672). Thus, by the action of chlorine or bromine upon benzene in sunlight, di-, tetra-, and hexa-halogen addition products are obtained, and by heating benzene with a large excess of strong hydriodic acid, it is converted into hexahydrobenzene, C^6H^{12}. In the latter case the benzene nucleus is said to be *reduced*, the six latent atomicities being satisfied with hydrogen. When the nucleus is only *partially* reduced, that is to say when only two or four atoms of hydrogen are added, the "aromatic" character of the original substance is destroyed, and the derivatives deport themselves like unsaturated compounds of the fatty series.

Now the terpenes of the formula $C^{10}H^{16}$ contain two atoms more of hydrogen than cymene, and they are readily converted into this hydrocarbon, or derivatives of it, by various reactions. Moreover, their behavior towards the halogens and halogen acids is that of unsaturated compounds. They must be considered as dihydrocymenes, and the existence of numerous isomerides is explained by assuming that the added hydrogens occupy different positions. According to Wallach, who has made a most careful study of this group, the structure of pinene and limonene, for example, may be thus represented:



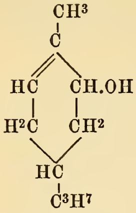
Pinene.



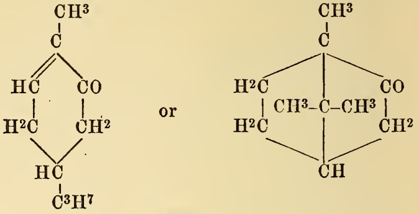
Limonene.

The camphors are oxygenized derivatives of partially reduced cymenes. Borneol contains the group CH.OH, and is derived from a tetrahydrocymene (dihydrocamphene). Ordinary camphor is the corresponding ketone.

Their constitutions are probably expressed by the formulæ



Borneol.



Camphor.

Menthol appears to be an oxyhexahydrocymene.

CAMPHORIC ACID.

$$C^{10}H^{16}O^4 = C^8H^{14} < \begin{matrix} CO.OH \\ CO.OH \end{matrix}$$

This acid, which has long been known, is obtained by boiling camphor with dilute nitric acid. The camphor, which at first floats as an oily liquid, finally disappears, and camphoric acid deposits as the solution cools. It is purified by dissolving it in caustic soda solution and precipitating with hydrochloric acid.

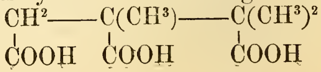
Camphoric acid crystallizes in colorless plates. It is only slightly soluble in cold water, but quite soluble in alcohol. It melts at 187°, and if heated above its fusing-point becomes converted into *camphoric anhydride*, $C^8H^{14} < \begin{matrix} CO \\ CO \end{matrix} > O$, which sublimes in brilliant needles, fusible at 221°.

$$\underset{\text{Calcium camphorate.}}{CaC^{10}H^{14}O^4} = CaCO^3 + \underset{\text{Camphorone.}}{C^9H^{14}O}$$

Besides ordinary camphoric acid, which is dextro-rotatory, there are two other modifications,—*levo-camphoric acid*, obtained from matricaria camphor, and *meso-camphoric acid*, formed by the union of equimolecular quantities of the two active varieties.

Camphoric acid is dibasic; its calcium salt yields by dry distillation the compound *camphorone*, $C^9H^{14}O$, a liquid boiling at 208°.

Camphoronic acid, $C^6H^{11}(COOH)^3$, is produced by the further oxidation of camphoric acid. It is a crystalline compound fusible at 135°. By its synthesis it was recognized as *trimethyl-tricarballylic acid,*



$$\begin{matrix} CH^2 & — & C(CH^3) & — & C(CH^3)^2 \\ | & & | & & | \\ COOH & & COOH & & COOH \end{matrix}$$

Among the other benzene addition compounds we can mention only the following:

Quercite, $C^6H^7(OH)^5$.—This compound is pentahydroxyhexahydrobenzene, but was formerly considered to be related to the sugars, and was called *acorn-sugar*, having been first obtained from acorns. It forms monoclinic crystals, fusible at 222°, and subliming at 235°. It is soluble in water and in dilute alcohol, and its solutions are dextro-rotatory, a fact which is easily explained, as it contains two similar asymmetric carbon atoms. Hydriodic acid converts it into benzene, and finally into hexyl iodide.

Inosite, $C^6H^6(OH)^6$.—In 1850, Scherer extracted a sweet substance from the muscles, and the same compound has since been found in the lungs, kidney, spleen, and liver. Under the name inosite it was long classified with the sugars, but Maquenne has shown that it is no other than hexahydroxyhexahydrobenzene.

Inosite forms large rhombic tables or transparent, colorless prisms having a sweet taste. The crystals contain one molecule of water of crystallization, and effloresce in the air. Inosite is soluble in water, but insoluble in absolute alcohol and in ether. It is optically inactive, is not fermentable, and will not reduce alkaline cupric solutions.

Dambonite, $C^6H^6(OH)^4(CH^3)^2$.—This substance is the dimethyl ether of inosite, and was first obtained by A. Girard from Gaboon caoutchouc. It forms colorless needles, fusible at 190° and subliming at 210°. It is soluble in water, only slightly soluble in alcohol. Hydriodic acid reduces it to methyl iodide and inosite.

UNSATURATED AROMATIC COMPOUNDS.

The benzene derivatives so far considered are formed by the replacement of the hydrogen of benzene by saturated groups. There are, however, compounds which contain unsaturated groups, and which can so combine directly with chlorine, bromine, or hydrogen. Among these we will describe only styrolene and some of its derivatives.

STYROLENE, OR PHENYLETHYLENE.

$C^8H^8 = C^6H^5\text{-}CH{=}CH^2$

This compound, which may be considered as ethylene in which one atom of hydrogen is replaced by phenyl (C^6H^5), exists in storax, the thickened juice of the bark of *Liquidambar orientale.* It is extracted by passing steam through this balsam, fused under boiling water; the styrolene is carried over with the steam. It is also formed when cinnamic acid is heated with lime; for this reason it has been sometimes called *cinnamene.*

It is a colorless, mobile, strongly-refracting liquid, having an agreeable odor. The styrolene obtained from storax is optically active, a property which appears due to some impurity, for the hydrocarbon obtained artificially is inactive. Its density at 0° is 0.925, and it boils at 145°. When long kept, it becomes polymerized, and more rapidly if heated, into *metastyrolene*, a transparent, amorphous mass, which is reconverted into styrolene when distilled.

Styrolene, being unsaturated, can combine directly with chlorine and bromine. The bromide, $C^8H^8Br^2$, crystallizes in needles or plates, fusible at 74°. When heated with hydriodic acid, styrolene is converted into ethylbenzene.

$$C^6H^5\text{-}CH{=}CH^2 + 2HI = C^6H^5\text{-}CH^2\text{-}CH^3 + I^2$$

CINNAMIC ALDEHYDE.

$C^9H^8O = C^6H^5\text{-}CH{=}CH\text{-}CHO$

Cinnamic aldehyde exists in the essential oils of cinnamon and cassia. It is formed during the distillation of a mixture of cinnamate and formate of barium, by a reaction similar to that which yields the fatty aldehydes under the same conditions. It is made synthetically by passing hydrochloric acid gas into a mixture of ordinary aldehyde and benzaldehyde.

$$\underset{\text{Benzaldehyde.}}{C^6H^5\text{-}CHO} + \underset{\text{Aldehyde.}}{CH^3\text{-}CHO} = \underset{\text{Cinnamic aldehyde.}}{C^6H^5\text{-}CH{=}CH\text{-}CHO} + H^2O$$

Cinnamic aldehyde is a colorless oil, heavier than water. It has an aromatic odor. When exposed to the air it becomes oxidized into cinnamic acid. It reacts with hydroxylamine and phenylhydrazine, and forms a crystallizable compound with sodium acid sulphite, a property which permits of its ready separation from oil of cinnamon.

CINNAMYL ALCOHOL, OR STYRONE.

$$C^9H^{10}O = C^6H^5\text{-}CH{=}CH\text{-}CH^2.OH$$

Styracin, which may be extracted from storax, is a cinnamyl cinnamate, a compound of cinnamic acid and cinnamic alcohol, and may be readily saponified by potassium hydroxide.

$$C^9H^7O^2.C^9H^9 + KOH = C^9H^7O^2K + C^9H^9.OH$$

Cinnamic alcohol crystallizes in brilliant needles, soluble in alcohol, and slightly soluble in water. It melts at 33°, and distils without change at 250°.

CINNAMIC OR PHENYLACRYLIC ACID.

$$C^9H^8O^2 = C^6H^5\text{-}CH{=}CH\text{-}CO.OH$$

This acid exists in Tolu and Peruvian balsams, in storax, and in certain gum benzoins. It is formed by the careful oxidation of cinnamic alcohol or aldehyde, and has also been obtained synthetically by heating benzaldehyde with acetic anhydride and dry sodium acetate.

$$C^6H^5\text{-}CHO + CH^3\text{-}COOH = H^2O + C^6H^5\text{-}CH{=}CH\text{-}CO.OH$$

According to Perkin, who discovered this important reaction, the condensation is caused by the dehydrating action of the sodium salt, but Fittig's researches render it probable that the latter enters into the reaction and the anhydride is the dehydrating agent.

"Perkin's reaction" has been extensively applied in the preparation of unsaturated acids, especially of the homologues of cinnamic acid.

Cinnamic acid is colorless and odorless. It crystallizes from hot water in fine needles, and from alcohol in large prisms. It melts at 133°. When rapidly heated, it distils almost without alteration at 290°. When distilled with lime, or heated to 200° with water, it is decomposed, yielding styrolene and carbon dioxide.

$$C^9H^8O^2 = CO^2 + C^8H^8$$

By fusion with potassium hydrate it is converted into acetic and benzoic acids.

$$C^6H^5\text{-}CH{=}CH\text{-}CO.OH + 2KOH = C^6H^5\text{-}CO.OK + CH^3\text{-}CO.OK + H^2$$

Concentrated nitric acid converts it into two isomeric *nitrocinnamic acids*, $C^9H^7(NO^2)O^2$; orthonitrocinnamic acid, fusible at 240°, and paranitrocinnamic acid, fusible at 288°.

Cinnamic acid can fix directly two atoms of chlorine, bromine, or hydrogen, so forming saturated compounds. Sodium amalgam converts it into *hydrocinnamic* or *phenylpropionic* acid, $C^6H^5-CH^2-CH^2-CO.OH$, a compound crystallizing in fine, colorless needles, fusible at 47.5°, and boiling at 280°. The following formula will show the relations between acrylic and propionic acids, on one hand, and on the other those between cinnamic and hydrocinnamic acids.

$CH^2{=}CH-CO.OH$ Acrylic acid.	$CH^3-CH^2-CO.OH$ Propionic acid.
$CH(C^6H^5){=}CH-CO.OH$ Cinnamic acid. (Phenylacrylic.)	$CH^2(C^6H^5)-CH^2-CO.OH$ Hydrocinnamic acid. (Phenylpropionic.)

The cinnamates resemble the benzoates. Ferric chloride produces a yellow precipitate in their solutions.

Phenylpropiolic Acid, $C^6H^5-C{\equiv}C-CO.OH$, is formed when the dibrom-addition product of cinnamic acid, *phenyldibromopropionic acid*, is boiled with alcoholic potash.

$$C^6H^5-CHBr-CHBr-CO.OH = C^6H^5-C{\equiv}C-CO.OH + 2HBr$$

It crystallizes in needles which melt at 137°. At higher temperatures the acid is resolved into *phenylacetylene* and carbon dioxide.

$$C^6H^5-C{\equiv}C-CO.OH = C^6H^5-C{\equiv}CH + CO^2$$

The ortho-nitro-derivative has been used in the artificial preparation of indigo blue.

INDIGO.

$C^{16}H^{10}N^2O^2$

Indigo is obtained from different species of the genus *Indigofera;* it is also found in woad (*Isatis tinctoria*), but is no longer extracted from this plant.

In India, indigo is prepared by macerating the stems and leaves of the indigofera, collected at the time of flowering, with water, in vats where they are allowed to ferment. In 12 or 15 hours the liquid is drawn off into other vats, where it is agitated so as to bring it in contact with the air, an operation which occasions the formation of a blue precipitate. The brown liquor is then drawn off, and the deposit is boiled in copper vessels; it is then pressed between cloths and cut into cubical pieces and dried. In this form the indigo is delivered to commerce.

Indigo is not contained ready formed in the plants which serve for its manufacture. Schunck considers that these plants contain a substance analogous to the glucosides, *indican*, which is decomposed by fermentation into indigo, and *indoglucin*, $C^6H^{10}O^6$.

The indigo of commerce contains from 50 to 90 per cent. of coloring matter. It generally occurs in irregular masses, of which the shade varies from violet-blue to blackish-blue. The most valued varieties present a brilliant coppery reflection.

Pure indigo is called indigotin. It may be obtained by heating the indigo of commerce in a current of hydrogen, or by subliming it in small quantities between two watch-glasses (Chevreul). It then forms right rhombic prisms. Indigotin is insoluble in water, in cold alcohol, and in ether, but dissolves in hot oil of turpentine and in aniline. When carefully heated, and in small quantity, it volatilizes, and its vapor density corresponds to the formula $C^{16}H^{10}N^2O^2$.

Concentrated, or, better, fuming sulphuric acid dissolves indigo at 50 or 60°, forming a beautiful blue solution, which contains two acids, *indigomonosulphonic acid*, $C^{16}H^9N^2O^2.SO^3H$, and *indigodisulphonic* or *sulphindigotic acid*, $C^{16}H^8N^2O^2(SO^3H)^2$. The solution of indigo in sulphuric acid is used in dyeing; it is prepared by dissolving indigo in a hot mixture of fuming and ordinary sulphuric acids. The blue solution thus obtained is known as sulphate of indigo, Saxon blue, or composition blue.

Indigo carmine is the soluble sodium salt of the disulphonic acid. It is employed in dyeing animal fibres.

Boiling dilute nitric acid converts indigo into isatin. The concentrated acid converts it first into nitrosalicylic acid, $C^7H^5(NO^2)O^3$, and then into picric acid.

When heated with potassium hydrate, indigo is converted into *anthranilic* (orthamidobenzoic) *acid*, $C^7H^5(NH^2)O^2$, or into salicylic acid, which is formed at the expense of the anthranilic acid.

$$\underset{\text{Anthranilic acid.}}{C^7H^5(NH^2)O^2} + KOH = \underset{\text{Potassium salicylate.}}{KC^7H^5O^3} + NH^3$$

When indigo is distilled with potassium hydrate, aniline passes over, being formed at the expense of the anthranilic acid first formed.

$$\underset{\text{Anthranilic acid.}}{C^7H^7NO^2} = CO^2 + \underset{\text{Aniline.}}{C^6H^7N}$$

Synthesis of Indigo.—Various reactions have been discovered which are applicable to the synthesis of indigo. The most important of these are due to von Baeyer, to whom also belongs the honor of having first (1878) prepared indigo artificially. Only a few syntheses of indigo blue can be considered here.

1. Isatin chloride, which will be described farther on, when dissolved in acetic acid and treated with zinc dust yields a colorless liquid, which, when exposed to the air, assumes a blue color, and deposits crystals of indigotin. Ammonium sulphhydrate effects the reduction more rapidly than zinc and acetic acid (Baeyer and Emmerling).

2. There exists normally in human urine a compound which may also be prepared artificially, *indoxylsulphate of potassium.* When it is heated in the air, or treated with feeble oxidizing agents, it is converted into indigo (Baumann and Tiemann).

Potassium indoxylsulphate, $C^8H^6NO.SO^3K$, is a derivative of *indoxyl*, $C^8H^6(OH)N$, and the conversion of the latter into indigo is represented in the equation,

$$\underset{\text{Indoxyl.}}{2C^8H^6(OH)N} + O^2 = \underset{\text{Indigo.}}{C^{16}H^{10}N^2O^2} + 2H^2O$$

3. A much better yield of indigo blue is obtained by the action of reducing agents upon orthonitrophenylpropiolic acid (Baeyer, 1880).

$$\underset{\text{o-nitrophenylpropiolic acid.}}{C^6H^4(NO^2)C{\equiv}C{-}CO.OH} + 2H^2 = C^{16}H^{10}N^2O^2 + 2CO^2 + 2H^2O$$

For this purpose orthonitrocinnamic acid is converted into its dibromide and the latter boiled with alcoholic potash. The resulting nitro-acid, by careful treatment with glucose and potash, is reduced to indigo. The high price of the required materials has caused this process of manufacture to be abandoned.

4. Baeyer has made an interesting synthesis of indigo from orthonitrobenzaldehyde, $C^6H^4{<}\genfrac{}{}{0pt}{}{CHO(^1)}{NO^2(^2)}$. This compound reacts with acetone, in presence of sodium hydrate, forming a compound, $C^{10}H^9NO^3$, which contains the elements of acetone and orthobenzoic aldehyde, less one molecule of water.

$$\underset{\text{Orthobenzoic aldehyde.}}{C^7H^5(NO^2)O} + \underset{\text{Acetone.}}{C^3H^6O} = \underset{\substack{\text{Acetonic derivative of ortho-}\\\text{benzoic aldehyde.}}}{C^{10}H^9(NO^2)O} + H^2O$$

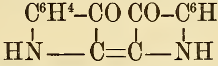
An excess of caustic soda converts this last body into acetic acid and indigo.

$$2C^{10}H^9NO^3 = C^{16}H^{10}N^2O^2 + 2C^2H^4O^2$$

5. According to Heumann, indigo is produced when phenylglycocoll is fused with potash.

$$C^6H^5NH.CH^2.COOH + O^2 = C^{16}H^{10}N^2O^2$$

Baeyer's researches indicate that the molecular structure of indigo is expressed by the following formula:



$$\begin{array}{llll} C^6H^4\text{–}CO & & CO\text{–}C^6H^4 & \\ \;\;| \qquad\;\; | & & \;| \qquad\quad | & \\ HN\text{—}C & = & C\text{—}NH & \end{array}$$

Indigo White, $C^{16}H^{12}N^2O^2$.—This body, which was discovered by Chevreul in 1812, results from the action of nascent hydrogen on indigo. It is produced when the latter substance is submitted to the action of alkaline solutions in presence of reducing matters, such as sulphurous or phosphorous acid, hydrogen sulphide, zinc, ferrous hydroxide, or grape-sugar.

$$C^{16}H^{10}N^2O^2 + H^2 = C^{16}H^{12}N^2O^2$$

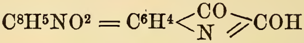
Indigo white is ordinarily prepared by introducing a mixture of indigo, ferrous sulphate, slaked lime, and water into a vessel, which should be entirely filled with the mixture and then hermetically sealed and allowed to stand for two days. A clear, alkaline solution is thus obtained, which is decanted, and supersaturated with hydrochloric acid, out of contact with the air. A deposit of indigo white is formed, and must be collected on a filter, rapidly washed with boiled water, and dried in a vacuum.

The body thus obtained has a dirty-white color, and is without either taste or smell. It is insoluble in water, but dissolves with a yellow color in alcohol, ether, and alkaline solutions. On contact with air it absorbs oxygen, and is converted into indigo blue. Nitric acid rapidly brings about this transformation.

Uses.—Indigo is largely used in dyeing. The principle of its application depends on the conversion of the indigo blue into indigo white by reducing agents. The reduced indigo white is soluble in alkaline solutions, and in this form is fixed on the fabrics: it is reconverted into indigo blue by exposure to the air. The mixture just indicated for the preparation of indigo white (ferrous sulphate, indigo, lime, and water) is most frequently employed. It constitutes what is known as the *vitriol vat.*

Schützenberger and de Lalande have described a process of dyeing with indigo, based on the employment of sodium hydrosulphite as the reducing agent.

ISATIN.



$$C^8H^5NO^2 = C^6H^4 \left< \begin{matrix} CO \\ N \end{matrix} \right> COH$$

This body was discovered by Erdmann and Laurent in 1841. It is a product of the oxidation of indigo by dilute nitric acid.

$$C^8H^5NO + O = C^8H^5NO^2$$

Pure isatin crystallizes sometimes in large, dark, gold-colored prisms, sometimes in small, reddish-yellow prisms having a brilliant lustre. It is only slightly soluble in cold water and in ether, but more soluble in boiling water, and very soluble in alcohol. Its solutions are brown-red. As it contains a carbonyl group, CO, isatin forms, like other ketones, crystallizable compounds with sodium acid sulphite, hydroxylamine, and phenylhydrazine. Isatin gives a characteristic reaction with thiophene. When a trace of the latter is added to a solution of isatin in sulphuric acid, a blue solution is obtained from which water precipitates *indophenin*, $C^{12}H^7NOS$. When distilled with potash, isatin yields aniline.

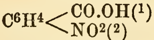
$$\underset{\text{Isatin.}}{C^8H^5NO^2} + 4KOH = 2K^2CO^3 + \underset{\text{Aniline.}}{C^6H^7N} + H^2$$

It dissolves in solutions of the alkaline hydroxides, forming violet solutions, which become yellow when boiled, the isatin being converted into *isatic* acid.

$$\underset{\text{Isatin.}}{C^8H^5NO^2} + H^2O = \underset{\text{Isatic acid.}}{C^8H^7NO^3}$$

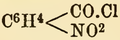
Synthesis.—Among various methods by which isatin may be prepared synthetically, the following, discovered by Baeyer, is most interesting:

Orthonitrobenzoyl chloride is converted into a cyanide, which, by hydrolysis, yields orthonitrobenzoyl-carbonic acid. By reduction of the latter, the corresponding amide, isatic acid, is obtained, and this is converted into isatin by dehydration.



$$C^6H^4 < \begin{matrix} CO.OH(^1) \\ NO^2(^2) \end{matrix}$$

Orthonitrobenzoic acid.

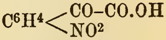


$$C^6H^4 < \begin{matrix} CO.Cl \\ NO^2 \end{matrix}$$

Orthynitrobenzoyl chloride.

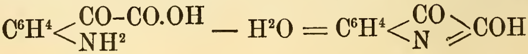
$$C^6H^4 < \begin{matrix} CO.CN \\ NO^2 \end{matrix}$$

Orthonitrobenzoyl cyanide.



$$C^6H^4 < \begin{matrix} CO-CO.OH \\ NO^2 \end{matrix}$$

Orthonitrobenzoyl carbonic acid.



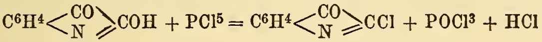
$$C^6H^4 < \begin{matrix} CO-CO.OH \\ NH^2 \end{matrix} - H^2O = C^6H^4 \left< \begin{matrix} CO \\ N \end{matrix} \right> COH$$

Isatic acid. Isatin.

By the action of chlorine, isatin yields substitution products These latter break up, like isatin itself, by the action of potassium hydrate, yielding *chloranilines* (Hofmann).

$$\underset{\text{Monochlorisatin.}}{C^8H^4ClNO^2} + 4KOH = 2K^2CO^3 + \underset{\text{Monochloraniline.}}{C^6H^6ClN} + H^2$$

When isatin is heated with phosphorus pentachloride, in presence of benzene, isatin chloride is obtained. This may serve, as has been seen, for the synthesis of indigo.



$$C^6H^4\left\langle{}^{CO}_{N}\right\rangle COH + PCl^5 = C^6H^4\left\langle{}^{CO}_{N}\right\rangle CCl + POCl^3 + HCl$$

Isatin. Isatin chloride.

Products of the Reduction of Isatin.—To isatin are related certain products of its reduction, which are interesting and which have been studied by Knop and Baeyer. They are

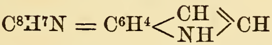
Dioxindol	$C^8H^7NO^2$;
Oxindol	C^8H^7NO;
Indol	C^8H^7N.

Isatic acid, which has been mentioned, may be considered as trioxindol, $C^8H^7NO^3$. Dioxindol and oxindol are formed successively by the action of sodium amalgam on an aqueous solution of isatin.

$$\underset{\text{Isatin.}}{C^8H^5NO^2} + H^2 = \underset{\text{Dioxindol.}}{C^8H^7NO^2}$$

$$\underset{\text{Dioxindol.}}{C^8H^7NO^2} + H^2 = \underset{\text{Oxindol.}}{C^8H^7NO} + H^2O$$

INDOL.

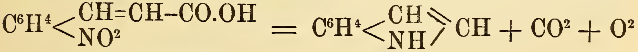


$$C^8H^7N = C^6H^4\left\langle{}^{CH}_{NH}\right\rangle CH$$

By reducing oxindol by zinc powder with the aid of heat, Baeyer obtained indol, the parent substance of the indigo group.

$$\underset{\text{Oxindol.}}{C^8H^7NO} + Zn = \underset{\text{Indol.}}{C^8H^7N} + ZnO$$

He has also made the synthesis of indol by heating orthonitrocinnamic acid with potassium hydroxide and iron filings.



$$C^6H^4\left\langle{}^{CH=CH-CO.OH}_{NO^2}\right. = C^6H^4\left\langle{}^{CH}_{NH}\right\rangle CH + CO^2 + O^2$$

Orthonitrocinnamic acid. Indol.

This reaction is a proof of the constitution of indol and its derivatives.

Properties.—Indol is a solid, crystallizing in brilliant colorless plates. It melts at 52°, and boils with partial decomposition at 245°. Its vapor is carried over by vapor of water. Its odor recalls that of naphthylamine. It dissolves readily in boiling water and in alcohol and ether. It has feebly basic properties.

Indol is formed normally during the pancreatic digestion by the breaking up of albuminoid matters. It occurs, together with its methyl derivative, *skatol*, in human excrements.

Skatol, C^9H^9N, has also been obtained synthetically in shining leaflets, having a strong fæcal odor, and melting at 95°.

NAPHTHALENE.

$C^{10}H^8$

This important compound was discovered by Garden in 1820, in coal-tar. Its composition was determined by Faraday, and its properties and transformations were principally studied by Laurent.

It is a frequent product of the dry distillation of organic matters, and is formed in abundance when these matters, or the products of their decomposition, are heated to high temperatures. Thus it is formed in large quantities when tar is passed through red-hot tubes.

Naphthalene is extracted from coal-tar, and is purified by crystallization in alcohol, or by sublimation.

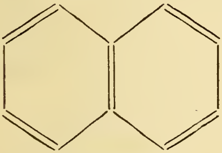
Properties.—Naphthalene occurs in rhombic tables when it has been sublimed, and is deposited in prisms from its ethereal solution. It melts at 79.2°, and boils at 218°. It is inflammable, and burns with a very smoky flame. It is insoluble in water, slightly soluble in cold alcohol, freely soluble in boiling alcohol and in ether.

By its general properties naphthalene is closely related to benzene: reagents affect it in a similar manner, and the compounds which result from the replacement of its hydrogen atoms, or the addition of hydrogen or chlorine, are analogous to the corresponding benzene derivatives.

Nitric acid attacks naphthalene, forming nitro-derivatives, among which is *nitro-naphthalene*, $C^{10}H^7(NO^2)$, which crystallizes in sulphur-yellow, rhombic prisms, fusible at 61°. By long boiling with dilute nitric acid, naphthalene is converted into phthalic acid and carbon dioxide. Nitronaphthalene oxidized in the same manner yields nitrophthalic acid.

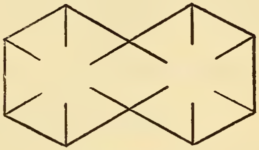
By the action of reducing agents nitronaphthalene is converted into *amidonaphthalene* (α-naphthylamine), just as aniline results from the reduction of nitrobenzene. This amidonaphthalene, upon oxidation, gives phthalic acid.

These facts are readily explained by assuming that the naphthalene molecule is formed by two benzene nuclei joined together, or condensed, in such a manner that two adjacent carbon atoms are common to both (Erlenmeyer), thus,—



Kekulé's formula.

or



Centric formula.

When phthalic acid is produced by the oxidation of naphthalene, one of the nuclei is destroyed, and the two carbon atoms which remain attached to the other nucleus become oxidized to carboxyl. In nitronaphthalene, under the same conditions, the nucleus which does not contain the nitro-group is oxidized, while in the case of amidonaphthalene the other nucleus, which contains the amido-group (in exactly the same place as the nitro-group of the former acid), is destroyed.

This view of the constitution of naphthalene derives support from various syntheses (see α-naphthol), and satisfactorily accounts for all known cases of isomerism in the naphthalene group.

According to the positions occupied by the substituting atoms or groups, we have two series of mono-derivatives. The *α-compounds* are those which result from the replacement of one of the four hydrogen atoms which occupy an ortho-position with respect to a carbon atom common to both nuclei; and in the *β-compounds* one of the remaining four positions is taken by the entering atom or group.

Numerous isomers are known of many of the disubstituted naphthalenes. When the substituting atoms or groups are identical, ten are theoretically possible, and when the substituents are different, as many as fourteen isomers may exist.

Chlorine acts on naphthalene in two ways: it combines directly, forming chlorides of naphthalene, and produces numerous substitution products which generally combine with an excess of chlorine. Bromine yields only substitution compounds.

Among all these products, we may mention the following:

$C^{10}H^8Cl^2$	naphthalene dichloride.	$C^{10}H^7Cl$	monochloronaphthalene.
$C^{10}H^8Cl^4$	naphthalene tetrachloride.	$C^{10}H^6Cl^2$	dichloronaphthalene.
$C^{10}H^6Cl^2Cl^4$	dichloronaphthalene tetrachloride.	$C^{10}H^5Cl^3$	trichloronaphthalene.
$C^{10}Cl^8Cl^2$	perchloronaphthalene dichloride.	$C^{10}Cl^8$	perchloronaphthalene.

Concentrated sulphuric acid dissolves naphthalene, forming

α- and β-Naphthalenesulphonic acids, $C^{10}H^7.SO^3H$

Naphthalenedisulphonic acids, $C^{10}H^6\left\{\begin{matrix}SO^3H\\SO^3H\end{matrix}\right.$

The formation of the first of these acids is expressed in the following equation:

$$\underset{\text{Naphthalene.}}{C^{10}H^8} + SO^4H^2 = H^2O + \underset{\text{Naphthalenesulphonic acids.}}{C^{10}H^7.SO^3H}$$

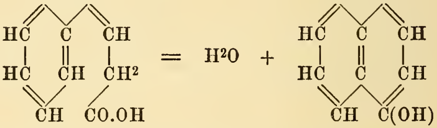
NAPHTHOLS.

$C^{10}H^7.OH$

These bodies are formed artificially by treating naphthalene with sulphuric acid, and fusing the naphthalenesulphonic acids so obtained with potassium hydrate (see page 678).

$$\underset{\text{Potassium naphthalene-sulphonate.}}{C^{10}H^7.SO^3K} + KOH = K^2SO^3 + \underset{\text{Naphthols.}}{C^{10}H^7.OH}$$

α-Naphthol is formed by heating *phenylisocrotonic acid** to its boiling-point (Fittig and Erdmann).



α-Naphthol forms silky needles or laminæ, soluble in alcohol, ether, and benzene, almost insoluble in cold water, slightly soluble in boiling water. It melts at 94°, and boils

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* This is obtained by the action of benzaldehyde upon succinate of sodium in presence of succinic anhydride.

$$C^6H^5.CHO + CO.OH–CH^2.CH^2.COOH = C^6H^5–CH=CH–CH^2CO.OH + CO^2 + H^2O$$

at 278–280°. Its aqueous solution produces a violet color with chloride of lime. When treated with reagents, it forms derivatives analogous to those of phenol.

β-naphthol is prepared from sodium β-naphthalenesulphonate. It crystallizes in small rhombic tables, fusible at 122°, and boils at 285–290°.

The mono- and di-sulphonic acids, obtained by heating the naphthols with sulphuric acid, are used in the preparation of many important coloring matters. Naphthol yellow, for example, is dinitro-α-naphthol sulphonic acid, and β-naphthol orange and rocellin (a substitute for cochineal) are complex derivatives of β-naphthol.

NAPHTHYLAMINES.

$$C^{10}H^{9}N = C^{10}H^{7}.NH^{2}$$

Zinin obtained amidonaphthalene in 1842 by reducing nitronaphthalene by ammonium sulphydrate, which may be advantageously replaced by iron and acetic acid.

$$\underset{\text{Nitronaphthalene.}}{C^{10}H^{7}(NO^{2})} + 3H^{2} = 2H^{2}O + \underset{\text{Naphthylamine.}}{C^{10}H^{7}(NH^{2})}$$

This *a-naphthylamine* forms fine, colorless needles. It sublimes at a gentle heat, melts at 50°, and boils without alteration at 300°. It has a fetid odor. Its reaction is not alkaline, although it perfectly neutralizes the acids, with which it forms well-defined and crystallizable salts. When exposed to the air, the salts of naphthylamine acquire a violet color, probably due to an absorption of oxygen.

β-naphthylamine is prepared by heating β-naphthol with ammonia in presence of zinc chloride. It crystallizes in pearly needles, fusible at 112°, and boils at 294°.

The reactions of the naphthylamines are analogous to those of aniline. Their diazo- and diazoamido-derivatives are applied in the preparation of valuable dyes.

ANTHRACENE AND PHENANTHRENE.

$$C^{14}H^{10}$$

Anthracene, which is solid, exists in the less volatile products of the distillation of coal-tar. It is obtained from the last products of this operation. The mass, which has a buttery consistence, is squeezed in a filter-press, and the residue is submitted to repeated distillations; it is finally purified by compression and several crystallizations in benzene.

Anthracene may be formed artificially by several processes.

1. By passing the vapor of toluene and various derivatives of that body through a tube heated to bright redness. Under these conditions, two molecules of toluene lose six atoms of hydrogen, and are converted into anthracene.

$$\begin{matrix} C^6H^5{-}CH^3 \\ C^6H^5{-}CH^3 \end{matrix} - 3H^2 = \begin{matrix} C^6H^4{=}CH \\ | \\ C^6H^4{=}CH \end{matrix}$$

2 mol. toluene. Anthracene.

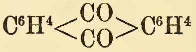
2. By heating phthalic anhydride with benzene in presence of aluminium chloride, orthobenzoylbenzoic acid is obtained; this, upon treatment with phosphorus pentoxide, is converted into anthraquinone, which, when reduced with zinc dust, yields anthracene.

In the pure state, anthracene forms monoclinic tabular crystals which are colorless, and present a magnificent blue fluorescence (Fritzsche). They melt at 213°, and distil without alteration at 345°.

By the action of oxidizing agents, such as chromic acid, anthracene is converted into a solid body, which crystallizes in beautiful yellow needles, fusible at 276°, and which can be sublimed without alteration. It is *anthraquinone*, $C^{14}H^8O^2$, a body which bears the same relations to anthracene as quinone to benzene.

C^6H^6 Benzene.	$C^{14}H^{10}$ Anthracene.
$C^6H^4O^2$ Quinone.	$C^{14}H^8O^2$ Anthraquinone.

The constitution of anthraquinone is expressed by the formula

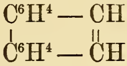


$$C^6H^4{<}\begin{matrix} CO \\ CO \end{matrix}{>}C^6H^4$$

By treating anthraquinone with bromine, Graebe and Liebermann converted it into dibromanthraquinone, $C^{14}H^6Br^2O^2$, a solid body, which crystallizes in yellow needles.

Phenanthrene.—Besides anthracene, there is another hydrocarbon of the same composition, which exists in coal-tar, and may also be formed artificially. It is called phenanthrene, and forms colorless scales, having a bluish fluorescence. It melts at 100°, and boils at 340°. It is soluble in 50 parts of alcohol at 13°; very soluble in hot alcohol, and in ether and benzene.

Its constitution is expressed by the formula



$$\begin{array}{lcl} C^6H^4 & - & CH \\ | & & \| \\ C^6H^4 & - & CH \end{array}$$

ALIZARIN.

$$C^{14}H^8O^4 = C^{14}H^6(OH)^2O^2$$

Natural State and Synthesis.—Alizarin is the name applied to the coloring matter of madder (*Rubia tinctorum*) which Robiquet was the first to extract in a pure state. Graebe and Liebermann made its synthesis in 1868 by heating dibromanthraquinone to 200° with potassium hydroxide.

$$\underset{\text{Dibromanthraquinone.}}{C^{14}H^6Br^2O^2} + 2KOH = 2KBr + \underset{\text{Alizarin.}}{C^{14}H^6(OH)^2O^2}$$

Alizarin does not exist ready formed in the madder plant. The latter contains a glucoside to which Robiquet has given the name *ruberythric acid*, and which is decomposed by the action of acids into alizarin and glucose.

$$\underset{\text{Ruberythric acid.}}{C^{26}H^{28}O^{14}} + 2H^2O = \underset{\text{Alizarin.}}{C^{14}H^8O^4} + \underset{\text{Glucose.}}{2C^6H^{12}O^6}$$

Preparation.—Alizarin may be extracted from madder by boiling the latter with a solution of alum. The filtered liquid, left to itself for some days, deposits impure alizarin as a brown-red precipitate, and holds in solution another coloring matter which is called *purpurin*.

The precipitated alizarin is purified by washing with dilute hydrochloric acid, and crystallization in alcohol. The product thus obtained is exhausted with a boiling solution of alum, which removes the purpurin, and is finally dissolved in ether, which deposits it in crystals.

Alizarin is now almost exclusively obtained from anthracene. This hydrocarbon is oxidized to anthraquinone, and the latter body treated with fuming sulphuric acid to convert it into anthraquinonesulphonic acid. The sodium salt of this acid is fused with sodium hydroxide, and a small quantity of potassium chlorate is added to the fused mass.

$$C^{16}H^7(SO^3Na)O^2 + 3NaOH + O^2 = C^{14}H^6(ONa)^2O^2 + Na^2SO^4 + 2H^2O$$

The alkaline mass is dissolved in water, precipitated by hydrochloric acid, and the precipitate purified by crystallization from toluene and finally by sublimation.

The artificial product is delivered to commerce in the form of a paste, but the reaction by which it is formed produces, at the same time, isomerides which remain mixed with the alizarin, properly so called. Eight isomeric compounds are known having the composition $C^{14}H^8O^4$. One of them, purpuroxanthin, is contained in small quantity in madder.

Properties of Alizarin.—Alizarin forms long, brilliant, orange-yellow prisms. It is scarcely soluble in cold water, but dissolves better in boiling water, and is soluble in alcohol, ether, and carbon disulphide. It melts at 278°, and sublimes in long, orange-red needles. It dissolves in sulphuric acid with a blood-red color, and water precipitates it without alteration from this solution. Boiling dilute nitric acid converts it into oxalic and phthalic acids. When alizarin is heated to redness with zinc powder, it is reduced to anthracene (Graebe and Liebermann).

Alizarin forms combinations with the bases; it dissolves in ammonia, with a purple color, and in the caustic alkalies, yielding purple solutions which have a blue reflection.

Uses.—Alizarin produces a red color (Turkey red) on fabrics that are mordanted with alumina, or with ricinoleic-sulphonic acid,* and a violet on those which are mordanted with ferric oxide.

PURPURIN.

$C^{14}H^5(OH)^3O^2$

This name is given to another coloring matter which may be extracted from madder, and which has already been mentioned. It appears to exist in the plant as a glucoside. It dissolves readily in alcohol and ether, with a red color.

It crystallizes from weak alcohol in orange-colored needles, which contain one molecule of water of crystallization. From concentrated alcohol, it deposits in red, anhydrous needles. When heated, it melts at 254°, and sublimes in red needles. With aluminium mordants, it gives scarlet-red shades.

Purpurin is an oxyalizarin, or a trioxyanthraquinone, $C^{14}H^5(OH)^3O^2$: indeed, it may be obtained by treating a

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* This is prepared by treating castor oil with sulphuric acid.

solution of alizarin in concentrated sulphuric acid with an oxidizing agent, such as manganese dioxide (de Lalande). Inversely, the reduction of purpurin reproduces alizarin (Rosenstiehl). It undergoes a complete reduction, and is converted into anthracene, when heated with zinc-dust.

Anthrapurpurin and *flavopurpurin* are isomeric with the purpurin just described; they are contained in commercial alizarin.

The hydrocarbons of the aromatic series and the products obtained from them by substitution and addition all contain closed chains consisting of carbon atoms exclusively. There exist, however, very numerous compounds of an "aromatic character" whose nuclei are not made up entirely of carbon atoms, but in which other elementary atoms, such as oxygen, sulphur, and nitrogen, form part of the closed chains.

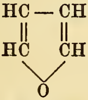
Among these bodies we will consider furfurane, thiophene, pyrrol, pyridine, and quinoline, and some of their more important derivatives.

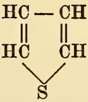
FURFURANE, THIOPHENE, AND PYRROL.

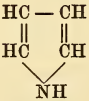
When the barium salt of pyromucic acid (page 662) is heated with a little soda-lime, a colorless liquid of peculiar odor, *furfurane*, C^4H^4O, distils.

Thiophene, C^4H^4S, and *pyrrol*, C^4H^4NH, are similar bodies which occur in small quantities in coal-tar.

The striking analogies in the chemical behavior of these bodies, as well as their close resemblance to benzene, are best accounted for in the formulæ


Furfurane.


Thiophene.


Pyrrol.

Furfurane is contained in pine-tar. It boils at 32°, is insoluble in water, but miscible with alcohol and ether.

Its most important derivative is *furfurol*, $C^4H^3O{-}CHO$, an aldehyde. This is formed in the dry distillation of many carbohydrates, and most readily by heating bran or sawdust with dilute sulphuric acid. Furfurol is a colorless liquid of peculiar odor. It boils at 162°. When heated with silver oxide and water it is oxidized to *pyromucic acid*, $C^4H^3O.COOH$, which also results from the dry distillation of mucic acid.

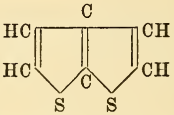
Pyromucic acid crystallizes in colorless leaflets, melting at 134°. Treated with bromine and water, it is converted into fumaric acid, carbon dioxide being given off.

Thiophene was discovered by V. Meyer in commercial benzene. Its isolation from this source offers considerable difficulty, but a very pure product may be obtained synthetically by heating a mixture of dry sodium succinate and phosphorus trisulphide (Volhard and Erdmann).

The physical as well as the chemical properties of thiophene are remarkably like those of benzene. It is a colorless, mobile liquid, which congeals at very low temperatures. Its boiling-point is at 84°. The derivatives of thiophene are made in the same manner as those of benzene, which they closely resemble in their properties.

Of the homologues of thiophene, *thiotolene*, $C^4H^3S.CH^3$, and *thioxene*, $C^4H^2S(CH^3)^2$, occur in coal-tar. Having nearly the same boiling-points as the corresponding benzene derivatives, they accumulate in the fractions constituting commercial toluene and xylene.

Thiophtene, $C^6H^4S^2$, may be regarded as the "naphthalene" of the thiophene group. Its constitution is expressed by the formula



Nitrothiophene, $C^4H^3S.NO^2$, is one of the products of the action of nitric acid upon thiophene. It is a solid, crystallizing in monoclinic prisms, and melting at 44°. It boils at 224°. Upon reduction with tin and alcoholic hydrochloric acid, it yields *amidothiophene*, $C^4H^3S.NH^2$. The free base, which is a colorless oil, is very unstable. It is not diazotized by treatment with nitrous acid, but it forms azo-compounds with diazo-derivatives of benzene.

Thiophenesulphonic acid, $C^4H^3S.SO^3H$, is easily obtained by the direct sulphonation of thiophene: by repeated treatment with sulphuric acid, commercial benzene may be deprived of the admixed thiophene. When superheated with water, the sulphonic acid is resolved into thiophene and sulphuric acid.

The very numerous derivatives of thiophene that have been described by V. Meyer and others also include phenols, aldehydes, ketones, carboxylic acids, etc.

The "indophenin" reaction, which has already been given (page 736), constitutes the most delicate test for thiophene.

Pyrrol was discovered by Runge. It is present in coal-tar and in bone-oil, and is produced in the dry distillation of ammonium mucate. When freshly prepared it is a colorless liquid, which turns brown in the air. It boils at 131°. Although practically insoluble in water, it mixes readily with alcohol and ether. Metallic potassium converts it into *potassium-pyrrol*, $C^4H^4(NK)$, a crystalline body which is decomposed by water into pyrrol and potassium hydroxide. When treated with nascent hydrogen, pyrrol is reduced to *pyrroline*, $C^4H^6(NH)$, a strong base, boiling at 91°. By heating this base with hydriodic acid, it takes up more hydrogen and is converted into *pyrrolidine*, $C^4H^8(NH)$, an alkaline liquid which boils at 83°.

The most characteristic test for pyrrol consists in exposing to its vapor a pine shaving moistened with hydrochloric acid: it assumes a deep-red color.

A great variety of substitution products of pyrrol have been obtained. Both the hydrogen of the imido-group and that united with the carbon atoms may be replaced by alkyl groups.

Iodol (tetraiodopyrrol), $C^4I^4(NH)$, is an odorless substitute for iodoform. It is made by the action of iodine and an alkali upon pyrrol. It crystallizes in yellow leaflets; soluble in alcohol.

PYRIDINE AND ITS DERIVATIVES.

From the oil obtained by the dry distillation of animal matters, and which was formerly known as the *bone oil of Dippel*, Anderson has extracted a series of bases isomeric with the aromatic amines. Among these bases are the following:

Pyridine, C^5H^5N.
Picolines, C^6H^7N, isomeric with aniline.
Lutidines, C^7H^9N, isomeric with toluidine.
Collidines, $C^8H^{11}N$, isomeric with xylidines.
Parvolines, $C^9H^{13}N$, etc.

These bases also occur in coal-tar; in fact, they are generally formed when nitrogenous organic matter is subjected to destructive distillation.

Some of the bases, as well as many of their derivatives, have been obtained synthetically. The following are the most important modes of formation that have been observed:

1. Pyridine is produced when a mixture of acetylene and hydrocyanic acid is passed through a red-hot porcelain tube.

$$2C^2H^2 + HCN = C^5H^5N$$

2. By the action of ammonia upon certain aldehydes, oxidized bases are formed, thus:

$$\underset{\text{Acrolein.}}{2C^3H^4O} + NH^3 = \underset{\text{Acrolein-ammonia.}}{C^6H^9NO} + H^2O$$

$$\underset{\text{Crotonaldehyde.}}{2C^4H^6O} + NH^3 = C^8H^{13}NO + H^2O$$

By dehydration these condensation products yield pyridic bases.

$$C^6H^9NO = \underset{\text{Picoline.}}{C^6H^7N} + H^2O$$

$$C^8H^{13}NO = \underset{\text{Collidine.}}{C^8H^{11}N} + H^2O$$

3. Baeyer and Ador have also obtained a collidine (aldehydine) by heating aldehyde-ammonia in closed vessels.

$$4C^2H^4O + NH^3 = \underset{\text{Collidine.}}{C^8H^{11}N} + 4H^2O$$

4. Pyridine is formed by the action of methylene iodide and sodium methylate upon potassium pyrrol.

5. *Piperidine* (hexahydropyridine) results when pentamethylene hydrochloride is rapidly heated.

$$C^5H^{10}(NH^2)^2.HCl = C^5H^{11}N + NH^4Cl$$

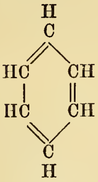
This base yields pyridine when heated with concentrated sulphuric acid.

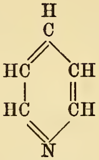
6. A dihydro-dicarboxylic acid of collidine is obtained when aldehyde-ammonia is heated with acetoacetic ether.

$$2C^6H^{10}O^3 + CH^3.CHO + NH^3 = C^5N(H^2)(CH^3)^3(CO.OH)^2 + 3H^2O$$

The two additive hydrogen atoms are removed by treatment with nitrous acid.

The first term of the series is pyridine. According to an ingenious hypothesis of Körner, this compound has a constitution analogous to that of benzene, the five carbon atoms and the nitrogen atom forming a closed chain similar to the benzene nucleus.


Benzene.


Pyridine.

The higher homologues of pyridine, such as picoline, lutidine, and collidine, then result from the substitution of one or more methyl or other alkyl groups for the hydrogen of pyridine. According to the position of these groups with relation to the nitrogen atom in the pyridic chain, isomerism will occur, precisely analogous to that which we have considered in the case of the aromatic amines.

Pyridine may, indeed, be regarded as a mono-substituted benzene, its nitrogen occupying the place of a CH group. The mono-derivatives of pyridine are therefore analogous to the di-derivatives of benzene. They exist in three isomeric forms, designated as α-, β-, and γ-derivatives, and corresponding to the ortho-, meta-, and para-disubstituted benzenes.

We cannot extend these theoretical considerations. However, the pyridic bases and quinoline, which is related to them, appear to take part in the constitution of the natural alkaloids. Indeed, some of the latter, such as cinchonine and brucine, yield by distillation with potassium hydrate a mixture of pyridic bases and quinoline.

Pyridine, C^5H^5N.—This base has been obtained from the animal oil of Dippel by Anderson, and from coal-tar by Greville Williams.

It may be prepared from these products, but is best obtained in a pure condition by heating nicotinic acid (see page 750) with lime.

$$C^5H^4N.COOH = C^5H^5N + CO^2$$

It is a colorless liquid, having a characteristic odor, and at 0° a density 1.003. It boils at 115°, and is soluble in water and alcohol. It is an energetic base, forming deliquescent salts. Sodium converts it into a polymeride, *dipyridine*, $C^{10}H^{10}N^2$.

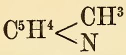
Piperidine, or hexahydropyridine, $C^5H^{11}N$, is formed by the action of sodium upon a hot alcoholic solution of pyridine.

It is a colorless liquid, whose odor suggests that of pepper. It boils at 106°, and is miscible with water and alcohol.

Piperidine is a powerful base which forms crystalline salts with acids.

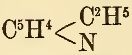
We cannot describe the other pyridic bases: they all exist in several isomeric modifications. Thus, there are three picolines, or methyl-pyridines, $C^5H^4(CH^3)N$; nine lutidines, of which six are dimethyl-pyridines and the others ethyl derivatives. The collidines comprise trimethyl-pyridines, methylethyl-pyridines (aldehydine), and propyl-pyridines.

Under the action of oxidizing agents, such as potassium permanganate in alkaline solution, the pyridic bases behave like aromatic hydrocarbons. The lateral chains are oxidized and converted into carboxyl, CO.OH. Thus methylpyridine (β-picoline) and ethylpyridine (β-lutidine) yield the same *pyridine-carboxylic* (*nicotinic*) *acid*.



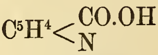
$$C^5H^4 < \begin{matrix} CH^3 \\ N \end{matrix}$$

and



$$C^5H^4 < \begin{matrix} C^2H^5 \\ N \end{matrix}$$

yield

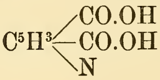


$$C^5H^4 < \begin{matrix} CO.OH \\ N \end{matrix}$$

Methylpyridine. Ethylpyridine. Nicotinic acid.

Picolinic acid and *isonicotinic acid* are the corresponding α- and γ-derivatives.

There are six *pyridine-dicarboxylic acids.*



$$C^5H^3 \begin{matrix} \diagup CO.OH \\ - CO.OH \\ \diagdown N \end{matrix}$$

QUINOLINE.

C^9H^7N

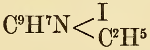
Gerhardt obtained this base by distilling certain natural alkaloids, among which are quinine and cinchonine, with potassium hydroxide. It is identical with a base which Runge had extracted, several years previous, from coal-tar, and which he named *leucol* or *leucoline*.

Considerable quantities of quinoline are found in bone-oil. Being accompanied by isomeric and homologous bases (isoquinoline, quinaldine, lepidine, etc.), the pure substance cannot readily be isolated from any of these sources. It may, however, be prepared synthetically by a method which was discovered by Skraup, and which consists in heating aniline with glycerol and sulphuric acid in presence of nitrobenzene.

$$\underset{\text{Aniline.}}{C^6H^5.NH^2} + \underset{\text{Glycerol.}}{C^3H^8O^3} + O = \underset{\text{Quinoline.}}{C^9H^7N} + 4H^2O$$

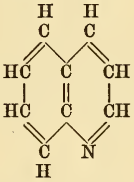
The sulphuric acid aids the condensation by its dehydrating action, and the nitrobenzene plays the part of an oxidizing agent.

Quinoline is a mobile, colorless, strongly refracting liquid. Its density at 0° is 1.081, and it boils at 238°. It has a penetrating odor and a very bitter taste. It is insoluble in water; with acids it forms well-defined salts, and behaves as a tertiary base. With ethyl-iodide it forms quinoline ethiodide.



$$C^9H^7N{<}^{I}_{C^2H^5}$$

Quinoline is related to the true aromatic compounds, and at the same time to the pyridic bases. Its synthetical formation and its reactions have led to the following representation of its constitution, which is that of naphthalene, in which a group CH is replaced by an atom of nitrogen.



Quinaldine, or *α*-methylquinoline, $C^9H^6(CH^3)N$, is present in coal-tar, and is formed when aniline is heated with paraldehyde and hydrochloric acid (Doebner and Miller).

$$C^6H^5.NH^2 + 2C^2H^4O + O = C^{10}H^9N + 3H^2O$$

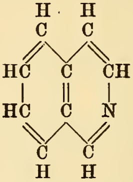
It is a colorless liquid, boiling at 246°.

Besides quinaldine, there exist six mono-methylquinolines and many higher homologues.

Isoquinoline is very similar to its isomeride, quinoline. It is present in coal-tar, and has been obtained synthetically.

It is a solid, melting at 22°. Its boiling-point is the same as that of quinoline.

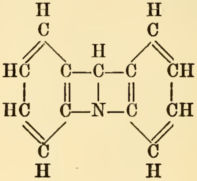
When oxidized with potassium permanganate it yields *cinchomeronic* and phthalic acids. The former is one of the pyridine dicarboxylic acids; its carboxyl groups are in the β- and γ-positions. Hence the constitution of isoquinoline must be



Acridine, $C^{13}H^{9}N$, is another solid base contained in coal-tar. It accompanies anthracene, from which it may be separated by treatment with sulphuric acid.

It crystallizes in colorless needles, fusible at 110°, but subliming even below this temperature. It boils at 360°. It forms salts, which in dilute solutions exhibit a blue fluorescence.

The constitution of acridine is expressed by the formula



ALKALOIDS.

This term has been applied to the nitrogenous organic bases which are derived from plants. Many of these substances are possessed of poisonous or medicinal properties; they constitute the "active principles" of vegetable drugs.

The alkaloids cannot be said to represent a sharply-defined group of compounds. While the constitution of only a small number of these complex bodies is clearly established, it is well known that the great majority are derivatives of pyridine, quinoline, and isoquinoline, others are closely related to uric acid, and still others belong to different groups of the fatty and aromatic series.

It is customary to divide the alkaloids into two classes, the first of which includes the liquid and volatile bases, the second those which are solid. The latter generally contain oxygen, the former do not.

With few exceptions the alkaloids are very sparingly soluble in water; most of them, however, dissolve readily in alcohol, ether, chloroform, benzene, etc., and they all form soluble salts with acids.

A number of special reagents are used to isolate and identify the alkaloids. Platinic and auric chlorides form well-defined crystalline double salts (chloroplatinates and chloraurates) with their hydrochlorides, and tannic acid, phosphomolybdic acid, potassium mercuric iodide, etc., produce precipitates in their solutions. From these insoluble compounds the alkaloids can be regenerated with the aid of alkalies.

CONINE.

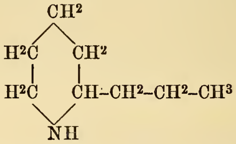
$C^8H^{17}N$

This is a liquid and volatile alkaloid which is extracted from the hemlock (*Conium maculatum*). The seeds of this plant are crushed and distilled with sodium hydrate. The alkaline liquid which collects in the receiver is neutralized by dilute sulphuric acid, evaporated to a syrupy consistence, and the residue exhausted with a mixture of alcohol and ether, which dissolves the conine sulphate, and leaves ammonium sulphate. The alcohol and ether are driven out by evaporation; a concentrated solution of sodium hydrate is added to the conine sulphate, and the liquid is distilled. The conine passes with a certain quantity of water, on which it floats. It is separated, dried over some fragments of calcium chloride, and rectified in a vacuum.

Ladenburg made the synthesis of conine by heating α-picoline with aldehyde and subjecting the resulting α-allylpyridine to the action of nascent hydrogen.

$$\underset{\alpha\text{-picoline.}}{C^5H^4(CH^3)N} + CH^3{-}CHO = H^2O + \underset{\alpha\text{-allylpyridine.}}{C^5H^4(CH{=}CH{-}CH^2)N}$$

Conine is therefore α-propylpiperidine.



It contains one asymmetric carbon atom, and exists in three stereoisomeric modifications. Natural conine is dextrorotatory, and the synthetic conine which is inactive can readily be broken up into the two active varieties of opposite rotatory power.

Conine is a limpid, oleaginous liquid, having a penetrating and nauseating odor, recalling that of hemlock. It boils at 168°. It is slightly soluble in water, more so in cold than in hot water, so that a cold, saturated solution becomes clouded when heated. It is very soluble in alcohol and in ether. It has a strongly alkaline reaction, immediately restoring the blue color to reddened litmus-paper. It precipitates many metallic oxides from solutions of their salts. On contact with the air it becomes brown and resinified. The density of conine at 0° is 0.886.

Conine is often mixed with methylconine, a compound derived from conine by the substitution of a methyl group for an atom of hydrogen, and formed artificially by the action of methyl iodide on conine.

Wertheim has obtained from the flowers and seeds of the hemlock a solid alkaloid, which he has named *conhydrine*, $C^{18}H^{17}NO$, and which contains the elements of conine plus a molecule of water.

NICOTINE.

$C^{10}H^{14}N^{2}$

This alkaloid exists in tobacco. It may be obtained by exhausting tobacco with boiling water and evaporating the liquid to a syrupy consistence on a water-bath; the still hot extract is then mixed with twice its volume of alcohol, allowed to settle, and the alcoholic liquid separated from the thick lower layer, which contains much calcium malate. The alcohol is distilled off, and the residue exhausted with strong alcohol, of which the greater part is then driven off by evaporation. Potassium hydrate is added to the alcoholic extract, which is then agitated with ether, which dissolves the nicotine set free. A few grammes of oxalic acid added to the ethereal solution causes the separation of a syrupy deposit which contains oxalate of nicotine. This salt is decomposed by potash and the nicotine set free is dissolved out by ether. After the ether has been expelled on a water-bath, the nicotine is distilled in a current of hydrogen, that part being retained which passes above 180° (Schloesing).

Properties.—Nicotine is a colorless liquid, having an offensive, penetrating odor. It rotates the plane of polarization to the left. It boils between 240 and 250°, not, however, without undergoing partial decomposition. Above 146°, it begins to distil slowly, and at 100° it emits white vapors; at ordinary temperatures it gives off so much vapor that a rod wet with hydrochloric acid will be enveloped in white fumes if held a little distance above the nicotine.

Nicotine dissolves in all proportions in water, alcohol, and ether. It has a strongly alkaline reaction, and perfectly neutralizes the acids, and precipitates the metallic oxides from solutions of their salts. It is one of the most violent poisons known. It is a diatomic base; its chloroplatinate, which crystallizes in red prisms, has the composition

$$C^{10}H^{14}N.(HCl)^2.PtCl^4$$

PIPERINE.

$C^{17}H^{19}NO^3$

This alkaloid occurs in various species of pepper, particularly in black pepper, from which it may be extracted by alcohol. It crystallizes in prisms, fusible at 129°, very soluble in alcohol and ether, and insoluble in water. Its reaction is neutral, and its salts are not well defined. Sulphuric acid dissolves it, producing a dark-red color. When heated with alcoholic potash, it yields piperidine (p. 750) and *piperic acid.*

$$C^{17}H^{19}NO^3 + H^2O = \underset{\text{Piperidine.}}{C^5H^{11}N} + \underset{\text{Piperic acid.}}{C^{12}H^{10}O^4}$$

ATROPINE.

$C^{17}H^{23}NO^3$

This alkaloid, which is largely used in the treatment of diseases of the eyes, was discovered in 1833 by Geiger and Hesse, and by Mein, in the deadly nightshade (*Atropa Belladonna*).

It has been obtained also from the thorn-apple (*Datura Stramonium*).

It appears that atropine does not exist already formed in the deadly nightshade, but that it is formed during extraction from an isomeric alkaloid, *hyoscyamine*, which, together with another alkaloïd, *hyoscine*, exists naturally in the plant.

Preparation.—Belladonna-root is reduced to powder and digested several days with alcohol. The solution is filtered, slaked lime, in quantity equal to one-twentieth of the weight of root employed, is added, the solution again filtered, and rendered slightly acid with sulphuric acid. It is again filtered, and $\frac{2}{3}$ of the alcohol distilled off. The residue is concentrated at a gentle heat, and a concentrated solution of potassium carbonate is added until the liquid, now neutral, begins to be clouded. After a few hours, the precipitate is separated by filtration, and potassium carbonate is added to the filtrate as long as impure atropine is precipitated. The next day, the deposit is collected on a filter, pressed, dried, and exhausted with 96 per cent. alcohol. The solution is decolorized with animal charcoal, the liquid diluted with six times its volume of water and put in a cool, dark place. The atropine is deposited in twenty-four hours in crystalline needles.

Properties.—Atropine crystallizes in delicate needles, fusible at 115°. It dissolves in 300 parts of cold water, and in almost all proportions of alcohol. It is less soluble in ether. At 140° it volatilizes, but the greater part of it is decomposed.

In burning, atropine diffuses the odor of benzoic acid. When it is treated with potassium dichromate and sulphuric acid, benzyl aldehyde distils and benzoic acid is formed (Pfeiffer).

Atropine is a virulent poison. The *sulphate of atropine* is much used in ophthalmic surgery. A single drop, even of a very dilute solution of this salt, produces dilatation of the pupil.

When a small quantity of atropine is moistened with nitric acid, evaporated to dryness, and the residue treated with alcoholic potash, a rich violet color is developed (Vitali).

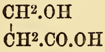
A solution of bromine in aqueous hydrobromic acid throws down from solutions of atropine a yellow amorphous precipitate which soon becomes converted into characteristic crystals (Wormley).

When heated with baryta water, or with hydrochloric acid, atropine breaks up into *tropine* and *tropic acid* (Lossen and Kraut).

$$\underset{\text{Atropine.}}{C^{17}H^{23}NO^{3}} + H^{2}O = \underset{\text{Tropic acid.}}{C^{9}H^{10}O^{3}} + \underset{\text{Tropine.}}{C^{8}H^{15}NO}$$

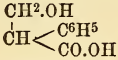
Tropine is an energetic base, soluble in water, alcohol, and ether: from the latter solvent it separates in tables, fusible at 61°. It is a derivative of piperidine.

Tropic acid is the phenyl derivative of hydracrylic acid.



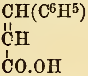
$$\begin{array}{l} CH^{2}.OH \\ | \\ CH^{2}.CO.OH \end{array}$$

Hydracrylic acid.



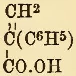
Tropic acid.

It forms small crystals, fusible at 117°. By long boiling with hydrochloric acid, or with baryta water, it loses a molecule of water, and is converted into atropic acid, $C^{9}H^{8}O^{2}$, which is isomeric with cinnamic acid.



$$\begin{array}{l} CH(C^{6}H^{5}) \\ \| \\ CH \\ | \\ CO.OH \end{array}$$

Cinnamic acid.



$$\begin{array}{l} CH^{2} \\ \| \\ C(C^{6}H^{5}) \\ | \\ CO.OH \end{array}$$

Atropic acid.

Tropic acid and tropine combine, forming a true salt. When long heated with dilute hydrochloric acid, this salt loses the elements of water, and atropine is formed.

$$\underset{\text{Tropine tropate.}}{C^{8}H^{15}NO.C^{9}H^{10}O^{3}} = H^{2}O + \underset{\text{Atropine.}}{C^{17}H^{23}NO^{3}}$$

This partial synthesis of atropine has been effected by Ladenburg.

COCAINE.

$C^{17}H^{21}NO^{4}$

Cocaine was obtained by Niemann from coca leaves (*Erythroxylon Coca*). It has been studied by Wöhler and Lassen.

Preparation.—Coca leaves are exhausted several times with water at a temperature between 60 and 80°, and the solution is precipitated by lead acetate, and filtered; the filtered solution is freed from excess of lead acetate by addition of sodium sulphate and then, after a new filtration, the solution is evaporated. Sodium carbonate is then added until it produces a faint alkaline reaction; the liquid is lastly agitated with ether, which takes up the cocaine and leaves it on evaporation.

Properties.—Cocaine crystallizes in monoclinic prisms which are colorless and odorless, and fuse at 98°. It is but slightly soluble in cold water, more soluble in alcohol, very soluble in ether. Its taste is bitter, its reaction slightly alkaline. When heated with hydrochloric acid, it absorbs two molecules of water and decomposes into methyl alcohol, benzoic acid, and a crystallizable alkaloid, *ecgonine*, $C^9H^{15}NO^3$.

$$C^{17}H^{21}NO^4 + 2H^2O = C^9H^{15}NO^3 + CH^4O + C^7H^6O^2$$

According to Einhorn, ecgonine is a carboxylic acid of tropine.

Cocaine has been made artificially by successively introducing the benzoyl and methyl groups into ecgonine.

It is used in surgery as a local anæsthetic.

ALKALOIDS OF CINCHONA.

The different cinchona barks owe their febrifuge virtues to several alkaloids, of which the more important, *quinine* and *cinchonine*, were discovered by Pelletier and Caventou in 1820. Since then, *quinidine* and *cinchonidine* have been isolated, the first isomeric with quinine, the second with cinchonine. All of these are crystallizable alkaloids. When their sulphates are heated with sulphuric acid, they are converted into two new isomerides, *quinicine* and *cinchonicine*. The latter are not crystallizable.

Hence the following six alkaloids are known:

Cinchonine, cinchonidine, cinchonicine . . .	$C^{19}H^{22}N^2O$
Quinine, quinidine, quinicine	$C^{20}H^{24}N^2O^2$

These alkaloids are by no means distributed in the same manner in the numerous species and varieties of cinchona bark, and these barks are not equally rich in alkaloids. The following summary gives some indications of this difference:

1 KILOGRAMME OF BARK YIELDS:		QUININE SULPHATE.	CINCHONINE SULPHATE.
Yellow bark (*Cinchona Calisaya*) . .		30–32 grammes.	6–8 grammes.
Red bark (*Cinchona succirubra*) . . .		20–25 "	8 "
Pale bark	Loxa (*Cinchona condaminea*)	8 "	6 "
	Huanuco (*Cinchona nitida*)	6 "	12 "

Quinic Acid.—In the cinchonas, the alkaloids are combined with a well-defined, crystallizable acid, whose composition is expressed by the formula $C^7H^{12}O^6$. It is *quinic acid.*

This acid is obtained from the calcium quinate which is deposited in a few days, when the liquid separated from the quino-calcium precipitate is concentrated and allowed to stand (see farther on).

This calcium quinate is purified by several crystallizations, and its solution decomposed by oxalic acid. The quinic acid remains in the solution, and separates in crystals when the liquid is properly concentrated.

Quinic acid crystallizes in beautiful, transparent, oblique rhombic prisms. It is very soluble in water, and but slightly soluble in absolute alcohol. It melts at 161.5°, losing at the same time the elements of water.

Its aqueous solution rotates the plane of polarization to the left.

Quinic acid is the benzene addition compound, hexahydro-tetrahydroxybenzoic acid, $C^6H^7(OH)^4CO.OH$. When distilled with a mixture of sulphuric acid and manganese dioxide, it yields quinone, $C^6H^4O^2$.

QUININE.

$C^{20}H^{24}N^2O^2$

When ammonia is added to a solution of sulphate of quinine, a white precipitate of quinine is obtained, which, when left to itself and moistened with water from time to time, becomes crystalline by combining with one molecule of water.

Quinine is very bitter. It dissolves in 2266 parts of cold, and in 760 parts of boiling water; in 1.33 parts of cold alcohol, and 22.6 parts of ether (Regnault). It is also soluble in chloroform. Its alcoholic solution turns the plane of polarization to the left. When water at 32° is added to the hot alcoholic solution until a cloud begins to form, resinous quinine is deposited, and also colorless, prismatic crystals containing three molecules of water. From its ethereal or alcoholic solution, quinine crystallizes in delicate silky needles, fusible at 177°.

Quinine is diacid, that is, each molecule of the base requires for the formation of saturated salts, two molecules of a monobasic or one of a dibasic acid. It is a tertiary base uniting directly with the alcoholic iodides to form quaternary iodides.

Quinine Sulphate, $2(C^{20}H^{24}N^2O^2).SO^4H^2 + 8H^2O$.—*Preparation.*—This salt, which is extensively used in medicine, is prepared by boiling yellow bark (*Cinchona Calisaya*) or red bark (*Cinchona succirubra*) with water acidulated with sulphuric or hydrochloric acid. A slight excess of milk of lime is then added in small quantities to the decoction, and precipitates not only the quinine and cinchonine, but all of the coloring matter (cinchonine red), which forms an insoluble compound with the lime. The quinic acid remains in solution as calcium quinate. The quino-calcium deposit contains also the excess of lime, and calcium sulphate, in case sulphuric acid has been employed. It is collected on a cloth, allowed to drain, pressed, and dried. It is then exhausted with boiling alcohol, which dissolves out the alkaloids.

The alcoholic solution, concentrated by distillation, deposits the cinchonine in crystals, in case the bark employed be rich in that alkaloid. The mother-liquor retains the quinine. It is neutralized by sulphuric acid, and the alcohol distilled off. The quinine sulphate crystallizes in a mass on cooling, and is purified by redissolving it in boiling water and adding animal charcoal.

It has been proposed to replace the alcohol, in the extraction of the quino-calcium deposit, by certain fixed or volatile oils, which dissolve quinine. For this purpose, petroleum and the heavy oils produced by the distillation of tar, and which are abundant in commerce, may be used with advantage. After having dissolved the alkaloids in these oils, the solutions are agitated with dilute sulphuric acid, which removes from them the quinine and cinchonine. Sulphates are thus obtained which may be crystallized.

Properties.—Quinine sulphate occurs in long, thin, light needles, which are somewhat flexible. It requires for its solution 740 parts of water at 13°, or about 30 parts of boiling water. The solution restores the blue color to reddened litmus-paper. It turns the plane of polarization to the left (Bouchardat). When crystallized in alcohol, quinine sulphate contains only two molecules of water.

If some quinine sulphate be suspended in cold water, and a few drops of sulphuric acid be added, the sulphate dissolves and the liquid acquires a blue fluorescence.

In this case, quinine sulphate, which is a basic salt, is converted into a salt, $C^{20}H^{24}N^2O^2.SO^4H^2$, which has an acid reaction, and is called *quinine acid sulphate.* This salt crystallizes in shining needles containing 8 molecules of water: it is the normal sulphate. A still more acid sulphate is known, $C^{20}H^{24}N^2O^2.(SO^4H^2)^2 + 7H^2O$.

If an excess of chlorine-water be added to a solution of quinine sulphate, and the liquid be supersaturated with ammonia, a beautiful green color will be produced.

This reaction is characteristic of quinine.

When tincture of iodine is added to a solution of quinine sulphate in hot acetic acid, in a few hours the liquid deposits large, thin plates. It is *iodoquinine sulphate*, $C^{20}H^{24}N^{2}O^{2}I^{2}.SO^{4}H^{2} + 5H^{2}O$ (Herapath).

These crystals appear green by reflected light, and are almost colorless by transmitted light. When two of them are crossed, the portions which are superposed almost entirely intercept the passage of light. In this respect, iodoquinine sulphate acts as a polarizer, like tourmaline.

Uses.—Quinine sulphate is a valuable remedy. It is principally employed as a febrifuge, and generally in the treatment of diseases of an intermittent type. It is successfully administered in other diseases, especially in acute articular rheumatism, gout, certain neuralgias, etc.

CINCHONINE.

$C^{19}H^{22}N^{2}O$

Cinchonine is obtained as an accessory product in the manufacture of quinine. It deposits from its alcoholic solution in brilliant, colorless, quadrilateral prisms. It is insoluble in water, but soluble in alcohol and chloroform. It is almost insoluble in ether, a property which distinguishes it from quinine. Its alcoholic solution turns the plane of polarization to the right.

Cinchonine has a bitter taste. It melts at 257°, and when cautiously heated in the bottom of a closed tube, it partly sublimes in very light, delicate crystals. The salts of cinchonine are antipyretics, like those of quinine; they are, however, much less effective than the latter.

In its chemical structure cinchonine is closely related to quinine.

When distilled with potassium hydroxide, cinchonine yields quinoline and a mixture of pyridine bases.

Among the oxidation products obtained by the action of nitric acid, or, better, potassium permanganate, on cinchonine, we may mention two; they are

$$C^7H^5NO^4 = C^5H^3N(CO.OH)^2$$

Cinchomeronic or pyridine dicarboxylic acid.

$$C^{10}H^7NO^2 = C^9H^6N(CO.OH)$$

Cinchoninic or quinoline-γ-carboxylic acid.

Weidel, who has studied these acids, has also described another oxidation product of cinchonine, an acid, $C^9H^6N^2O^6$.

From the nature of its decomposition products, it is probable that cinchonine contains a pyridine and a quinoline nucleus.

When oxidized by chromic acid, quinine yields methoxyquinoline-γ-carboxylic acid, which makes it appear probable that quinine is methoxycinchonine.

STRYCHNINE AND BRUCINE.

Pelletier and Caventou discovered these two alkaloids in various vegetable products derived from plants belonging to the genus *Strychnos*, such as nux vomica (seeds of the *Strychnos Nux vomica*), false angustura bark, which comes from the same Strychnos, Saint Ignatius bean (seeds of the *Strychnos Ignatii*), etc. These alkaloids appear to be combined in the Strychnos with an acid but little known, which Pelletier and Caventou called *igasuric acid*.

Strychnine, $C^{21}H^{22}N^2O^2$.—*Preparation.*—Strychnine is extracted from nux vomica by a process analogous to that which serves for the preparation of quinine. The crude strychnine which deposits in crystals from its alcoholic solution is always mixed with brucine. The two alkaloids are separated by converting them into nitrates, which are made to crystallize; the strychnine nitrate, less soluble than that of brucine, deposits in needles, and the concentrated solution afterwards deposits voluminous crystals of brucine nitrate. To isolate the alkaloids, the corresponding nitrates are precipitated by ammonia, and the alkaloid dissolved in boiling alcohol, which deposits it in crystals on cooling.

Properties.—Strychnine crystallizes in rectangular octahedra, sometimes in quadrilateral prisms terminated by four-sided pyramids. It is colorless and odorless, but extremely bitter. It is insoluble in water and in ether, and scarcely soluble in absolute alcohol. It dissolves readily in ordinary alcohol, in chloroform, and in the volatile oils. Its alcoholic solution turns the plane of polarization to the left.

When strychnine or one of its salts is moistened with strong sulphuric acid, and a little potassium dichromate added, a blue color is produced, which changes to violet and red, and at last disappears.

Among the products of the action of fused potassium hydroxide upon strychnine are quinoline, indol, and picoline.

Strychnine is one of the most active poisons known; even in very small doses it produces violent tetanic spasms.

Brucine, $C^{23}H^{26}N^2O^4 + 4H^2O$.—Brucine, separated from strychnine by the process above indicated, crystallizes by slow evaporation of its solution in weak alcohol in oblique rhombic prisms, which are often quite large. These crystals, which contain four molecules of water, rapidly effloresce in the air. Brucine is almost insoluble in water, but dissolves readily in alcohol and very slightly in ether. The alcoholic solution rotates the plane of polarization to the left.

If brucine be moistened with nitric acid, it immediately assumes a blood-red color and, by the aid of a gentle heat, disengages carbon dioxide and vapors which contain methyl nitrite (Strecker).

When fused with potash, it yields homologues of pyridine.

ALKALOIDS OF OPIUM.

Opium is the thickened juice of the capsules of the white poppy (*Papaver somniferum*). It is obtained by making incisions in these capsules from the base to the summit. A milky juice exudes, and in the course of a day thickens and solidifies in tears. These are removed, pressed together, and fashioned into variously-formed masses.

The basic nature of morphine, one of the crystallizable principles of opium, was recognized in 1806 by Sertürner. Besides this, opium contains a number of alkaloids combined with several acids. Among the latter are sulphuric acid, lactic acid, and *meconic acid*, $C^7H^4O^7 = C^5HO^2(OH)(COOH)^2$. The latter is one of the more important constituents of opium; it possesses the characteristic property of producing a blood-red color with ferric salts. Opium contains also a gummy matter, soluble in water, and a brown, insoluble, resinous matter, which remains in the mass when opium is exhausted with water. The aqueous solution of opium has a brown color. The following alkaloids have been obtained from opium:

Morphine	$C^{17}H^{19}NO^{3}$
Codeine	$C^{18}H^{21}NO^{3}$
Thebaine	$C^{19}H^{21}NO^{3}$
Papaverine	$C^{21}H^{21}NO^{4}$
Narcotine	$C^{22}H^{23}NO^{7}$
Narceine	$C^{23}H^{29}NO^{9}$

Still other alkaloids have been obtained from opium, but it is probable that some of them are produced during the process of extraction. Of those enumerated, we will describe only morphine, codeine, and narcotine.

MORPHINE.

$C^{17}H^{19}NO^{3}$

Preparation.—1. Opium is cut into slices and exhausted with water. The solution is evaporated to a syrupy consistence and the still hot extract is mixed with an excess of pulverized sodium carbonate. After the lapse of twenty-four hours, the precipitate is collected and exhausted with dilute acetic acid, which dissolves the morphine and leaves the narcotine. The liquid is filtered, decolorized by animal charcoal, and supersaturated with ammonia. The morphine is precipitated, and is purified by crystallization in alcohol (Merck).

2. One kilogramme of opium is exhausted with cold water; 100 grammes of pure lime are added to the liquid, which is then evaporated to a syrupy consistence at a temperature of 65 or 75°. After cooling, the mass is exhausted with 3 litres of water which leaves the meconate of calcium; the latter is separated by filtration. The liquid is then evaporated to one-fourth its volume, and while it is still hot, 50 grammes of calcium chloride dissolved in 100 grammes of water and 8 grammes of hydrochloric acid are added.

This mixture is left to itself for about two weeks, when it will be found to have set in a mass of crystals which are bathed in a colored mother-liquor. The deposit is pressed in a cloth, dissolved in boiling water, with addition of animal charcoal, and the solution filtered. On cooling, a mass of crystals is formed, consisting of a mixture of morphine hydrochloride and codeine hydrochloride. These are pressed, dissolved in water, and ammonia is added, which precipitates the greater portion of the morphine, while the codeine remains in solution. The deposit is collected on a filter and redissolved in boiling alcohol, from which the morphine crystallizes on cooling (Robertson and Gregory).

Properties.—Morphine crystallizes in small, colorless, right rhombic prisms, having a bitter taste. It is insoluble in ether, in chloroform, and in benzene. The alcoholic solution rotates the plane of polarization to the left. The crystals contain one molecule of water which they lose at 100°. Morphine dissolves easily in solutions of the caustic alkalies, from which it is reprecipitated by acids. It is but slightly soluble in ammonia; almost insoluble in water.

Tests.—1. If a few drops of a solution of iodic acid be added to an alcoholic solution of morphine, the liquid immediately assumes a brown or yellow color, due to the liberation of iodine. Iodic acid exerts an oxidizing action on morphine.

2. If a small quantity of morphine powder be added to a solution of ferric chloride, a blue color is produced. This characteristic recalls a reaction of the phenols, and leads to the belief that morphine contains a phenolic hydroxyl group (Grimaux).

3. Nitric acid produces an orange-red color with morphine.

The last two reactions are characteristic.

When morphine is heated to 200° with potassium hydrate, it disengages methylamine.

When heated with zinc dust, it yields phenanthrene, and various pyridic and quinolic bases studied by Gerichten and Schroetter.

Morphine Hydrochloride.—This salt, of which the preparation has already been indicated, crystallizes in silky needles, soluble in 1 part of boiling and 16 or 20 parts of cold water; it is very soluble in alcohol. The crystals contain $C^{17}H^{19}NO^{3}.HCl + 3H^{2}O$.

Platinic chloride forms a yellow precipitate of a double chloride in an aqueous solution of morphine hydrochloride.

$$(C^{17}H^{19}NO^{3}.HCl)^{2}.PtCl^{4}$$

Hydrochloride of morphine is much used in medicine.

When its solution is heated to 60° with silver nitrite, the base is oxidized and converted into oxymorphine, $C^{17}H^{19}NO^{4}$.

When morphine is heated to about 140° with concentrated hydrochloric acid, it is transformed into a new base, *apomorphine*, $C^{17}H^{17}NO^{2}$, derived from morphine by the removal of one molecule of water (Matthiessen). This base possesses special therapeutic properties. When administered by hypodermic injection or swallowed, it acts as an emetic.

CODEINE.

$C^{18}H^{21}NO^{3}$

Codeine is methylmorphine. It is obtained from the ammoniacal mother-liquor from which the morphine is deposited, in the preparation of the latter body by the process of Robertson and Gregory. For this purpose, the mother-liquor is concentrated and caustic potash is added, which precipitates the codeine. It is collected, dissolved in hydrochloric acid, the solution decolorized with animal charcoal, and the codeine again precipitated by potash. Lastly, the precipitate is dissolved in ordinary ether, which deposits the codeine in voluminous crystals by spontaneous evaporation.

These crystals are right rhombic prisms, and contain one molecule of water. Anhydrous ether deposits codeine in anhydrous rectangular octahedra, fusible at 150°.

Codeine dissolves in 89 parts of water at 15°, and is more soluble in boiling water. Alcohol and ether dissolve it readily, and the alcoholic solution rotates the plane of polarization to the left.

Starting with the idea that morphine contains a phenolic hydroxyl group, Grimaux conceived that the solution of morphine in potassium hydroxide should contain the compound $C^{17}H^{18}NO^{2}.OK$: indeed, by treating this alkaline solution with methyl iodide, he obtained codeine.

$$C^{17}H^{18}NO^{2}.OK + CH^{3}I = KI + C^{17}H^{18}NO^{2}.OCH^{3}$$

This reaction certainly demonstrates that codeine is methylmorphine.

If bromine-water be poured upon codeine in fine powder, the latter dissolves, and is converted into hydrobromide of *monobromo-codeine*. By the continued addition of bromine-water, a yellow precipitate is formed, consisting of hydrobromide of *tribromo-codeine*, that is, codeine in which three atoms of hydrogen are replaced by three atoms of bromine.

NARCOTINE.

$C^{22}H^{23}NO^{7}$

Narcotine may be extracted from the residue of opium which has been exhausted by water. This is treated with hydrochloric acid, filtered, and the filtrate precipitated by sodium carbonate. The precipitate is dissolved in alcohol, and the alcoholic solution decolorized by animal charcoal. The narcotine crystallizes out on cooling.

It forms brilliant, colorless prisms, belonging to the system of the right rhombic prism. It melts at 176°. It is insoluble in cold water, and requires for its solution about 60 parts of cold absolute alcohol, or 12 parts of boiling absolute alcohol. It is soluble in ether, a character which distinguishes it from morphine. Its alcoholic and ethereal solutions have a bitter taste, and turn the plane of polarization to the left.

If a few crystals of narcotine in a watch-glass be moistened with sulphuric acid containing a trace of nitric acid, an intense blood-red color is produced.

By the action of certain oxidizing agents, narcotine is decomposed into a new alkaloid, *cotarnine*, and an acid which is called *opianic acid* (Wöhler).

$$\underset{\text{Narcotine.}}{C^{22}H^{23}NO^{7}} + O = \underset{\text{Opianic acid.}}{C^{10}H^{10}O^{5}} + \underset{\text{Cotarnine.}}{C^{12}H^{13}NO^{3}}$$

Cotarnine crystallizes in colorless, silky needles, grouped in stars. They melt at 132°.

When heated with water, narcotine breaks up into cotarnine and *meconine*, which is also present in opium.

$$\underset{\text{Narcotine.}}{C^{22}H^{23}NO^{7}} = \underset{\text{Meconine.}}{C^{10}H^{10}O^{4}} + \underset{\text{Cotarnine.}}{C^{12}H^{13}NO^{3}}$$

When subjected to the action of hydriodic acid, narcotine loses successively three methyl groups, and yields hydriodides of three new bases. One of them contains $C^{19}H^{17}NO^{7}$, and has been designated as *nornarcotine* or *normal narcotine.* It is formed according to the equation

$$\underset{\text{Narcotine.}}{C^{22}H^{23}NO^{7}} + 3HI = \underset{\text{Nornarcotine.}}{C^{19}H^{17}NO^{7}} + \underset{\text{Methyl iodide.}}{3CH^{3}I}$$

Hence narcotine itself represents *trimethyl-nornarcotine*, $C^{19}H^{14}(CH^{3})^{3}NO^{7}$ (Matthiessen and Foster).

The intermediate terms between narcotine and nornarcotine are also known.

ACONITINE.

$C^{33}H^{45}NO^{12}$

The *Aconitum Napellus* contains, independently of aconitic acid, a base which was extracted by Geiger and Hesse. It occurs as a white powder, or as colorless, tabular crystals, only slightly soluble in water, very soluble in alcohol. Its taste is acrid and bitter. It is a violent poison. Its nitrate crystaltizes readily.

The following two alkaloids, theobromine and caffeine, are not derivatives of the fundamental alkaloidal nuclei; they are closely related to uric acid.

THEOBROMINE.

$C^{7}H^{8}N^{4}O^{2}$

Theobromine exists in the beans of the cocoa (*Theobroma Cacao*). To prepare it, the crushed cocoa beans are exhausted with water, and the aqueous extract is precipitated by lead acetate. The precipitate is separated by filtration, and the filtrate is freed from an excess of lead by hydrogen sulphide; it is then again filtered, and evaporated to dryness. The residue is dissolved in absolute alcohol and the solution concentrated; the theobromine separates as a crystalline powder, having a bitter taste, slightly soluble in alcohol and ether. It may be sublimed. It is soluble in ammonia.

CAFFEINE, OR THEINE.

$C^{8}H^{10}N^{4}O^{2}$

Caffeine was extracted from coffee in 1821 by Pelletier and Caventou, and by Robiquet and Runge. Liebig, Pfaff, and Wöhler determined its composition. It exists in coffee, tea, Paraguay tea (leaf of the *Ilex Paraguaiensis*), guarana (seeds of the *Paullinia Sorbilis*), and in kola-nuts. Caffeine is methyl-theobromine.

Preparation.—Caffeine, or theine, is generally obtained from tea. Powdered tea is exhausted several times with cold alcohol, and the tincture is precipitated by subacetate of lead, filtered, and a current of hydrogen sulphide passed through the filtrate to precipitate the excess of lead. The filtered liquid is then evaporated to one-fourth its volume, neutralized by potassium hydrate, and allowed to crystallize (Herzog).

Properties.—Caffeine forms long, colorless, silky needles, containing one molecule of water. It loses its water of crystallization at 100°, melts at 225°, and sublimes without alteration at a higher temperature. It is only slightly soluble in cold water, but dissolves readily in boiling water, and in alcohol. It is but slightly soluble in ether. It forms definite combinations with the acids. When boiled with concentrated potash, it disengages methylamine.

Heated with baryta water, it breaks up into carbon dioxide and *caffeidine*, $C^7H^{12}N^4O$, a base soluble in water, and which yields by prolonged boiling with water sarcosin and other products.

By the action of chlorine water or of nitric acid, caffeine forms methylamine, cyanogen chloride, and an acid, $C^{12}H^{12}NO^7$, which Rochleder has named *amalic acid*. The latter is tetramethyl-alloxantin, $C^8(CH^3)^4N^4O^7$, and the reaction indicates a relation between caffeine and the uric acid group.

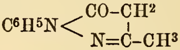
When caffeine is boiled for a few minutes with fuming nitric acid, the yellow liquid evaporated to dryness, and the residue moistened with ammonia, a purple color is produced, analogous to that of murexide.

SUBSTITUTES FOR NATURAL ALKALOIDS.

Among the more important medicinal properties of several of the natural alkaloids are those of relieving pain and of lowering the temperature of the body,—the analgesic and antipyretic effects. The use of the alkaloids possessing these properties in the most marked degree is often objectionable on account of other actions on the animal economy. Organic chemistry has placed a large number of compounds at the service of the physician, and several of these are extensively used as substitutes for natural alkaloids. We have space to mention only a few.

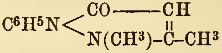
Paracetphenetidine, $C^6H^4.NH(C^2H^3O)\text{–}OC^2H^5$.—The ethyl ethers of the amidophenols, *e.g.*, $C^6H^4.NH^2.OC^2H^5$, are called *phenetidines*, and the acetyl compound formed by the replacement of one of the hydrogen atoms of the NH^2 group in paraphenetidine by the group acetyl is perhaps the most important of the antipyretics. It is a white crystalline powder, almost insoluble in cold water, more soluble in hot water, and freely soluble in alcohol and in ether. It is employed in medicine under the name *phenacetin.*

Phenyldimethylpyrazolon, or *antipyrine*, is a derivative of acetoacetic ether. By the reaction of phenylhydrazine and ethylacetoacetate, phenylmethylpyrazolon is formed, having the composition



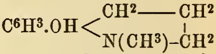
$$C^6H^5N\left<\begin{array}{l}CO-CH^2\\ \qquad | \\ N=C-CH^3\end{array}\right.$$

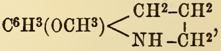
If methylphenylhydrazine be substituted for the phenylhydrazine, phenyldimethylpyrazolon results.



$$C^6H^5N\left<\begin{array}{l}CO\text{——}CH\\ \qquad\qquad \| \\ N(CH^3)-C-CH^3\end{array}\right.$$

This is the medicinal antipyrine. It forms monoclinic crystals, easily soluble in water, alcohol, and chloroform, almost insoluble in ether. It melts at 113°, and cannot be distilled without decomposition.

Hydroxymethyltetrahydroquinoline,  $C^6H^3.OH\left<\begin{array}{l}CH^2\text{——}CH^2\\ \qquad\qquad | \\ N(CH^3)-CH^2\end{array}\right.$ a derivative of orthoamidophenol, has been used as an antipyretic under the name *kairine*, and

Methoxytetrahydroquinoline,  $C^6H^3(OCH^3)\left<\begin{array}{l}CH^2-CH^2\\ \qquad | \\ NH-CH^2\end{array}\right.$, has been recommended for the same purpose, being called *thalline.* Neither of these appear to have any advantages over phenacetin and antipyrine, and, moreover, their employment is not without danger by reason of special actions they exert on certain nerve-centres.

ALBUMINOID MATTERS—PROTEIDS.

The albuminoid matters are complex organic substances, containing carbon, hydrogen, oxygen, and nitrogen, associated with a small proportion of sulphur. Their composition and properties generally are represented by those of the coagulable matter which exists in white of egg and in the serum of blood, and which is called albumen. They are closely related to the epidermic productions and insoluble substances which are converted into gelatin or chondrin by boiling, although differing from these latter in chemical composition and in many properties. These compounds appear to be the closest approximation of unorganized matter to organized matter; that is the living cell, and they have therefore been called proteids.

The following reactions serve to characterize albuminoid substances:

In contact with water containing one or two thousandths of hydrochloric acid most insoluble albuminoid matters swell up and are finally converted into a transparent jelly, which is partially soluble in water.

Concentrated hydrochloric acid dissolves albuminoid substances by the aid of heat, assuming a deep violet or blue color.

Concentrated nitric acid colors them yellow.

Albuminoid substances are precipitated from neutral or slightly alkaline aqueous solutions by alcohol, tannin, phenol, and the salts of heavy metals such as lead, mercury, and copper. The copper precipitate is soluble in strong potassium hydroxide solution, the liquid assuming a rich violet color.

A solution of mercuric nitrate in dilute nitric acid is colored red when boiled with albuminoid substances (*Millon's reagent*.

The albuminoid substances are levo-rotatory, the optical activity varying in wide limits.

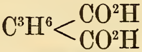
The insoluble albuminoid bodies, such as coagulated albumen, fibrin, and casein, dissolve by the aid of a gentle heat in potassium hydroxide, to which they yield a portion of their sulphur. The alkaline liquid, supersaturated with acetic acid, precipitates the dissolved matter in flakes.

The molecular composition of these bodies is very complex, as will presently be seen when we consider the compounds into which they can be split up, and their molecular weights are consequently very great. Their centesimal composition is comprised within the following limits:

Carbon	50.0	to	53.5
Hydrogen	6.6	“	6.9
Nitrogen	16.8	“	15.6
Oxygen	26.1	“	22.4
Sulphur	0.5	“	1.6
	100.0		100.0

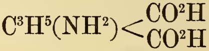
Concentrated and boiling solutions of the alkalies decompose all albuminoid substances, the principal products of the decomposition being carbon dioxide, formic acid, *glycocoll*, and its homologue *leucine*, $C^6H^{13}NO^2$, as well as *tyrosine*, $C^9H^{11}NO^3$, *aspartic acid*, $C^4H^7O^4$, and *phenylalanine*, $C^6H^4–CH^2–HC(NH^2)–COOH$. The other decomposition products will be indicated when treating of albumen.

Leucine and tyrosine are also formed when albuminoid substances are long boiled with dilute sulphuric acid. At the same time, aspartic acid, and glutamic acid, $C^5H^9NO^4$, which is the acid amide of normal pyrotartaric acid, is formed.



$$C^3H^6<\begin{matrix}CO^2H\\CO^2H\end{matrix}$$

Pyrotartaric acid.



$$C^3H^5(NH^2)<\begin{matrix}CO^2H\\CO^2H\end{matrix}$$

Glutamic acid.

By the action of energetic oxidizing agents, such as chromic acid, or manganese dioxide and sulphuric acid, albuminoid bodies produce various products of oxidation and decomposition, among which we may note particularly: (1), the volatile acids of the series, $C^nH^{2n}O^2$, from formic acid to caproic acid inclusive; (2), the corresponding aldehydes; (3), the nitriles (hydrocyanic ethers), propionitrile (ethyl cyanide), and valeronitrile (butyl cyanide); (4), benzoic acid and benzaldehyde.

By subjecting albumen and its analogues to the action of an aqueous solution of barium hydrate at a temperature of 140 or 150°, Schützenberger observed that these bodies decompose, by hydration, into ammonia, carbon dioxide, oxalic, sulphurous, and acetic acids (the latter three bodies in very small proportion), and into other products, which are mostly crystallizable. These products are tyrosine and the acid amides of the fatty series $C^nH^{2n+1}NO^2$, from amidobutyric acid, $C^4H^7(NH^2)O^2$, to amid-œnanthic acid, $C^7H^{13}(NH^2)O^2$, inclusive. With these products are others which are also crystallizable, but contain less hydrogen; lastly, more highly oxidized amides are formed in the same reaction, such as malamic, diamidocitric, aspartic, and glutamic acids.

From these results, it may be inferred that albumen and its analogues contain the elements of urea, tyrosine, acid amides of the fatty series, and more oxidized amides analogous to aspartic acid, all of these bodies being combined together, with elimination of water. The presence of a certain proportion of a dextriniform body in the products of the decomposition of albumen permits the supposition that the complex molecule of the latter body contains also an amide of cellulose or an amylaceous body.

It can now be understood that an exact chemical classification of the proteids is not yet possible. They may, however, be conveniently arranged as follows:

1. TRUE ALBUMENS, soluble in pure water and coagulable by heat. Egg albumen and serum albumen are types of this variety. There are analogous vegetable albumens.

2. GLOBULINS, insoluble in water, but soluble in solutions of neutral salts, such as sodium chloride, magnesium sulphate: the solutions are coagulable by heat. Examples are vitellin, the albumen of yolk of egg, cryosine, serum globulin, fibrinogen. There appear to be no exactly corresponding vegetable substances.

3. FIBRINS, insoluble in water, swell up in solutions of neutral salts and in dilute acids; coagulated by boiling water, blood fibrin is the best type, and *gluten fibrin* is an analogue of vegetable origin.

4. COAGULATED ALBUMENS, insoluble in water, and only slightly swelled by saline solutions and dilute acids. These substances are not colored by iodine.

5. AMYLOID, insoluble, colored red, brown, or violet by iodine. This substance appears to be a pathological modification of albuminoids, and cannot be prepared artificially from other varieties.

6. ACID ALBUMENS, insoluble in water, saline solutions or alcohol, but dissolved by dilute acids and alkalies: a small quantity of calcium carbonate suspended in water prevents their solution.

7. ALKALI ALBUMENS, very slightly soluble in water, saline solutions, and hot alcohol; soluble in water holding suspended calcium carbonate, in which they replace the carbonic acid.

8. ALBUMOSES, apparently transition products between the preceding bodies and the next class; soluble in dilute solutions of common salt.

9. PEPTONES, very soluble in water, not coagulable by heat, and not precipitated by acids or salts.

10. TRUE PROTEIDS, capable of being broken up into an albuminoid body with some other substance; such as hemoglobin, oxyhemoglobin, casein, chondrin, nuclein.

11. ALBUMOIDS, insoluble matters, in general not dissolved by the digestive juices: these occur in the skin and in the strong integuments.

12. GELATINOIDS, soluble in hot water without alteration: gelatin is the type.

13. SPONGY MATTERS, such as compose sponge.

We will briefly consider the more important of these bodies.

TRUE ALBUMENS.

Soluble albumen exists in solution in white of egg, and in other liquids of the animal economy. The coagulable principle of the serum of blood is a liquid analogous to the albumen of white of egg, and has been called *serin.*

When a filtered solution of white of egg is evaporated at a low temperature or in a vacuum, the soluble albumen at length dries to a transparent, yellowish mass, having a gummy appearance. In this state it is not pure; it remains combined with a trace of alkali and mixed with a small quantity of salts. When treated with water, it again dissolves. When it is perfectly dry, it may be heated to even 100° without losing all of its water. The greater part, if not all, of the salts which exist in white of egg with the albumen may be removed by dialysis (Graham).

When a solution of white of egg or of the serum of blood is heated, the liquid begins to be clouded at 70°, and coagulates at about 73°, sometimes in flakes, sometimes in a white mass, according to the concentration of the solution; heat converts albumen into the insoluble variety.

When white of egg is diluted with eight or nine times its volume of water and the carbonic acid gas which is dissolved or combined with the albumen is carefully expelled at a low temperature, a solution is obtained which is not coagulable by heat. The lost property may, however, be restored by passing carbon dioxide through the liquid.

If strong alcohol be added to a solution of albumen, a white coagulum of insoluble *coagulated albumen* is produced.

Action of Acids on Albumen.—Sulphuric, hydrochloric, and nitric acids precipitate albumen in thick flakes, which retain a certain quantity of acid; the latter may be removed by prolonged washings with water, the residue constituting an *acid albumen.*

The action of nitric acid upon albumen is often used for the detection of that substance in pathological urine. A still more sensitive reagent is metaphosphoric acid, which precipitates the smallest traces of albumen contained in a solution.

Ordinary phosphoric acid, acetic acid, and lactic acid, do not precipitate solutions of albumen.

Action of Alkalies on Albumen.—When white of egg is beaten up with a few drops of a very concentrated solution of potassium hydrate, it sets in a few minutes in a soft, transparent, semi-solid mass, from which the excess of potash may be removed by washing with cold water. The residue is albuminate of potash, from which all of the excess of potash may be removed by prolonged washings. The gelatinous albuminate of potash dissolves in boiling water. Acetic acid precipitates from the solution an *alkali albumen*, which may be freed from salts by dialysis.

Coagulated albumen dissolves in the alkalies and alkaline carbonates, forming albuminates.

Albumen combines with calcium hydrate, as with potassa; a mixture of white of egg and slaked lime constitutes a very hard cement.

Action of the Salts on Albumen.—Many salts precipitate solutions of albumen. Acetate and subacetate of lead form dense precipitates of albuminate of lead. Cupric sulphate produces a blue precipitate. Corrosive sublimate yields a white precipitate, even in very dilute solutions of albumen. The insolubility of this precipitate explains the use of albumen as an antidote to corrosive sublimate.

Solutions of albumen are not precipitated by solutions of sodium chloride or sodium sulphate, but when acetic acid is added to the mixture a precipitate forms. Reciprocally, a solution of albumen to which acetic acid has been added is precipitated by solutions of sodium chloride and sodium sulphate (Panum). In this case an *acid albumen* is formed.

In general, the properties of ovalbumen and those of serum albumen are very similar; the latter, however, resists the action of acids much more than the former, while it is more readily modified by the action of alkalies.

GLOBULIN—FIBRIN.

Berzelius gave the name *globulin* to the coagulable albuminoid that can be obtained from red blood-corpuscles, and which is probably a decomposition product of hemoglobin. It resembles albumen in many properties, but coagulates completely only at 93°. It is not precipitated by either acetic acid or by alkalies, but is thrown down when a current of carbon dioxide is passed through its solution.

When recently-drawn blood is left to itself, it coagulates spontaneously in a few minutes, and soon separates into a yellow liquid called the *serum*, and a red coagulum, which is the *clot*. The clot contains the red corpuscles, imprisoned in an insoluble albuminoid matter. This matter is fibrin; it is formed by the reaction of two globulins which exist in solution in the liquid portion of blood, which is called *plasma*. One of these substances is called *fibrinogen*, the other is *serum globulin*, sometimes called *fibrinoplastin*, or *paraglobulin*. These two bodies have been isolated: when they are mixed in presence of water and a certain proportion of sodium chloride, the whole dissolves at first and the liquid soon coagulates spontaneously; the coagulum is fibrin (Hoppe-Seyler).

Fibrin may be obtained in fibrous masses by beating fresh blood. The latter does not coagulate in this case, but the coagulable constituent attaches itself in red flakes to the rods with which the blood is agitated. By washing these flakes in running water, they are freed from the adhering red corpuscles, and obtained in white or grayish elastic masses of a fibrous appearance. This substance is entirely insoluble in pure water, but dissolves in slightly alkaline solutions, and, by the aid of a gentle heat, even in solutions of certain salts which have an alkaline reaction. It decomposes hydrogen dioxide into oxygen and water.

When left to itself during the heat of summer, it putrefies very rapidly, and is converted into a blackish liquid, which contains albumen. Leucine, and butyric and valeric acids are formed at the time.

When treated with concentrated hydrochloric acid, fibrin dissolves, forming a blue solution. When still moist fibrin is introduced into water containing one or two thousandths of concentrated hydrochloric acid, it swells and becomes transparent, forming a jelly. After some time it dissolves in the liquid, although with difficulty, and the solution then contains an *acid albumen*, syntonin.

Dilute sodium chloride solutions dissolve fibrin. When such a solution is dialyzed, most of the salt passes into the exterior liquid, and there remains in the dialyzer a limpid solution of the two globulins, coagulable by heat, and presenting many of the properties of egg albumen (A. Gautier).

Myosin.—Kühne designated by this name the albuminoid matter existing in solution in the sheaths of the muscular fibres (sarcolemma), and which has the property of coagulating spontaneously after death, thus producing cadaveric rigidity.

Myosin is insoluble in water as well as in a saturated solution of common salt, but it dissolves in a solution containing ten per cent. of salt. It may be extracted from the muscles by the following process: the flesh is chopped up, and decolorized by washing with water; it is then triturated with pulverized common salt, and enough water is added to produce a 10 per cent. solution of salt. After digestion for a few hours in the cold, the liquid is filtered and brought into contact with rock salt; as the latter dissolves, it precipitates the myosin in flakes.

Recently-precipitated myosin dissolves in a ten per cent. solution of salt, but it loses this property by desiccation. Very dilute hydrochloric acid dissolves it, and soon transforms it into syntonin.

ACID ALBUMENS—SYNTONIN.

Syntonin is the type of acid albumens: it may be prepared from muscular tissue. The latter is hashed, washed with water, and suspended in a large quantity of water containing one-thousandth of hydrochloric acid. The particles of meat swell and dissolve abundantly in the liquid, which is then pressed through a cloth, filtered, and exactly neutralized with sodium carbonate. The syntonin is precipitated in gelatinous, colorless flakes, which collect and dry upon the filter in elastic films.

Syntonin dissolves in water slightly acidulated with hydrochloric acid. It also dissolves in lime-water, and in a one per cent. solution of sodium carbonate.

PEPTONES—PEPSIN.

The gastric juice contains a ferment called *pepsin*, which is capable under certain conditions of profoundly modifying all the proteids. The change appears to be an hydrolysis, and by it the albuminoids are rendered soluble in water; the solutions are dialyzable and non-coagulable by heat; they are converted into peptones. In this condition they are ready for absorption into the animal system. Pepsin displays its greatest activity at about 35°, and in dilute hydrochloric acid solution; a given quantity of the ferment is capable of peptonizing an apparently unlimited quantity of albumen, provided the peptone formed be removed from the liquid as rapidly as it is produced. Whether the peptones are as numerous as the albuminoids from which they are derived is as yet undecided; it is certain, however, that there are several varieties, and that after absorption into the body they again become true albuminoids.

The pancreatic juice contains a ferment similar to pepsin, called *trypsin*.

TRUE PROTEIDS—HEMOGLOBIN.

This name is given to the crystalline matter which may be extracted from red blood-corpuscles, and which was first called *hematocrystalline*.

Preparation.—Clotted blood is broken up and triturated with its own volume of water until it is entirely reduced. It is then passed through a cloth, and the liquid is frozen, or agitated with small quantities of ether until the corpuscles are dissolved. The thawed liquid, or that which has been treated with ether, deposits a coagulum which imprisons all of the unbroken corpuscles. The liquid is filtered, rendered slightly acid by acetic acid, and alcohol is added as long as the precipitate first formed continues to dissolve. When cooled to 0° for several hours, the red liquid sets in a mass of crystals; these are collected on a filter, pressed, and washed with dilute alcohol and water, both at 0°. They are purified by dissolving them in water at 40° and evaporating the solution in a vacuum, or by adding alcohol and cooling the liquid to 0°.

Composition.—Hemoglobin so prepared has about the same composition as albuminoid bodies, but contains a little iron. According to Hoppe-Seyler, its composition is

Carbon	54.18
Hydrogen	7.2
Nitrogen	16.2
Oxygen	21.5
Iron	0.42
Sulphur	0.7

Properties.—Hemoglobin forms crystals which differ according to the blood from which they have been obtained. They generally belong to the type of the right rhombic prism. Those from human blood present, under the microscope, the forms indicated in Fig. 136. They are red, and doubly refracting. They contain water of crystallization.

They dissolve in water, and more readily in slightly alkaline solutions.

The red solution of hemoglobin (oxyhemoglobin) has an important optical property. When light which has traversed a dilute solution of hemoglobin is decomposed by a prism, the spectrum so formed shows two black bands (absorption bands) between Fraunhofer's lines D and E (Stokes).

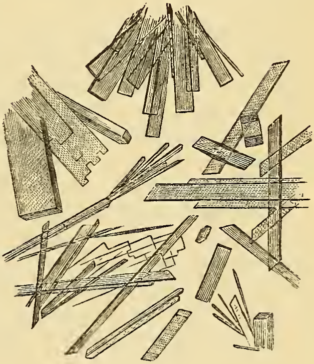


FIG. 136.

The crystals of hemoglobin contain oxygen which is weakly combined, and which may be removed by exposing the crystals in a vacuum (Hoppe-Seyler). Oxygenated hemoglobin is known as *oxyhemoglobin*, and hemoglobin deprived of oxygen reabsorbs that gas when brought into contact with it. It is curious that carbon monoxide will expel the oxygen from hemoglobin, at the same time replacing it (Cl. Bernard). The combination of hemoglobin and carbon monoxide is soluble in water.

The solution of oxyhemoglobin yields its oxygen to certain reducing agents, such as hydrogen sulphide. *Reduced* hemoglobin gives an absorption spectrum containing one single band, situated in a position between the two absorption-bands of oxyhemoglobin.

Hemoglobin decomposes hydrogen dioxide. It is very unstable, and if the crystals be dried at a temperature above 100° they rapidly become altered. The aqueous solution decomposes spontaneously in a few hours at 15°, or temperatures above that point. The acids, even the weak ones, favor this decomposition, which is manifested by a change of color, the fine red tint of the hemoglobin being replaced by a brown. In these cases, hemoglobin decomposes into an albuminoid matter (globulin), and a ferruginous pigment called hematin. At the same time, small quantities of fatty acids are set free (Hoppe-Seyler).

Hematin.—This substance has received different names. Lecanu, who first studied it, named it *hematosin.* When properly purified, it forms a blackish-blue, amorphous powder, which is quite stable, since it resists a temperature of 180°. It contains carbon, hydrogen, nitrogen, oxygen, and iron. When incinerated, it leaves 12.8 per cent. of oxide of iron.

It is insoluble in water, alcohol, ether, and chloroform. It dissolves in the alkalies, in ammonia, and in the acids, and is readily soluble in ammoniacal alcohol and in alcohol containing hydrochloric acid. These solutions are reddish-brown. With hydrochloric acid, hematin forms a compound which crystallizes in rhomboidal laminæ; the crystals are characteristic and may be recognized by means of the microscope (hydrochloride of hematin).

Hematoidin.—This body is doubtless a product of the decomposition of hemoglobin. Virchow found it in orange-colored crystals in the remains of old hemorrhages of the brain. It is also found in blood which has been exposed to air, and in extravasated blood in the Graefian follicles. It may easily be obtained from the yellow bodies contained in the ovaries of the cow, by triturating them with glass, and digesting for a few days with chloroform. After evaporation of the yellow chloroform solution, the residue is treated with ether to dissolve out the fat.

Hematoidin crystallizes in small, orange-red, transparent prisms. It is insoluble in water and alcohol, slightly soluble in ether; it is soluble in chloroform, which it colors golden-yellow. It presents certain analogies with bilirubin (page 786).

CASEIN.

When an acid is added to milk, a thick precipitate of casein is at once formed. The lactic acid which forms in milk by the fermentation of the milk-sugar produces the same precipitation. The milk is then said to curdle.

Casein dissolves in alkaline liquids and even in certain alkaline salts, such as carbonate and phosphate of sodium. It exists in this state in milk, which is alkaline when fresh. When this solution of alkaline albuminate, to which the name soluble casein has been given, is evaporated, it becomes covered with a pellicle. Acetic acid precipitates it in flakes, combining with the alkali. It is also coagulated by the gastric juice, by the action of the ferment known as *pepsin*. This ferment exists in *rennet* which is prepared from the fourth stomach of the calf, and which serves to coagulate skimmed milk in the preparation of cheese. Indeed, casein, more or less altered by putrefaction, is the basis of the different kinds of cheese.

GELATIN.

The bones contain a cartilaginous substance, which may be isolated by dissolving out the mineral salts, which consist of calcium carbonate and phosphate, with hydrochloric acid. There remains a semi-transparent, elastic substance, which retains the form of the bone. This substance, which has been called *ossein*, or *collagene*, is insoluble in cold water, but by prolonged boiling, or more rapidly by digestion with water heated to a few degrees above 100°, it dissolves and forms a solution, which sets in a transparent jelly on cooling. The body formed by this transformation dissolves slightly in cold water, and abundantly in boiling water, and the hot solution forms a jelly on cooling. Hence the name gelatin.

Other tissues of the animal economy may be converted into gelatin by boiling with water. It is so with the cellular tissue, the skin, the scales, and swimming-bladder of fishes. The swimming-bladder of the sturgeon, known in commerce as fish-glue, furnishes very pure gelatin by boiling with water.

The substances which may be converted into gelatin possess very nearly the same composition as gelatin itself; hence nothing precise is known concerning the nature of the change produced in them by the action of boiling water.

Dry gelatin occurs in transparent sheets, which are sonorous, and of which the color varies from yellowish to brown, according to their thickness and purity.

The aqueous solution is precipitated in white flakes by alcohol. The acids do not precipitate it, with the exception of tannic acid, with which it forms a thick coagulum, a combination of tannin and gelatin. This action of tannin on gelatinous matters is applied in the manufacture of leather, which is obtained by leaving fresh or green skins, previously swelled by soaking in water, in contact with tan, that is, coarsely-ground oak-bark, which is well known to contain tannin.

When chlorine-water is added to a solution of gelatin, a white cloud is formed which an excess of chlorine converts into a white, flocculent precipitate.

Solutions of gelatin are precipitated by platinic chloride and by corrosive sublimate, but not by alum or the salts of lead, copper, silver, etc. When boiled with dilute sulphuric acid, gelatin is converted into leucine and a substance to which Braconnot gave the name sugar of gelatin, and which is glycocol.

Chondrin.—When the cartilages of the short ribs are boiled for a very long time with water, they dissolve, forming a liquid which sets in a jelly on cooling. This gelatinous matter is chondrin. It is distinguished from gelatin by the property of its aqueous solution to form precipitates with all the acids, and with a great number of metallic salts. Alum forms in it an abundant, flocculent precipitate.

The substances which have just been summarily described, and others which form the liquids and tissues of the animal economy, undergo various transformations in the organism. They are derived from the vegetable kingdom, which alone can elaborate such complex matters. They pass with the aliments into the animal organisms, which assimilate them, and this work of assimilation does not profoundly modify the nitrogenized matters. But once fixed in the tissues, they do not remain there indefinitely, for there is a continual change and renewal of the whole economy. They become unfitted for the requirements of life, and disappear in their turn, eliminated by that continual oxidation which makes of the body a permanent hearth of slow combustion. A notable portion of the oxygen which enters the lungs at each inhalation penetrates into the blood, and is converted in the capillary system and the intricacies of the tissues into carbon dioxide. This gas, which returns to the lungs with the venous blood, is exhaled at each exhalation. Expired air contains 4 to 5 per cent. of carbon dioxide.

The carbon dioxide eliminates the greater portion of the carbon contained in the organic bodies burned during the phenomenon of respiration. The hydrogen of these bodies is eliminated in the form of water. But what becomes of their nitrogen? In man, and a great number of the higher animals, it is eliminated in the urea contained in the urine. Such are the principal features of this grand function of respiration, the source of heat in all animals.

But how is this slow oxidation which constitutes the object of respiration, as first shown by Lavoisier, accomplished? Are the organic matters ready to be oxidized and consumed at once, or does the oxidation take place in successive phases, so that there are a certain number of intermediate terms between the complex products which must disappear and the final products of their oxidation? All facts lead to the adoption of the latter conclusion. Indeed, there are found in the tissues and liquids of the economy a great number of bodies having compositions more or less complex, and which are the products, and, as it were, the testimony of a successive simplification,—of *disassimilation*, as it is called.

But it must not be supposed that all of the reactions which take place in the economy are phenomena of oxidation. Before being definitely oxidized and rejected from the body, the ingested organic matters and those which form our humors and tissues, may undergo various transformations and sometimes molecular complications. Thus, when benzoic acid is taken internally hippuric acid is found in the urine (Wöhler and Keller). Analysis has shown the presence in the animal economy of a multitude of more or less complex organic compounds, nitrogenized and non-nitrogenized, having definite compositions, and which are the products of varied reactions. Such reactions take place in the blood and in the tissues, principally in glandular organs, such as the liver. As it would be impossible to consider all of these products of disassimilation, we can only briefly notice the more important.

LECITHINE.

$C^{42}H^{84}NPO^9$

Gobley gave this name to a phosphorized fatty matter he obtained from yolk of egg, and which had been previously obtained from brain-tissue by Vauquelin. It exists in the brain and in the nerves, and in the seeds of plants.

Lecithine forms a homogeneous, translucent mass, which, as well as all its compounds, is very alterable. It decomposes rapidly when the alcoholic solution of its hydrochloride is boiled with baryta-water; oleate and palmitate of barium are precipitated, phosphoglycerate of barium is formed, and *choline* remains in solution (Liebreich).

Strecker represents this interesting decomposition by the equation

$$\underset{\text{Lecithine.}}{C^{42}H^{84}NPO^9} + 3H^2O = \underset{\substack{\text{Phospho-}\\\text{glyceric acid.}}}{C^3H^9PO^6} + \underset{\text{Choline.}}{C^5H^{15}NO^2} + \underset{\substack{\text{Oleic}\\\text{acid.}}}{C^{18}H^{34}O^2} + \underset{\substack{\text{Palmitic}\\\text{acid.}}}{C^{16}H^{32}O^2}$$

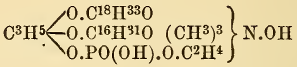
Choline is an oxygenized base of which the constitution is known. It is hydroxyethyl-trimethylammonium hydroxide.

$$\left.\begin{matrix}(C^2H^4.OH)'\\(CH^3)^3\end{matrix}\right\}N.OH$$

The chloride of this base is formed by synthesis by the action of ethylene chlorohydrin on trimethylamine (A. Wurtz).

$$C^2H^4\left\{\begin{matrix}OH\\Cl\end{matrix}\right. + (CH^3)^3N = \underset{\substack{\text{Hydroxyethyl-trimethyl-}\\\text{ammonium chloride.}}}{\left.\begin{matrix}(C^2H^4.OH)\\(CH^3)^3\end{matrix}\right\}NCl}$$

The constitution of lecithine may be represented by the formula—



$$C^3H^5\left\langle\begin{matrix}O.C^{18}H^{33}O\\O.C^{16}H^{31}O\ \ (CH^3)^3\\O.PO(OH).O.C^2H^4\end{matrix}\right\}N.OH$$

CHOLESTERIN.

$C^{26}H^{44}O$

This body is largely diffused in the organism. It exists in the bile, and is the principal constituent of most biliary calculi. It is found also in small quantity in the serum of blood, in the brain, in yolk of egg, pus, the liquid of hydrocele, etc.

Its solubility in alcohol and especially in ether, and the facility with which it crystallizes from its solutions, permits

its easy isolation, and it may readily be prepared by extracting biliary calculi with ether, or with boiling alcohol, and allowing the solution to evaporate. Cholesterin ordinarily deposits in thin and brilliant, rhombic leaflets or needles. It melts at 145°, and can be distilled, out of contact with air, at 360°.

It forms neutral compounds with acids, analogous to the ethers; it seems to be a monohydric alcohol.

The principal organic constituents of the bile are two complex acids, both nitrogenized, and one of which contains sulphur. These are glycocholic and taurocholic acids. They are not contained in the bile of all animals, and are generally extracted from that of the ox. They enter into the composition of human bile, which contains in addition coloring matters of which the most important are bilirubin and biliverdin. We will briefly describe these bodies.

GLYCOCHOLIC ACID.

$C^{26}H^{43}NO^{6}$

This body exists in the bile in the form of sodium glycocholate, which salt may be obtained in crystals from ox's bile. The latter is decolorized by animal charcoal, filtered, the liquid evaporated, and the residue perfectly dried and dissolved in absolute alcohol; the solution is introduced into a flask, and ether is cautiously added so that the two liquids may not mix, but form two layers. The latter gradually mingle and the sodium glycocholate deposits in crystals (Plattner).

When dilute sulphuric acid is added to a solution of this salt, a cloud is formed, and glycocholic acid is soon deposited in fine needles.

This acid is only slightly soluble in water and ether, but dissolves in alcohol. It is dextrogyrate (Hoppe-Seyler). By the action of hydrochloric acid, it is decomposed into *cholalic acid* and glycocoll (Strecker).

$$\underset{\text{Glycocholic acid.}}{C^{26}H^{43}NO^{6}} + H^{2}O = \underset{\text{Cholalic acid.}}{C^{24}H^{40}O^{5}} + \underset{\text{Glycocoll.}}{C^{2}H^{5}NO^{2}}$$

Cholalic Acid deposits from its ethereal solution in colorless prisms, containing two molecules of water of crystallization.

TAUROCHOLIC ACID.

$C^{26}H^{45}NSO^7$

The sodium salt of this acid remains dissolved in the ethereal solution from which sodium glycocholate has deposited. It has not yet been obtained crystallized. It is dextrogyrate. When boiled with dilute acids, or with alkalies, it breaks up into cholalic acid and taurine (Strecker).

$$\underset{\text{Taurocholic acid.}}{C^{26}H^{45}NSO^7} + H^2O = \underset{\text{Cholalic acid.}}{C^{24}H^{40}O^5} + \underset{\text{Taurine.}}{C^2H^7NSO^3}$$

The presence of biliary acids may be detected in a liquid, such as urine, by Pettenkofer's reaction: a little powdered sugar is dissolved in the liquid, and concentrated sulphuric acid is added with continual agitation, carefully avoiding an elevation of temperature. The presence of glycocholic or taurocholic acid causes the production of a rich purple color.

BILIARY PIGMENTS.

Bilirubin, $C^{16}H^{18}N^2O^3$, exists in human bile and in biliary calculi, and may be extracted from the latter. They are crushed, and exhausted, first with ether, which removes the cholesterin, then with boiling water, and finally with chloroform. The coloring matter remains in the residue as a calcareous combination; this is decomposed by adding hydrochloric acid, evaporating to dryness, and exhausting the dried residue with chloroform. After evaporation, the chloroform solution leaves a residue which contains, independently of bilirubin, three other biliary pigments which we will only mention: biliprasin, bilifuscin, and bilihumin. Alcohol dissolves the bilifuscin from this residue, and the new residue is exhausted with chloroform, which takes up the bilirubin, which alcohol precipitates in orange-colored flakes from the chloroform solution.

Bilirubin is obtained in small, dark-red crystals by evaporation of its solution in chloroform. It is insoluble in water, and very slightly soluble in ether and alcohol, but dissolves in chloroform, benzene, and carbon disulphide. It is very soluble in the alkalies, forming an orange-red solution, which becomes pure yellow on addition of water, and from which hydrochloric acid precipitates bilirubin. The ammoniacal solution of bilirubin gives precipitates with calcium chloride, barium chloride, and lead acetate.

Biliverdin, $C^{16}H^{18}N^2O^4$.—When a solution of bilirubin in sodium hydrate is agitated with air, it absorbs oxygen and becomes green. Hydrochloric acid precipitates biliverdin from the solution.

It is a bright-green powder, insoluble in water, ether, and chloroform, but soluble in alcohol. It contains one more atom of oxygen than bilirubin.

We may add that other coloring matters have also been derived from bile. They are bilifuscin, $C^{16}H^{20}N^2O^4$, and biliprasin, $C^{16}H^{22}N^2O^6$.

Biliary pigments are found in certain pathological urines, and may be detected by Gmelin's reaction. The urine is placed in a test-glass and strong nitric acid containing nitrous acid in solution is carefully added, so that it may not mix with but underlie the urine. Richly colored zones appear at the union of the two liquids, passing from green to blue, violet, and red. The green color is characteristic, the others being also produced by albumen and other substances.

Among the products of disassimilation we may also mention:

Leucine, $C^6H^{13}NO^2$, which belongs to the homologous series of glycocoll, and is found in many organs, especially in the pancreas, the salivary glands, the spleen, and the liver (page 604).

Tyrosine, $C^9H^{11}NO^3$, a body crystallizing in fine needles, may be obtained from the pancreas and the spleen (page 712).

It is known also that leucine and tyrosine may be obtained directly by the action of alkalies upon complex nitrogenized matters (page 772).

Hippuric Acid, $C^9H^9NO^3$, the origin of which has already been indicated (page 707).

Uric Acid, $C^5H^4N^4O^3$, which exists in small quantity in human urine, and which constitutes a large proportion of the urine of birds and reptiles (page 624).

Allantoin, $C^4H^6N^4O^3$, a product of the oxidation of uric acid, which Vauquelin and Buniva formerly extracted from the amniotic liquor of the cow, and which has also been found in the urine of young calves (page 628).

Various other products are related to uric acid. They are:

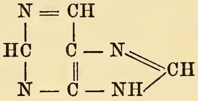
Xanthine, $C^5H^4N^4O^2$, a yellow matter, which Proust discovered in certain rare calculi (xanthic calculi), and which has also been found in small quantity in the muscles, pancreas, liver, and urine.

Adenine, $C^5H^5N^5$, has been obtained from the tissue of the pancreas. It crystallizes in leaflets containing three molecules of water of crystallization. When treated with nitrous acid it yields hypoxanthine.

Hypoxanthine or *sarcine*, $C^5H^4N^4O$, a white, amorphous substance which Scherer obtained from the spleen, and of which Strecker has noticed the existence in muscular tissue. Hypoxanthine forms a crystallizable combination with hydrochloric acid.

When hypoxanthine is boiled with nitric acid, it is converted into a nitrogenized body. By the action of reducing agents, such as ferrous sulphate, this nitrogenized body is converted into *guanine*, $C^5H^5N^5O$. The latter body was first obtained from guano. It has been found in the tissue of the pancreas.

According to E. Fischer, uric acid, xanthine, hypoxanthine, adenine, and guanine, are all derived from the same parent substance, to which he has given the name *purine*. The composition of this substance is $C^5H^3N^4$, and it possesses basic as well as acid properties. It is quite soluble in water, and melts at 217°. Its constitution is



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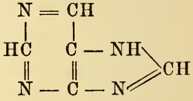

MEASURES OF WEIGHT.

		GRAINS.	OUNCES TROY = 480 GRAINS.	POUNDS AVOIRDUPOIS.
1 Milligramme	=	0.01543	0.000032	0.0000022
1 Centigramme	=	0.15432	0.000321	0.0000220
1 Decigramme	=	1.54323	0.003215	0.0002204
1 Gramme	=	15.43234	0.032150	0.0022046
1 Decagramme	=	154.32349	0.321507	0.0220462
1 Hectogramme	=	1543.23488	3.215072	0.2204621
1 Kilogramme	=	15432.34880	32.150726	2.2046212

1 Grain = 0.064799 grammes.
1 Oz. Troy = 31.103496 "
1 Lb. Avoirdupois = 0.453495 kilogrammes.

1 Cubic Centimetre of water at 4° C. weighs 1 gramme.

To convert Centigrade degrees into Fahrenheit degrees, multiply by 9 and divide by 5; add 32°.

To convert Fahrenheit degrees into Centigrade degrees, subtract 32°, then multiply by 5 and divide by 9.

1 Metre = 39.370708 inches.
1 Centimetre = 0.39370 "
1 Millimetre = 0.03937 "

1 Inch = 2.539954 centimetres.

MOHS'S SCALE OF HARDNESS.

1. Talc.
2. Gypsum.
3. Calcite.
4. Fluor spar.
5. Apatite.
6. Feldspar.
7. Quartz.
8. Topaz.
9. Corundum.
10. Diamond.

INDEX.

THE END.