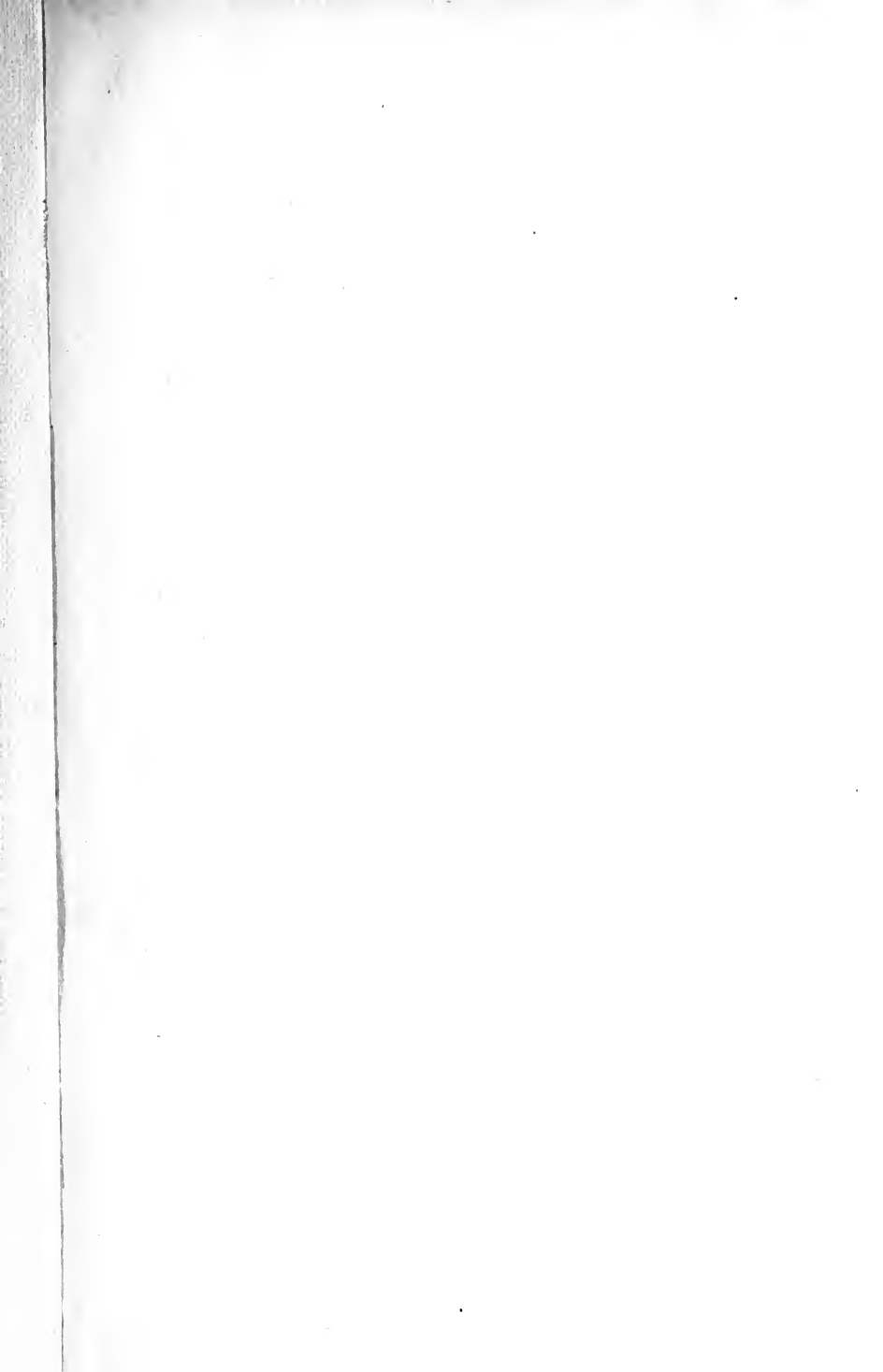


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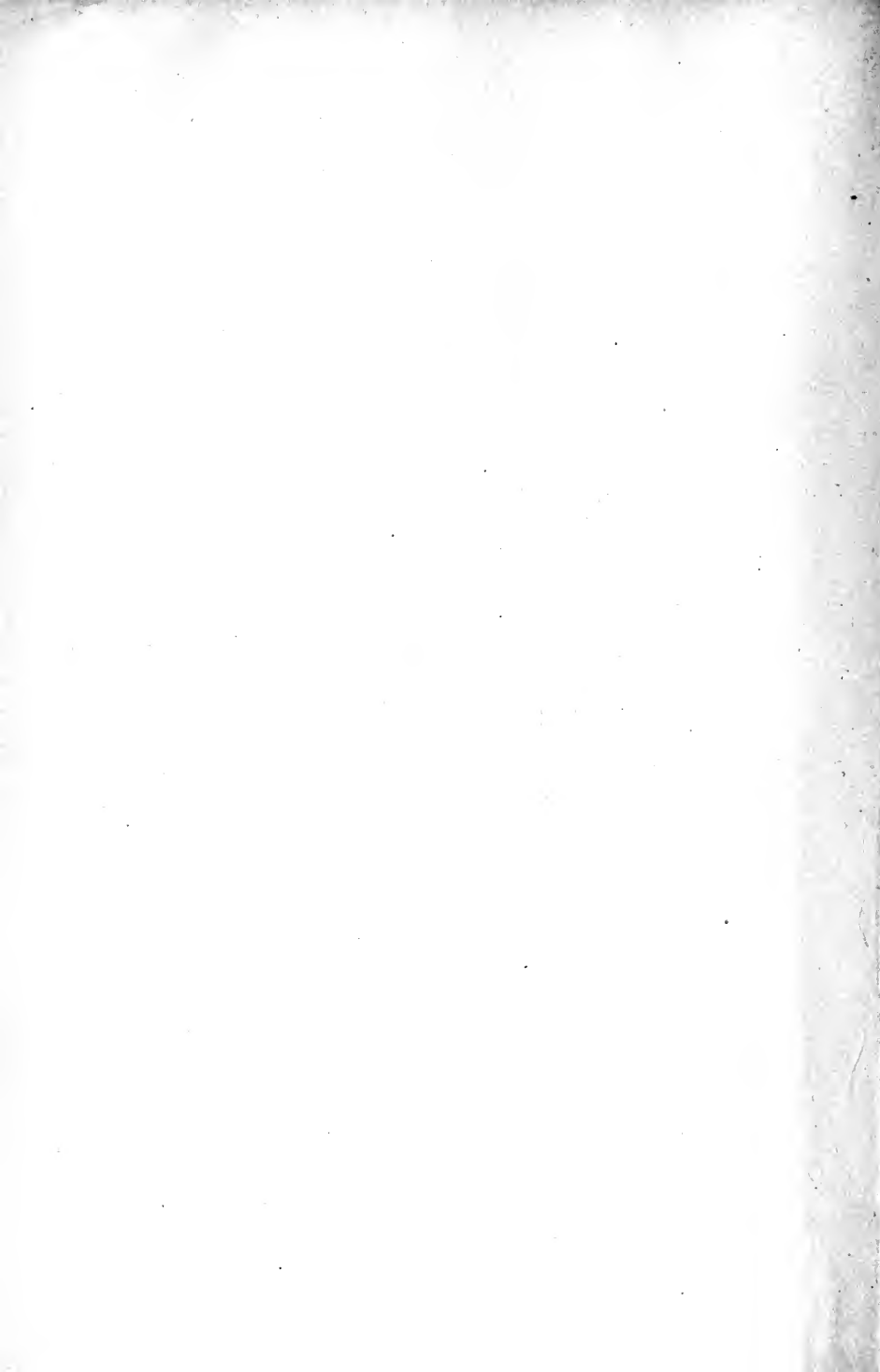


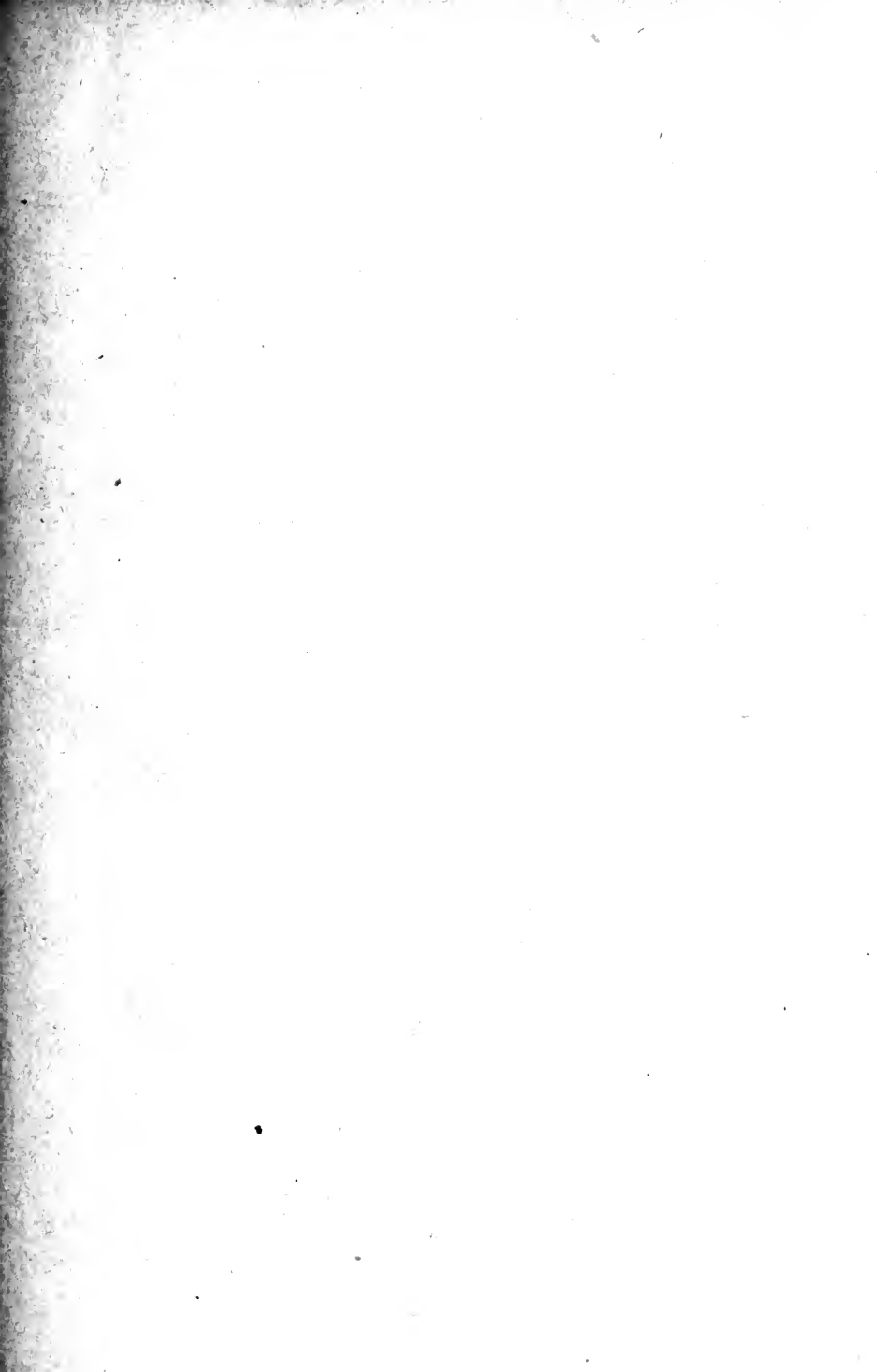
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INTERNATIONAL CHEMICAL SERIES

JAMES F. NORRIS, PH.D., CONSULTING EDITOR

INORGANIC CHEMISTRY





# Plate of Spectra

80 75 70 65 60 55 50 45 40

Ar

N<sub>2</sub>

He

H<sub>2</sub>

Sun

A a B C D E b F G h H<sub>1</sub>H<sub>2</sub>

Na

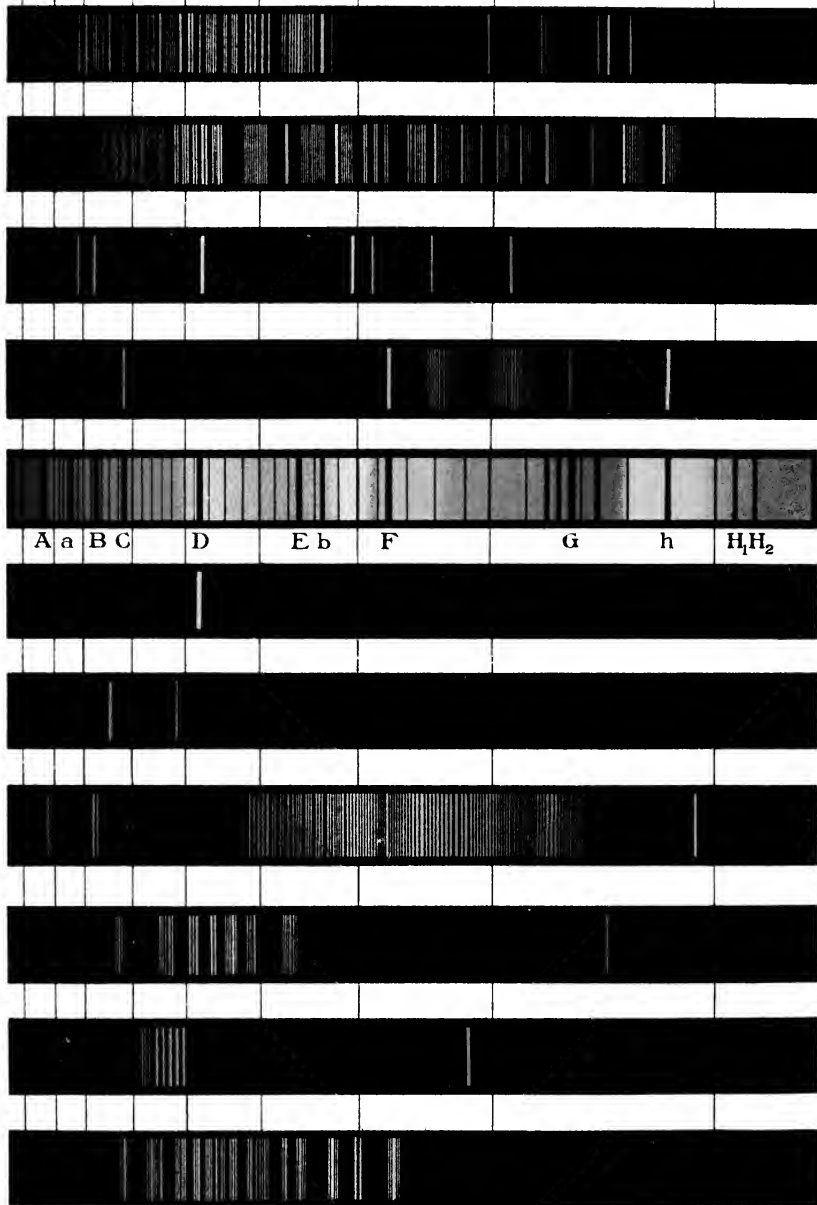
Li

K

Ca

Sr

Ba





# INORGANIC CHEMISTRY

BY

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*Professor of Chemistry in the University of Kansas*

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## PREFACE

Thirteen years ago the author of this book began to teach qualitative analysis from the standpoint of the law of mass action and the theory of electrolytic dissociation. The results were encouraging in spite of the difficulty that as yet no suitable text in general inorganic chemistry had been written to prepare the student for a course of this character. When a few years later Ostwald's masterly *Grundlinien* was translated into English, the need seemed to be met and the book was used as a text for a number of years at Kansas University.

Experience showed that Ostwald's fundamental idea was right; that inorganic chemistry can be most profitably taught from the standpoint of elementary physical chemistry; but because of its length, and of the presumption of maturity on the part of the reader, the book proved not well adapted to the average college student. In the meantime a number of other books appeared written along the same general lines, each with many excellent points, but none of which seemed to satisfy exactly the requirements. So with reluctance, which would have been greater if he had realized the magnitude of the task, the author undertook the preparation of this volume.

It has been through a number of mimeographed editions and has been used by six classes; consequently it represents several years of effort and experience. While aware that it is not perfect, the author is convinced that it is thoroughly teachable and adapted to students in the early part of their college course.

The general plan adopted was to avoid a long more or less theoretical introduction, but to develop the subject as logically as possible from the descriptive and experimental side, presenting each law or theory at the point best fitted both to the student and to the subject. This plan has met general approval during the past generation.

The order in which the non-metallic elements are discussed is that sanctioned by time and custom. When the metals are taken up, the subject has sufficiently advanced for the student to appreciate the Periodic System and thereafter the order is based upon this system except that for reasons which are obvious to every experienced teacher, copper, silver and gold are not treated until the student has become familiar with metals which are less exceptional in their properties.

The author believes that the more logically a subject is presented the easier it is to master. He has taken particular pains on this point, and also to see that the definitions and laws are as clearly and accurately worded as possible. After the introduction of a law, it is applied frequently so that the student may acquire a familiarity and working facility with the fundamental principles of chemistry.

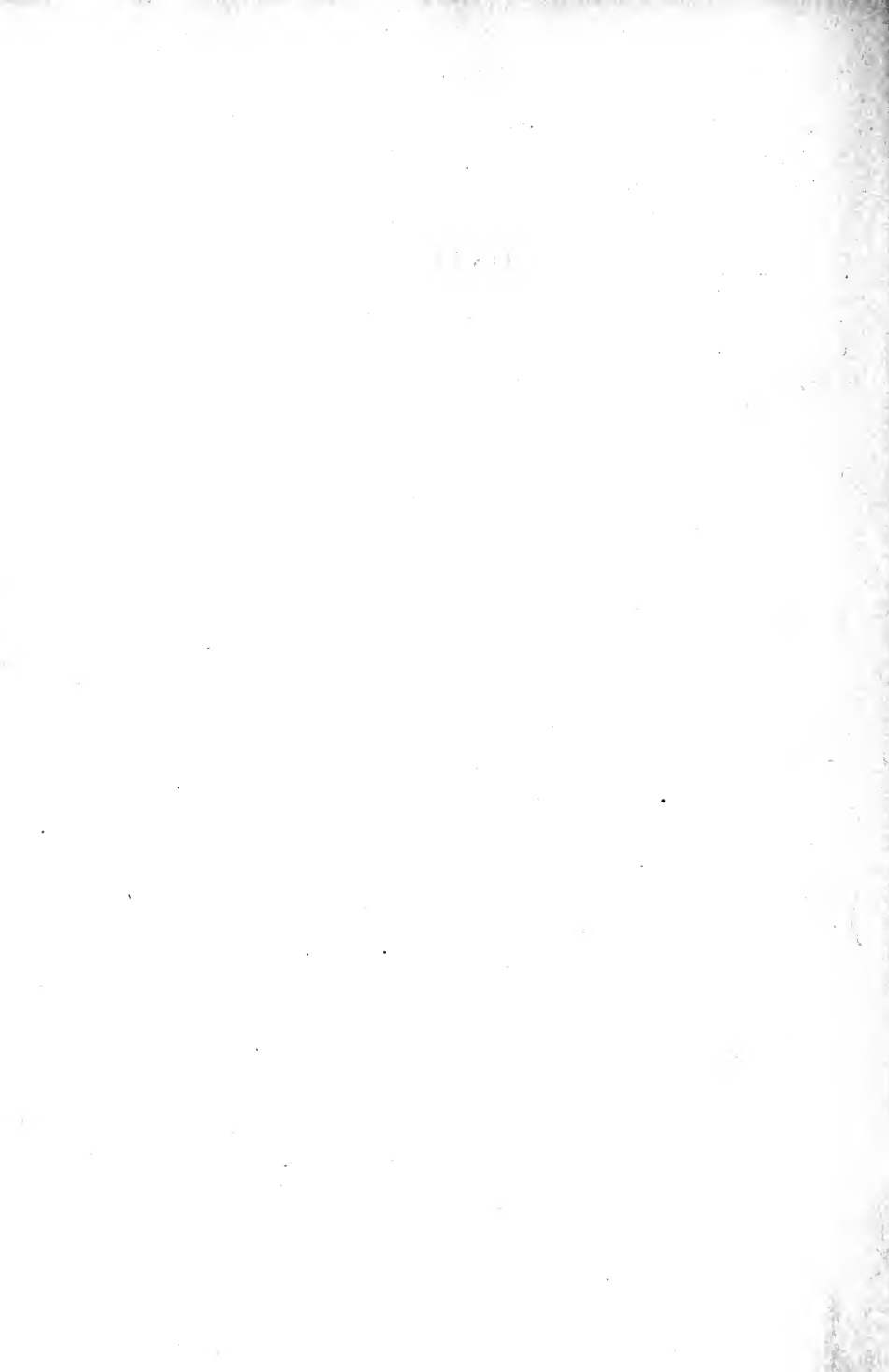
Statements of fact have been carefully and repeatedly checked with the standard books of reference, and the original literature, and it is hoped that satisfactory accuracy has been attained. Where, as was often the case, the data were discordant, the author has used his judgment aided by the principle that, other things being equal, the lower boiling-points and higher freezing-points are those of the purer substances and hence the more accurate.

Throughout the preparation and revision of the book the author has been given loyal aid by his assistants Dr. H. C. Allen, Dr. Frank Rupert, Mrs. Florence Hedger Duke, Mr. Edward R. Weidlein and Mr. Paul V. Farragher. Especial acknowledgment should be given Dr. David F. McFarland, formerly of the University of Kansas but now Assistant Professor of Applied Chemistry in the University of Illinois, who wrote the sections on the metallurgy of lead, copper, silver and gold. In the final revision of these portions, considerable help was received from Mr. W. A. Whittaker, Associate Professor of Metallurgy. The author wishes to express his feeling of great indebtedness to Dr. H. P. Talbot and to Dr. F. B. Dains for their valuable suggestions—made by the one after reading the copy and the other the galley proof. He is especially grateful to his wife Stella C. Cady for most efficient assistance given throughout the work. The illustrations with the exception of the frontispiece and those on

the metallurgy of iron and steel were made by Mr. Charles Robinson. The copy for the frontispiece was prepared by Mr. Emil Grignard, while the cuts for the iron and steel were taken from Bradley-Stoughton's "Metallurgy of Iron and Steel."

HAMILTON P. CADY.

LAWRENCE, KANSAS,  
*September, 1912.*



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# INORGANIC CHEMISTRY

## CHAPTER I

Chemistry is a branch of natural science and deals principally with the properties of substances, the changes which they undergo, and the natural laws which describe these changes.

It is a very difficult matter to convey thought from one person to another by means of words, and anything like accuracy can only be attained when the words have as nearly as possible the same meaning to each. For this reason it is necessary to discuss at some length the significance, in connection with chemistry, of some of the terms used in the opening statement.

**Properties of Substances.**—We are able to perceive objects around us. Each of these objects is called a body and the signs by which it makes its presence known to us are called the properties of the body. When we find ourselves surrounded by a number of different bodies we instinctively begin to arrange them into groups according to certain points of similarity in their properties. We may for example form a class of bodies called bottles and group together all objects having the general shape of bottles. When we come to examine the different members of the class, we find that they possess marked differences in properties, other than those of shape or size. Accordingly, we at once set up a number of sub-classes such as glass bottles, stoneware bottles, rubber bottles, etc., and say that these differ because they are made of different substances. Substances then, are the things of which bodies are made. As examples of substances we may give iron, salt, sugar, lead, etc.

It now remains to distinguish between the properties of bodies and those of substances. This distinction may be brought out by considering what we do in forming the sub-class glass bottles. In grouping the glass bottles together, we pay slight attention to the properties of shape and size, but look to other character-

istics which we say are the properties of the substance glass. Every part of a glass bottle presents the properties of the substance glass, and to precisely the same degree as every other part; further, if the bottle be broken into pieces that body will cease to exist and in its place there will be a collection of bodies called pieces of glass. If we neglect shape and size, the properties of all these bodies are alike and identical with those of the glass bottle from which they were formed. The properties of bodies, then, aside from those of shape and size are the properties of the substance from which the bodies are made. The properties of the body, as such, are those of shape and size. A given body cannot be a barrel unless it has a certain shape and is of a definite size; if it is larger it is a hogshead; if smaller a keg.

**Changes.**—Experience shows us that the properties of substances can be altered in various ways.

Every alteration constitutes a change, and for purposes of convenience, changes are arbitrarily divided into two classes, physical and chemical.

A physical change is one which alters only a very few of the properties of a substance. The moving about of a body or the heating of a piece of iron are examples of physical changes.

A chemical change is one which alters all or nearly all of the properties of a substance. In fact, after a substance has undergone a chemical change, we are unable to recognize the presence of the original substance, and in its place we find one or more new substances with different properties. The burning of wood or the rusting of iron are familiar examples of chemical changes.

From these definitions it would seem to be an easy matter to decide whether a given change is physical or chemical. And so it is in most cases. However, there are all gradations in the number of properties altered in the change, and in many cases it becomes really impossible to decide definitively to which class they belong. This is due to the fact that there is no real difference between the two changes; we having simply arbitrarily drawn a distinction as a matter of convenience in our general scheme of classification. The freezing of water is an example of a change which it is difficult to classify. So many of the properties of ice are different from those of water that one is inclined to call freezing a chemical change, but on the other hand

the transformation takes place so easily, simply upon changing the temperature, that probably the majority of people consider it a physical change.

In most cases there is no difficulty. For example, a piece of rubber when rubbed with woolen acquires the property of attracting bits of paper, but is not otherwise altered. Without question this is a physical change. If the rubber be brought in contact with a flame, it will take fire and burn with a smoky flame and continue to do so until all the rubber has disappeared. Soon after the rubber begins to burn a very strong odor will be noticed which must be due to something produced from the rubber. Since we have in this case the complete disappearance of the properties of rubber and the appearance of the properties of a new substance this is a chemical change.

**Natural Laws.**—Having discussed the properties of substances and the changes which they undergo, we may now turn to the natural laws which describe these changes.

Experience tells us that under like conditions events repeat themselves in a very large measure, and that the more nearly the conditions are reproduced the more closely are the events duplicated. So generally is this the result of our experience that we finally become convinced that if it were possible to reproduce the conditions exactly, the events would be exactly duplicated. This however we know to be impossible; for if every other condition were duplicated, the time of the taking place of the two events would be different since otherwise the two would be one event. As a result then of our experience we are able to say, after repeated trials, just what takes place under certain conditions. Such a statement is a law of nature. A law of nature differs then essentially from a law of man in that it is simply a statement of what does happen and has in it no element of compulsion. Man is so insignificant a part of nature that he cannot presume to dictate to her but can only observe, and learn to make the condition such that the operations of nature shall be as favorable to himself as possible. A law of nature is a statement of the way nature works and should be so worded that it describes as large a number as possible of single phenomena and gives us the maximum amount of information concerning each.

As an illustration of a law of nature, we may select the law

of falling bodies. We know as a matter of common experience that heavy bodies if unsupported fall to the earth, and a statement to this effect is a law of nature. It would be much more useful if it gave us the results of our experience as to the velocity of the bodies after falling for given times and in addition the space passed over during certain times of fall. The law might then be worded as follows: "All heavy bodies fall toward the earth with a velocity which is equal to the force of gravity times the time that the body has been falling and the space passed over is equal to one-half the force of gravity times the square of the time of fall."

Obviously from what has been said the wider our knowledge of the laws of nature the better equipped we are for life. They are all directly or indirectly the results of experience and their formulation is one of the most important works of science.

**The Fundamental Law of Chemistry.**—We find upon examining the properties of different bodies composed of the same substance that they agree exactly in all their essential properties, that is, the properties of the substance in distinction from those of the bodies. We find too that other substances have radically different properties and that the change from one to another is sudden, leaving gaps which are not filled in by gradual alterations in the properties. We have then as many absolutely distinct sets of unvarying properties as there are substances.

*Bodies may be arranged in classes such that the different members of each class agree exactly with each other in all their essential properties.* The different members of each class are the bodies composed of the same substance. The law just given is known as the law of the definiteness of properties and is often called the fundamental law of chemistry.

**Properties of a Substance and the Substance.**—We have defined properties as the signs through which objects manifest themselves to us and have spoken of them as though they belonged to substances, and of the substances as though they in some way possessed the properties. Indeed the original meanings of the words would convey these ideas, and it is very hard to get away from them. However, when we come to consider just what there is about a substance which is not a property of that substance and which might be that which possessed the proper-



ties we are completely at a loss. Everything that we know about a substance is a property of that substance and if by experimentation we find out anything more, that will also be a property; farther than this it seems to be impossible for us to conceive of anything concerning a substance that is not a property of that substance. One can be readily convinced of this by trying to think of anything about a familiar substance that is not a property of that substance. A realization of this fact does not make our conceptions of the substance any the less definite because these properties are the real things, about the substance, which we can know and measure. In fact our idea of the substance is simply the sum of all these properties which we know. For us then a substance is simply *a specific group of essential properties which always occur together and to an unvarying degree under given conditions*. This may be used as a working definition of a substance. If there is anything more to a substance than its properties we can know nothing of it. We cannot even imagine anything about it. So we will leave the question of the actual existence of a possessor of properties to speculative philosophy, and in matter of fact chemistry when we say substance we will mean properties.

Every known substance has a name which in a way stands for the properties of the substance. These names can mean to us only as much as we know of the properties of the substances. So in studying chemistry we must take care that we do not merely learn the names of the various substances with which we deal, but also that we make these names mean something to us by learning the more important properties of the substances. Some of the properties of substances, as for example color, can be ascertained by simple inspection, while others require more or less elaborate experiments to bring them to light. The constant aim is to represent these properties by numbers. To do this a unit must be decided upon and the property carefully measured in terms of this unit. Almost all of the units used in scientific work are derived directly or indirectly from three fundamental units, the centimeter, the gram, and the second, and the whole scheme of units is called the C. G. S. system. The second is the unit of time. It is in use in daily life and is familiar to everyone. The centimeter is the unit of length and is the

one hundredth part of the length of a certain bar of platinum carefully preserved in Paris, which is called the "Standard Meter." This standard meter was intended to be the  $1/10,000,000$  of the earth's quadrant measured on the meridian of Paris, but afterward turned out to be something different from this owing to an error in the measurement. An inch is equal to a little more than 2.5 cm. The gram is the unit of mass and will be defined in the next chapter.

**Physical and Chemical Properties.**—It is convenient to divide properties into two classes—physical and chemical. A physical property is one which can be detected and measured without causing the substance to undergo more than a physical change. As examples we might give color, density, conductivity for heat or electricity, etc.

A chemical property is one which is only revealed when the substance is transformed into something else and consequently undergoes a chemical change. One of the properties of sulfur is that it burns with a pale blue flame, and finally all disappears, leaving behind something which is invisible but which has a very strong smell. Since this property is shown only when the sulfur is transformed into a new substance, this is, therefore, a chemical property.

Of course there is no real difference between physical and chemical changes, and thus there is none between the two sets of properties, but nevertheless, it is convenient to make the arbitrary distinction.

**Identification of Substances.**—The chemist is very often confronted with the problem of deciding as to whether two different bodies are composed of the same or of different substances. The decision rests upon the answer to the question, Do the bodies have exactly the same essential properties? If they do, they are composed of the same substance; if they do not, of different substances. Evidently the question can only be answered after carefully investigating the properties. To be perfectly sure, it would seem to be necessary to compare all of the properties because two substances might agree in most of their properties and yet differ enough in some to make them different substances. The labor required for the comparison of all of the essential properties is so great that it is never done. The chemist com-

pares some of the essential properties, and if these agree exactly he decides that the two bodies are composed of the same substance. In doing this he takes advantage of a law which states that if two bodies agree exactly in some few of their essential properties they will agree exactly in all and are composed of the same substance.

**The Characterization of a Substance.**—The properties chosen for investigation in order to characterize a substance vary with the case, but naturally they are, in general, those which can be most readily observed and measured, or else they are the ones in which the substance differs most from other substances.

The impressions produced upon our sense of sight, taste, and smell can be very easily determined, and are but rarely omitted. The physical state (solid, liquid, or gaseous) of the substance at ordinary temperature and pressure and the conditions under which it changes from one state to another are easily determined and important properties. The solubility of a substance in water is another valuable characteristic. A few words concerning some of these frequently studied properties would seem to be in order here.

**Color.**—A substance has color because it has the power of absorbing some of the light with which we view it, while it allows the rest of it to pass on to our eye, thereby giving us the impression of the kind of light which is not absorbed. In general it is only light of a definite color which is absorbed so we get the sensation of the complementary color. Complementary colors are any two colors which together will produce the sensation of white. The following are complementary colors:

red	green
orange	blue
yellow	violet

If a substance absorbs one of these colors, the color of that substance will be the complement of the color absorbed. For example if yellow is absorbed the substance will appear violet, or if violet is absorbed the substance will appear yellow. Red paint then absorbs green light. The amount of light taken up, and consequently the depth of color will depend upon the thickness of the layer of the substance through which the light

passed and naturally the color will be the lighter, the thinner the layer is. For substances that are transparent the thickness of the layer will depend upon the size of the piece and so the smaller the individual bodies composed of a given substance, the lighter will appear to be the color of that substance. Blue vitriol is a transparent substance of a deep blue color as seen in crystals of the ordinary size, but if one of these crystals be very finely powdered, it will appear to be very light blue or almost white.

**Physical States.**—We distinguish three different ways in which substances fill space and call these the physical states, giving them the names solid, liquid, and gaseous states.

**The Solid State.**—A substance is a solid if a given body composed of this substance has both definite volume and definite shape of its own independent of its surroundings.

**The Liquid State.**—A substance is a liquid if a given body composed of this substance has a definite volume but takes its shape from its surroundings. A liquid always runs down to the lower part of the vessel in which it is placed and takes on the shape of the vessel in so far as it can fill the container. The free surface of a liquid tends to be flat and parallel to the surface of the earth unless the body of the liquid is small, when the surface is rounded. If the body of liquid be very small and the surface entirely free, the liquid takes on the form of a sphere modified more or less by the action of gravity.

**The Gaseous State.**—The gaseous state is characterized by the fact that a gaseous substance has neither definite volume nor shape, but always fills the container in which it is placed and consequently takes its shape and volume from the surroundings.

It is a very easy matter to tell, in the great majority of cases, whether a given substance is solid or gaseous. There are, however, a few substances which are like wax in that they keep a fairly definite shape for some time and so give the impression that they are solids. If left for a longer time they slowly change their shape and flow, thus showing that they are really viscous liquids. But such substances are comparatively rare and give but little trouble in classification.

The physical state of a substance may vary with the conditions such as temperature, etc. With rising temperature, solids always tend to become either liquid or gaseous, and liquids to become

gaseous. With falling temperatures gaseous substances always tend to become either liquids or solids, and liquids to become solids.

**Solubility and Solution.**—Many substances when brought in contact with water mix with the latter in varying proportions and form a homogeneous liquid which has in a general way the properties of the water and of the other substance. Such a homogeneous mixture *i.e.*, one in which every particle is exactly like every other particle in essential properties, is called a solution. The ability of a substance to form a solution is called its solubility and is an important property of the substance. A more extended discussion of solution will be given at a later point, where it will be shown among other things that solutions are not necessarily liquid but may be solid or gaseous as well.

**Mechanical Mixtures.**—Substances are often present together in such a way that they do not form a homogeneous mixture but the different parts may be distinguished and more or less easily separated. Such mixtures are called mechanical mixtures. Muddy water may be given as an example of such a mixture. Examine it with a lens and the particles of silt can be seen. Allow it to stand or pass it through a filter and the silt may be separated from the water. Muddy water is not homogeneous and hence is not a solution. Solutions stand between mechanical mixtures and a very important class of substances, with which we will become familiar in a little time, known as chemical compounds.

## CHAPTER II

The development of the conceptions of mass and energy belongs to the domain of physics, but they are so important in the study of chemistry that a brief discussion of them is necessary at this point.

The mass of a body is often defined as the quantity of matter in that body. But since the conception of matter is very vague, it makes that of mass exceedingly indefinite also. Now the mass of a body is the same as its inertia, and the inertia of different bodies can be easily compared and measured by determining their velocity after a definite quantity of work has been expended upon them. Inertia may be defined as the resistance which a body that is in motion or free to move, offers to forces tending to change its rate or direction of motion.

Inertia then is something definite which can be accurately measured, and by saying that the mass of a body is equal to its inertia we have obtained a definition of mass which is free from the vagueness of the conception of matter. The unit of mass is the gram, the 1/1000 of the standard mass, called the kilogram.

An important point in this connection is that the conception of mass should carry with it no idea of volume. It is a very familiar fact that bodies of the same size may have quite different inertias and consequently different masses. For example, a baseball and a lead ball of the same diameter; it will require very much greater exertion to impart a given velocity to the lead ball than to impart the same velocity to the baseball.

There is considerable confusion between weight and mass, although the two are entirely different. What we call weight is in general the force of attraction existing between two bodies, and this force is proportional to the products of the masses of the bodies and inversely proportional to the square of the distance between their centers of mass. As it is ordinarily used the weight of a body is the force of attraction between the body and the earth. In accordance with what has been said above, the weight

of a body will decrease as it is taken farther and farther from the center of the earth, while its inertia, and consequently its mass will be found unaltered. The weight of different bodies compared at the same spot on the earth's surface will stand to each other as their masses. In other words weight is proportional to mass at a given place.

Since weight is force, it is measured in terms of the unit of force, the dyne. A dyne is that force which acting on a gram for 1 second will generate a velocity of 1 cm. per second.

The weight of a gram varies from place to place on the earth's surface, but on an average is 981 dynes.

If one takes as the unit of weight, not the dyne, but, as is commonly done the weight of 1 gm., then the numerical value of the weight of a body in terms of this unit is the same as the mass of that body. The statement that a body has a weight of 10 gm. means that its weight is the same as that of 10 gm., 9810 dynes say, and consequently the mass is 10 gm.

**Energy.**—Work is usually defined as the product of a force and the distance through which it acts: energy as the ability to do work. It has been further shown that there are many forms of energy such as heat, light, electrical energy, chemical energy, etc., and that these forms may be changed one into another without loss. In fact *in an isolated system of bodies, energy can be neither created nor destroyed, but remains present in unchanged amount.* This is the law of conservation of energy.

Whenever energy is expended in doing work, say in raising a heavy body from the earth, the work done is equal, when measured in the proper units, to the energy expended, or expressed in symbols, representing energy by E and work by W

$$E = W$$

But the work is equal to the force times the distance through which it acts; in this case the force is the weight, wt., and the distance the height, h, through which it is raised, or

$$E = \text{wt.} \times h$$

Now the raised body because of its elevation possesses the ability to do work, or energy, which in this case is usually called potential energy. And this energy is equal to the weight times

the height or the potential energy is equal to the energy which was expended in doing the work which produced the potential energy.

A simpler way of looking at the matter is to regard work as being something that can be added to or taken away from bodies and to say that the body, in the case given above, possessed more work after being raised than before, and that it can give this work to other bodies and so possesses energy. From this way of looking at the matter energy may be defined as follows:

*Energy is work and everything which may be obtained from work and changed back into work.* This definition greatly simplifies the application of the law of the conservation of energy, but requires that work be looked upon in the way given in the preceding paragraph.

The unit of energy is the erg, and this is the work done by a force of one dyne acting through a distance of 1 cm. This unit is rather small, and so we have the joule, which is 10,000,000 ergs, and the kilojoule, which is 1000 joules.

**Conservation of Weight and of Mass.**—One of the most useful instruments to the chemist is the balance. This is a device by means of which the weights of bodies may be compared and since the weights are proportional to the mass, the relative masses may be determined.

If we ask the question, how are the masses of substances affected when they undergo chemical change, we can obtain the answer by weighing the reacting substances before and after the change. We will find that in many cases there are apparent losses in weight, as in the case of burning a piece of wood and in other cases a gain in weight, as in the rusting of iron. But these changes take place in contact with air and hence the changes in weight may be due to something escaping to the air in the case of the wood, or coming in from the air in the case of the iron.

This possible source of change in weight may be excluded by sealing the whole reacting substance air-tight in a flask. When this is done, it will be found that whatever changes in weight may be observed will be inside the limits of experimental error, for all but the very most refined experiments, and even in these cases the small changes observed, may perhaps be due to some source of error as yet unknown.



Neither is there any known physical change which will alter the weight of the substance undergoing the transformation and therefore we at once set up the law of the conservation of weight which is, that *neither a physical nor a chemical change alters the total weight of the system undergoing change.*

Since mass is proportional to weight we may get from the above the law of the conservation of mass. *The total mass of a system is the same before and after any chemical or physical change which may take place within the system.* This simply means that although chemical changes alter so radically the other properties of substances they do not change that property called mass.

**Density.**—The density of a substance may be defined as the ratio of the mass of a given body composed of that substance to the volume of the body. It is expressed in terms of grams per cubic centimeter.

**Specific Gravity.**—The specific gravity of a substance is the ratio of the weights of equal volumes of that substance and of some other substance taken as a standard. Water is usually taken as the standard. The temperature of both substances must be stated in order that specific gravity may be definite. If water at 4° Centigrade is taken as the standard substance, since at that temperature its density is one, the numerical value of the specific gravity will be the same as that of the density, although the conceptions are entirely different.

**Extensity.**—The extensity of a substance is the reciprocal of its density, or is the ratio of the volume of a given body composed of the substance to the mass of that body. It is then the volume of 1 gm. of the substance and is sometimes called the specific volume.

## CHAPTER III

### OXYGEN

**Discovery of Oxygen.**—Oxygen was discovered August 1, 1774, by the English chemist Priestly who prepared it by heating mercuric oxide. It was independently discovered something like a year earlier than by Priestly, by the Swedish chemist Scheele, but his results were not published until 1777. Scheele obtained it by heating saltpeter, mercuric oxide, manganese dioxide, and a number of other substances.

Priestly's original experiments, in a somewhat modified form, may be easily repeated. Mercuric oxide, which is a reddish powdery substance, is placed in a doubly bent tube (Fig. 1) which must be of hard glass. It is then strongly heated, and soon the mercuric oxide darkens in color and becomes almost black. If the heating be continued a bright metallic film appears on the cooler part of the tube, and at the same time, if the end of the delivery tube be placed under water, bubbles of gas will be seen to rise through the water. This gas may be collected by filling a vessel with water and placing it mouth downward in a trough of water. Upon bringing the mouth of the vessel over the delivery tube, the bubbles of gas will pass up into the vessel and gradually displace the water. When the vessel is full of the gas it may be removed from the water and placed mouth upward on the table for experimentation, taking care to keep it covered with a glass plate. It will be as transparent as air and in fact will appear just like air. It may, however, be distinguished from air by its action toward a feebly glowing spark on the end of a splinter. In oxygen the spark bursts into flame, while in air it barely continues to glow.

If the process of heating the mercuric oxide be continued, the oxide will be seen to gradually diminish in quantity and the bright metallic film to increase, and all the while the gas—oxygen—will be given off. This will go on until the mercuric oxide has all disappeared, then the process comes to an end. If the bright metallic film be examined it will be found to consist of drops of

mercury, which is often called quicksilver. So we have the one substance, mercuric oxide, decomposing into two substances, oxygen and mercury which have entirely different properties from the mercuric oxide; therefore, this is a chemical change.

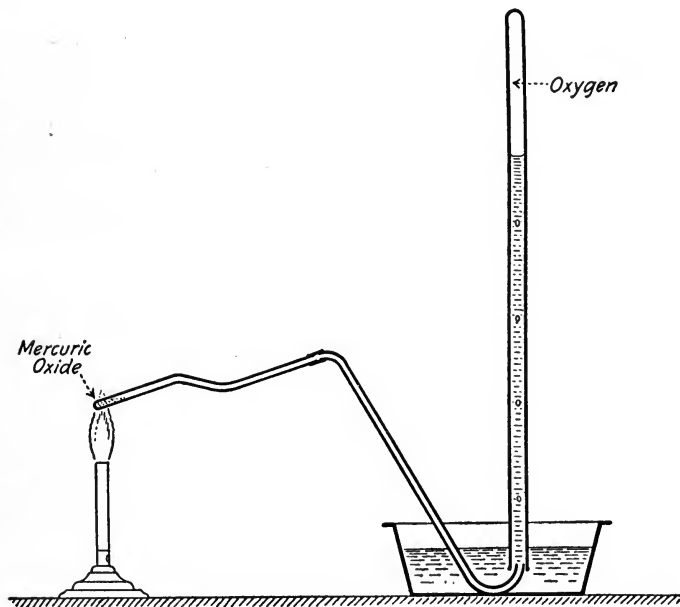


FIG. 1.

**Combustion.**—Experience from infancy has made us familiar with that most important set of chemical phenomena called combustion. We see the coal or wood burn in the stove, the oil or gas in the lamps. We know that a great amount of heat is universally given off during such a process. In most of the above-mentioned cases, it is very apparent that the burning substance decreases in weight. There are, however, other cases which we would certainly classify as combustion in which the weight is increased during the process of burning. For example, if a piece of metallic magnesium, in the form of a ribbon, be held in the flame of a match it will take fire and burn with an exceedingly bright light. The metal disappears and in its place is left a white powdery substance which weighs two-thirds more than the metal did before

burning. Finely divided iron will burn when brought into a flame, forming a black brittle substance which weighs more than the original iron. In these and other instances of the same kind which might be mentioned the products of combustion are solids, and hence easily obtained in a weighable form. This suggests that perhaps in every case of combustion the products are really heavier than the combustible substance, and that in the case of the wood, etc., first mentioned, the products are gaseous and hence escape our observation. That this is so may be easily shown in the case of a lamp by holding a cold object over the burning lamp when it at once becomes covered with a film of liquid. If proper arrangements are made for keeping the object cool, considerable quantities of the condensed liquid may be obtained, when it will be found to be identical in its properties with water. Since this water will not accumulate if the lamp is not lighted, we conclude that the water is one of the products of the combustion of the oil. If a drop of lime water, on the end of a glass rod or a loop of wire, be brought over the flame of a lamp it will quickly become clouded. Now water vapor will not produce this cloud nor will it appear unless the lamp is burning, and therefore we conclude that something besides water is formed during the burning of the oil. One of the characteristic properties of carbon dioxide is its ability to cloud lime water, and we then conclude that carbon dioxide as well as water is formed during the combustion of the oil. Processes by which the presence of certain substances may be detected are called tests or reactions, and the substances used, such as the lime water in this case, are called reagents. By applying these same tests to the coal, the wood and the gas, it will be found that in these cases also, carbon dioxide and water vapor are formed.

There is a solid white substance called caustic potash which has the power to take up both water vapor and carbon dioxide, and to hold them in such a form that they may be weighed.

If a glass cylinder loosely filled with this substance be placed over an unlighted candle and the whole counterpoised upon a balance and the candle then lighted (Fig. 2), the caustic potash will absorb the water vapor and carbon dioxide produced during the burning, and it will be very quickly seen that the weight of the whole is increasing, although the candle is visibly becoming smaller. In some such a way as this it may be shown that the

weight of the products of combustion is always greater than that of the combustible substance. Since in every case the products of combustion have different properties from the original substance, the changes that take place are chemical changes.

The law of the conservation of weight states that the weight of the products of a chemical change is the same as that of the substances before the change. We must conclude then that there is some other substance than that which burned taking part in the chemical change which we call combustion, and that the weight of this other substance is equal to the difference in weight

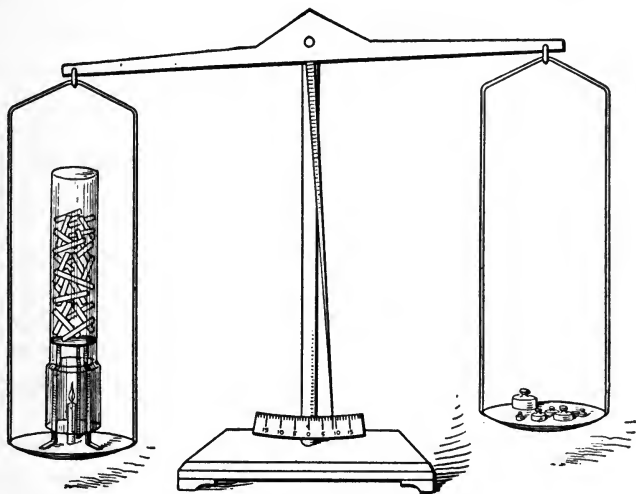


FIG. 2.

between that of the products of combustion and the combustible substance.

**Rôle of the Air.**—All these changes which we have been considering take place in contact with the air, so it is very probable that this other substance is present in the air. This is confirmed by the fact that it is impossible to make a combustible substance burn in a vacuum, and further, when it burns in a limited amount of air a part of the air is used up, or disappears, but never more than one-fifth of the total volume of the air. After one kind of combustion has used up one-fifth of the air, no other substance will burn in the remaining four-fifths. This indicates clearly that the air consists of at least two gaseous

substances, one present to the extent of one-fifth of the total volume; and taking a most important part in the phenomenon of combustion.

If mercury be heated for a number of days to a temperature a little below its boiling point in contact with a limited volume of air a reddish substance is formed on the mercury, and the air gradually decreases in volume. After about 12 days the process comes to an end. If the reddish powder be separated from the mercury and examined it will be found to be identical with the mercuric oxide used above, and like it to yield oxygen on being heated to a temperature above the boiling point of mercury.

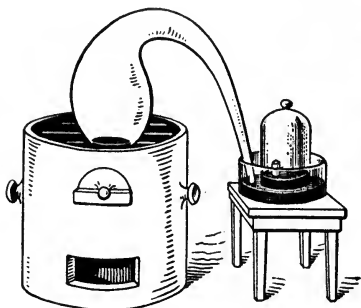


FIG. 3.

The volume of oxygen so produced is just equal to the decrease in the volume of air. The oxygen so obtained has the power of supporting combustion to an extraordinary degree and in the burning all the oxygen may be used up. The residual air will not support combustion, but if the oxygen obtained by decomposing the mercuric oxide be added to it the air regains all its original properties.

These experiments were first performed by the French chemist Lavoisier shortly after the discovery of oxygen, and had much to do with our present conception of combustion. The apparatus which he used is shown in Fig. 3.

**Combination and Decomposition.**—We have seen above that mercuric oxide may be transformed into mercury and oxygen. This process is an example of what is called decomposition, and the reversed process, the formation of the mercuric oxide from oxygen and mercury, is an example of combination. Processes like these compose a large part of the changes studied in chemistry.

**Preparation of Oxygen.**—Although free oxygen is present in the air in such enormous quantities, the problem of separating it from the substances with which it is mixed is by no means simple. (See liquid air, pp. 30 and 236.)

There are many other substances in addition to those already

given which will yield oxygen upon being heated. Among these may be mentioned potassium chlorate and potassium permanganate, and in addition oxygen may be obtained by the decomposition of water by the electric current and by acting upon sodium peroxide with water or dilute acid. The method most in use in the laboratory is that of heating potassium chlorate. This is a white crystalline substance<sup>1</sup> which melts at about 360° C. and decomposes at a higher temperature into oxygen and potassium chloride. The rate of decomposition increases rapidly as the temperature is raised. Curiously enough if it be mixed with something like one-third its weight of manganese dioxide the decomposition takes place much more rapidly than with the potassium chlorate alone, being quite active at as low a temperature as 200° C., and after the operation the manganese dioxide is found to be unaltered except, perhaps, that the particles may be a little finer than before. Although manganese dioxide will yield oxygen at a high temperature, it will not do so in noticeable quantity at 200° C., and its action here seems to be to greatly increase, by its mere presence, the rate at which the potassium chlorate decomposes. Actions of this kind are common and are known as catalytic actions. They will be considered more in detail later.

The decomposition of the potassium chlorate when mixed with manganese dioxide may be carried out in a hard glass flask (Fig. 4). The oxygen is collected by the displacement of water as explained above.

**Physical Properties.**—The gas so obtained is colorless and not very soluble in water or it could not be collected in this manner. If it has been allowed to stand for some time over water containing a little sodium hydroxide, it will be found to be tasteless and odorless. When freshly prepared, it contains a little chlorine and hence has an odor and taste.

One of the important physical properties of every substance is its density. In the case of oxygen, the density is so small that it is not a simple matter to determine it directly, since its mass would be so small in comparison to that of the vessels

<sup>1</sup> Potassium chlorate does not occur in nature and was first prepared many years after the discovery of oxygen, and therefore was not the substance from which oxygen was obtained at its discovery.

necessary to contain it, as to make the error in weighing large. The simplest way is to decompose a known weight of either mercuric oxide or potassium chlorate and weigh the residue. The loss in weight is the weight of the oxygen. If the unit of weight is the weight of 1 gram, the loss in weight gives at once the mass of the oxygen; and to obtain its density it will only be necessary to measure the volume of the oxygen, and divide the mass by the volume. For example, 1.6000 gram. of mercuric oxide gave 0.1111 gram. of oxygen which measured 87.15 c.c. under a pressure of 74 cm. of mercury and at

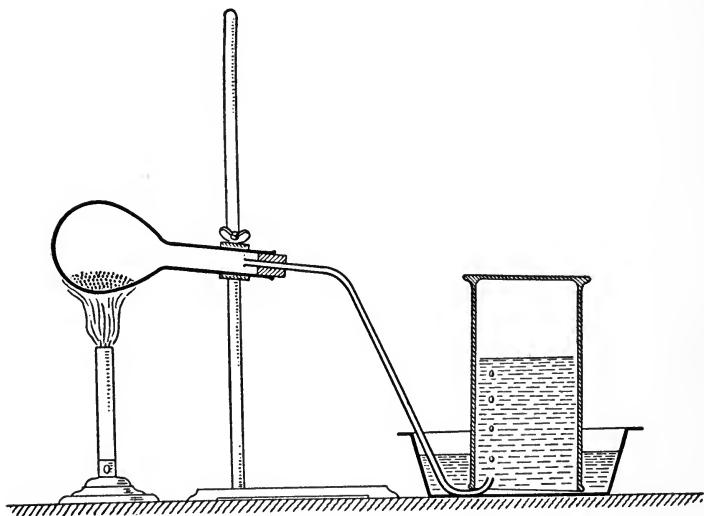


FIG. 4.

25° C. The density of oxygen under these conditions is therefore  $0.1111/87.15 = 0.0012752$ .

**Standard Conditions.**—If the volume of a gram of oxygen, or of any other gas for that matter, be determined under different atmospheric conditions it will be found to vary widely. Other things being the same, the higher the temperature, the greater the volume, and the higher the pressure the smaller the volume. It can be readily seen from this that the density of a gas is not definite unless the volume of a given mass of the gas be measured



at a certain definite temperature and pressure. For sake of uniformity it is the universal custom to take the temperature of melting ice or  $0^{\circ}$  C. as the standard temperature since this can be so easily reproduced. As the standard pressure, is taken the mean pressure of the air at the sea level, which is equal to that of a column of mercury 76 cm. in height. Since the density of the mercury changes with the temperature, the mercury should also be at  $0^{\circ}$  C.

### THE GAS LAWS

**Boyle's.**—As it is usually not convenient to measure the volume of gases under standard conditions, it is a matter of great importance to know just how they change their volumes with changes in pressure and temperature, so that their volumes may be read under any convenient conditions and corrected to what they would be under standard conditions. Fortunately it has been found that gases behave so nearly alike that the same corrections will do for all unless extreme accuracy is demanded.

The simplest relationship is that between the volume and the pressure, and this has been known ever since 1660, when it was discovered by the English scientist Robert Boyle.

Boyle found that if the pressure upon a fixed mass of a given gas, at constant temperature, be doubled, trebled, or quadrupled, the volume of the gas would be reduced to one-half, one-third, or one-fourth of its original volume, or in other words *the volume of a fixed mass of a given gas at constant temperature is inversely proportional to the pressure.* This is known as Boyle's law, and may be represented as follows:

$$(1) \quad v = k \frac{1}{p}$$

when  $v$  and  $p$  are the simultaneous values of the volume and pressure under which the gas is measured.

The above relation may also be expressed in the following form:

$$(2) \quad p_1 v_1 = p_2 v_2 = pv = \text{const.}$$

where  $p_1 v_1$  and  $p_2 v_2$  are pairs of simultaneous values of pressure and volume. In words this is expressed as follows: *The product of the simultaneous values of the pressure and the volume for a*

*fixed mass of a gas at constant temperature is a constant.* This is simply another way of wording Boyle's law.

As an example of the practical application of this law we may take the data given above for the density of oxygen. There we had 87.15 c.c. of oxygen at 25° C. and a pressure of 74 cm. of mercury. What would be the volume at the same temperature but under the standard pressure of 76 cm. of mercury?

Taking equation (2) we have

$$P_1V_1 = P_2V_2$$

and letting  $p_2=74$ ,  $v_2=87.15$  c.c. and  $p_1=76$  cm. of mercury,  $v_1$ =volume at this standard pressure. Solving for  $v_1$  we get:

$$v_1 = \frac{P_2V_2}{P_1}$$

$$v_1 = \frac{74 \times 87.15}{76} = 84.85 \text{ c.c.}$$

This would be the volume of the gas if measured at the temperature 25° C. under the standard pressure.

In order to calculate the volume which the gas would occupy at the standard temperature as well as pressure, it would be necessary to ascertain the influence of a given change in the temperature upon the volume of a fixed mass of a gas at constant pressure, and apply the proper correction to the calculated volume of the gas at the standard pressure. As indicated above, the volume of a fixed mass of gas increases with rising temperature, the pressure remaining constant. If we take the volume occupied by a certain mass of a gas at the melting-point of ice or 0° C. as unity, and then heat the gas to the temperature of water boiling under a pressure of 76 cm. of mercury, the volume of the gas will be found to be 1.367, so that the increase has been .367. If now we divide the difference in temperature between the melting-point of ice and the boiling-point of water into 100 equal parts, as has been done in the Centigrade thermometer system, the increase in volume for each degree is .00367 or 1/273 of the volume at 0° C. This is called the coefficient of expansion of the gas and is represented by alpha, "α".

The law describing this behavior is called **Gay Lussac's and Dalton's Law** or sometimes **Charles' Law** and was discovered simultaneously by Gay Lussac and Dalton in 1802. It may be

expressed as follows: *The volume of a fixed mass of a gas at constant pressure is increased by 1/273 of its volume at 0° Centigrade for each degree rise in temperature.*

The mathematical expression is

$$v_t = (1 + \alpha t)v_o$$

where  $v_o$  = volume at 0° C.,  $v_t$  = the volume at the temperature 't',  $t$  = the temperature, and  $\alpha$  the coefficient of expansion, 0.00367 or 1/273. The conditions under which this will hold are that both the mass of the gas and the pressure upon it must remain constant.

We are now in a position to make the full correction of the volume of the oxygen obtained on page 20. On page 22 we made the correction for pressure according to Boyle's law and found that at a temperature of 25° C. and under the standard pressure the volume would be 84.85 c.c. This volume is  $v_t$  in the Gay Lussac's Law equation and it only remains to find  $v_o$ . As given above

$$v_t = (1 + \alpha t)v_o$$

or

$$v_o = \frac{v_t}{1 + \alpha t}$$

or substituting

$$v_o = \frac{84.85}{1 + .00367 \times 25} = 77.74 \text{ c.c.}$$

To obtain the density of oxygen under standard conditions all that remains to be done is to divide the mass of the oxygen, 0.1111 gm. by this calculated volume, 77.74 c.c.

$$\text{Density} = \frac{.1111}{77.74} = .0014293 \text{ gm. per c.c.}$$

**Absolute Temperature.**—Since all gases are so regular in their behavior toward changes of temperature the change in the volume of a fixed mass of a gas under constant pressure has been taken as the measure of the change in temperature. Gas thermometers are really the standard instruments for the measurement of temperature at the present time. Mercury thermometers are used as working instruments because they are somewhat more convenient than gas thermometers.

In the Centigrade thermometer system, the melting-point of ice has been called  $0^{\circ}$  and the boiling-point of water  $100^{\circ}$ . If a fixed mass of a gas at constant pressure be raised in temperature from the melting-point of ice to the boiling-point of water (Fig. 5), its volume will be increased by  $100/273$  of its volume at  $0^{\circ}$  C. Since we have already decided to call the temperature interval

Volume Temp.

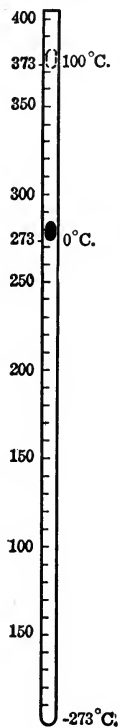


FIG. 5.

between the freezing- and the boiling-point of water  $100^{\circ}$  and to take the change in the volume of a gas as the measure of the change in the temperature, we say that if a fixed mass of a gas at constant pressure changes its volume by  $1/273$  of its volume at  $0^{\circ}$  C. its temperature has been changed by  $1^{\circ}$  C. If it changes its volume by  $20/273$  of its volume at  $0^{\circ}$  C. the change has been  $20^{\circ}$ .

It is a very simple matter to cool a gas to a temperature below  $0^{\circ}$  C. The gas contracts during the process and continues to do so as it is cooled to lower and lower temperatures. In accordance with what has been said above, we consider that the gas has been cooled  $1^{\circ}$  for each  $1/273$  of its volume at  $0^{\circ}$  C. which it has lost, the pressure and the mass of gas being constant. It is very obvious that a gas cannot lose more than  $273/273$  of its volume because this would reduce it to zero volume. Therefore, the lowest temperature to which a gas can be cooled is  $273$  Centigrade degrees below the Centigrade zero and this temperature is called absolute zero. As a matter of fact all gases are liquefied or solidified before they reach this temperature, and since the gas laws do not describe the behavior of liquids or solids the substances would doubtless have some volume even if cooled to

absolute zero. The lowest temperature yet reached is about  $3^{\circ}$  above absolute zero which is the temperature at which liquid helium will boil under diminished pressure.

Temperatures reckoned upward from this absolute zero are called absolute temperatures. The absolute temperature of melting ice is  $273^{\circ}$  A., and of boiling water  $373^{\circ}$  A. Temperatures on the Centigrade scale may be readily changed to the

absolute scale by adding 273 to the Centigrade temperature. Absolute temperatures are usually represented by T and Centigrade by t, so,

$$T = t + 273$$

There are two important advantages of the absolute over the Centigrade system. First, by its use one does away with all negative temperatures and second, we are enabled to state the law of Gay Lussac and Dalton in the following exceedingly simple manner. *The volume of a fixed mass of a gas at constant pressure is directly proportional to the absolute temperature.* In symbols this law is expressed as follows:

$$v = k'T$$

where v is the volume, k the proportionality factor, and T the absolute temperature. Boyle's law, it will be recalled, is similar to this in form. The volume of a fixed mass of gas at constant temperature is inversely proportional to the pressure. In symbols,

$$v = k \frac{1}{p}$$

in which p is the pressure and k and v have the same significance as before.

**The Combination of the Gas Laws.**—It is a very common problem in chemistry to have to calculate the volume of a gas under standard conditions from data taken at quite a different temperature and pressure. This may be done in two operations as we have shown above, but it is very desirable that we should be able to do it in one. The laws of Boyle and of Gay Lussac may be readily combined into one general gas law by paying attention to a few simple conditions.

According to Boyle's law the volume of a fixed mass of a gas at constant temperature is inversely proportional to the pressure, or

$$v = k/p$$

while Gay Lussac's law says that the volume of a fixed mass of a gas at constant pressure is proportional to the absolute temperature, or

$$v = k'T$$

Now a magnitude which is proportional to two other magnitudes is proportional to their product. So if the  $v$ , in the Boyle's law equation and the  $v$ , in the Gay Lussac's law refer to the volume of the same fixed mass of the same gas, in each case, then this volume becomes proportional to the product of the absolute temperature and the reciprocal of the pressure, or,

$$v = KT/p$$

Our general gas law then can be put in words as follows: The volume of a fixed mass of a gas is directly proportional to the absolute temperature and inversely proportional to the pressure upon the gas. The proportionality constant  $K$  is usually written " $r$ ," so that the law becomes

$$v = rT/p$$

or

$$pv = rT$$

Rearranging the equation, it becomes  $pv/T = r = \text{constant}$ , where  $p$ ,  $v$ , and  $T$  are simultaneous values of pressure, temperature and volume.

Then,

$$p_1 v_1 / T_1 = pv / T = p_{76} v_o / T_o$$

in which  $p_{76}$  is the standard pressure of 76 cm. of mercury,  $T_o$ , the standard temperature of  $0^\circ \text{C}$ . or  $273^\circ \text{A}$ ., and  $v_o$  the volume under standard conditions which is so often what we wish to find. Solving this equation for  $v_o$  we get,

$$v_o = vpT_o / p_{76}T$$

or putting in the numerical values of  $T_o$  and  $p_{76}$ ,

$$v_o = 273pv / 76T$$

in which  $p$ ,  $v$ , and  $T$  are the measured values and  $v_o$  that desired. This is a very convenient form to leave the equation in for many purposes, but if it is desired to use Centigrade temperatures it must be modified somewhat by substituting for  $T$  its value,  $273 + t$ , and then

$$v_o = \frac{273 pv}{76(273 + t)} = \frac{vp}{76(1 + t/273)}$$

or

$$v_o = \frac{vp}{76(1 + .00367t)}$$

**Graphical Representation of the Gas Laws.**—An equation like that for Boyle's law,

$$pv = \text{constant}$$

is very useful indeed, since it enables us to calculate the pressure corresponding to any volume or the volume corresponding to any pressure.

Let us assume for the moment, that in the equation given above,

$$pv = \text{constant}$$

that the value of the constant is 100. Then

$$pv = 100$$

For every value of  $p$ , there is one and only one value of  $v$ —arranging these in the form of a table,

$p$	$v$
1	100
2	50
5	20
10	10
20	5
50	2
100	1

Any intermediate values could be determined in the same way.

By employing a device which is very common in all branches of science, a clear picture of the relation can be obtained which tells the whole story at a glance (Fig. 6).

This is called the graphical or geometrical representation of the relation and the process of obtaining the representation is often called plotting a curve.

To represent the numerical relation given above for Boyle's law, let us say that in the diagram given above, distances measured toward

the right from the line  $OP$  shall represent volume, and that distances measured upward from the line  $OV$  shall repre-

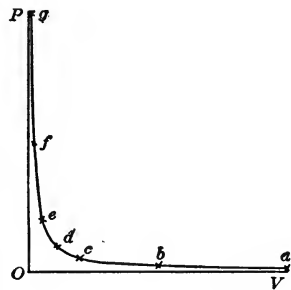


FIG. 6.

sent pressures. Every point then to the right of PO and above OV represents at the same time some definite pressure and volume. To represent the values for  $p$  and  $v$  from the equation  $pv=100$  as given above, divide the distance PO and OV each into 100 equal parts. When  $p=1$ ,  $v$  was 100. To represent this find a point one division above OV and 100 divisions to the right of OP. The point  $a$  fulfils these requirements. When  $p$  is 2,  $v$  is 50. This is represented by a point two divisions above OV and 50 to the right of OP. The point  $b$  is the required point. When  $p$  is 5,  $v$  is 20 and this is represented by the point  $c$ .

Correspondingly the points ( $p=10, v=10$ ), ( $p=20, v=5$ ), etc., (data given in the above table) are represented by the points  $d, e, f$  and  $g$ .

These points  $a, b, c, d, e, f$ , and  $g$  are then connected by a smooth line, and the resulting curve gives a complete picture of the relations contained in the equation

$$pv = \text{constant}$$

If the points corresponding to any values of  $p$  and  $v$  intermediate between those given in the table be calculated they will

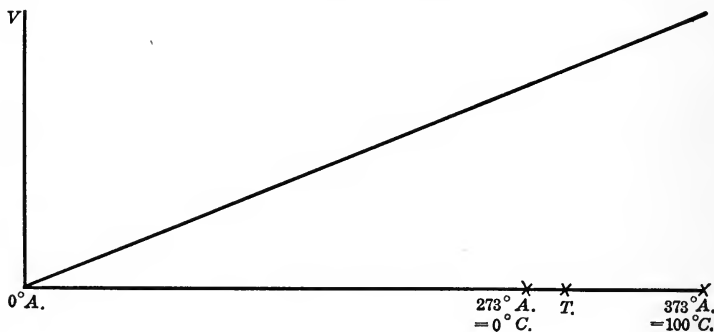


FIG. 7.

be found to lie on the curve as drawn. Since this is true for any given point we say it is true for all, and that the curve represents every simultaneous value of  $p$  and  $v$  between the limits  $p=1, v=100$ , and  $p=100, v=1$ .

The equation  $v=kT$  gives simultaneous values of  $v$  and  $T$  which when plotted yield the picture shown above (Fig. 7). This represents Gay Lussac's law.



Curves similar to these are so constantly used in all departments of science that it is highly advisable that everyone be able to prepare them and to read them at a glance. This is by far the best way to represent experimental results wherever it is applicable.

**Other Physical Properties of Oxygen.**—The solubility is one of the very important properties of a substance, a knowledge of which goes to make up our conception of the substance. As has been pointed out above, oxygen is not very soluble in water or it could not have been collected over this liquid. Its solubility in water, however, is easily measured since one volume of water at 0° C. dissolves .04890 volumes of oxygen. At higher temperatures the solubility is smaller. Many metals absorb noticeable quantities of oxygen. Melted silver, for example, takes up something like 10 times its own volume of oxygen, the greater part of which it gives off on cooling. The escaping gas causes particles of silver to grow out from the bead, and produces the phenomenon known to assayers as sprouting.

**Liquid Oxygen.**—If oxygen under atmospheric pressure be cooled below  $-182.5^{\circ}$  C. it becomes a pale blue liquid which boils under atmospheric pressure at  $-182.5^{\circ}$  C. If the pressure be lowered the boiling-point falls until under a pressure of 0.75 cm. of mercury the liquid boils at  $-211.2^{\circ}$  C. Upon raising the pressure the boiling-point rises, and finally under a pressure of 50.8 atmospheres the boiling-point is  $-118.5^{\circ}$  C. If the temperature be raised any higher than this the oxygen refuses to remain in or take on the liquid state no matter how great the pressure. To liquefy oxygen then it must be cooled to at least  $-118.5^{\circ}$  C., then upon the application of sufficient pressure which at  $-118.5^{\circ}$  C. is 50.8 atmospheres, but is lower if the temperature is lower, the liquid appears. At ordinary temperatures or at any temperature higher than  $-118.5^{\circ}$  C. it is not possible to liquefy oxygen by any pressure however great.

All other gases behave as oxygen does in this respect. Each gas has a certain temperature above which it is impossible to liquefy it. This temperature is called the **critical temperature**, and the pressure which will be just great enough to bring about the liquefaction at the critical temperature is called the **critical pressure**. In the case of oxygen, the critical temperature is

-118.5° C. and the critical pressure is 50.8 atmospheres. An atmosphere is a pressure equal to 76 cm. of mercury. For other gases, the critical magnitudes are different, and are characteristic for each substance. In forming a conception of any given gaseous substance, a fairly definite notion of its critical magnitudes and boiling-point should be obtained.

Air is a mixture of approximately one part by volume of oxygen and four parts by volume of other gaseous substances, chiefly nitrogen. Liquid air has something like the same composition but is a little richer in oxygen because this is more easily liquefied than the nitrogen. If the liquid air be allowed to boil away, the nitrogen will come off in relatively greater quantities than the oxygen and the liquid will gradually become richer and richer in oxygen, and finally will yield a gas containing 95 per cent. or more of oxygen. This is the basis of the most important method for the preparation of oxygen upon a commercial scale. The gas is put upon the market in strong steel cylinders under a pressure of 100 atmospheres.

Both gaseous and liquid oxygen are attracted by a magnet although the attracting force is very much smaller than that exerted upon an equal weight of iron.

**Solid Oxygen.**—When oxygen is cooled with liquid hydrogen, it freezes to a light blue solid which melts at -227° C.

**Chemical Properties.**—The ability to support combustion to an extraordinary degree is the chief chemical property of oxygen, and is made use of in its identification by introducing into a cylinder of the gas a glowing spark on the end of a stick, when it at once bursts into flame. This is the test or reaction for oxygen and the splinter or spark is the reagent.

There are two good reasons why the wood burns faster in the oxygen than in the air. The first is that since air is only one-fifth oxygen, more oxygen is in contact with the wood at a given time in the pure gas than in air, and naturally they combine more rapidly. Second, in the case of the combustion in the air, the heat given out in the burning of the wood is divided between the wood, the oxygen, the rest of the air and the products of combustion; and so of course the temperature cannot rise as high as in the case of the combustion in pure oxygen, where it has only the wood, the oxygen, and the products of combustion

to warm. Now the same thing is true in this case that was mentioned about the decomposition of potassium chlorate, that the reaction goes on much faster the higher the temperature. Therefore the rapid combustion in oxygen is due to the more abundant supply of the gas and to the higher temperature.

From this explanation we would expect that other things would burn more rapidly in oxygen than in air, and upon trial we would find our expectation realized. For example sulfur burns in the air with a pale blue flame of very little luminosity, while in oxygen it burns with a bright blue flame. Phosphorus burns in air with a yellowish-white flame, in oxygen the combustion is exceedingly rapid and the light is so intense as to be fairly dazzling.

Many substances which will not readily burn in the air will do so in oxygen, for example iron. If a piece of iron be heated in the air, it becomes covered over with a coating of something which may be separated rather easily from the iron, and at the same time that the coating is formed the iron increases in weight. If a thin piece of iron, say a watch spring, be heated white hot in oxygen it will take fire and burn vigorously, throwing off sparks in a very spectacular manner. The substance left after the combustion is the same as that formed by heating the iron in the air.

The easiest way to heat the watch spring to whiteness is to wrap the end of the spring with two turns of cotton string and dip the end in a little melted sulfur. If the sulfur be lighted and the spring thrust into a vessel of oxygen, the heat of the burning sulfur will make the iron white hot, when it will kindle and burn as described above.

We know as a matter of practical experience that in order to make things burn rapidly it is necessary to raise their temperature, and therefore it might seem natural to ask what the **kindling temperature** is in each case. Experiment will tell us that combustible substances combine with oxygen at temperatures far below that at which they burst into flame; that with rising temperature the rate at which the combination or combustion takes place increases very rapidly until finally the substance kindles into flame. It is not possible to locate this temperature at which kindling into flame takes place, very accurately, as it depends upon many factors, such as the state of subdivision of the sub-

stance, etc. Still less is it possible to locate a temperature above which a substance will combine with oxygen, while below it the reaction will not take place. The rate simply becomes smaller and smaller as the temperature falls. We therefore **must** conclude that all combustible substances combine with oxygen at all temperatures, although the rate may be immeasurably small.

We must look upon the coal, wood, etc., as combining with oxygen at ordinary temperatures, and the only reason that they have not disappeared is simply that they have not had time to do so.

The combination of oxygen with a combustible substance at temperatures below the kindling point is called **slow oxidation**. This is not essentially different from combustion, and with rising temperature gradually merges into the latter. As much heat is given off during slow oxidation as during the rapid combustion of the same quantity of the substance. If this heat is retained and goes to raise the temperature of the body, as for example, when the reaction takes place in the midst of a heap of coal, the temperature may rise high enough for the substance to burst into flame. When this happens we say it is a case of spontaneous combustion.

**Quantitative Relations.**—If we study with care the decomposition of mercuric oxide, taking into account the weights of the various substances, we will find that the weight of the oxygen formed plus that of the mercury is just equal to the weight of the mercuric oxide taken. This shows, of course, that nothing else than mercury and oxygen is formed from mercuric oxide. We will find too that, no matter how or where the mercuric oxide is prepared, there will always be a constant ratio between the weight of the mercuric oxide decomposed and the weight of the oxygen obtained; and that the same thing will be true for the ratio of the mercury to the mercuric oxide, although of course, the constants are very different. Letting A represent the weight of the oxygen, B that of the mercury, and C that of the mercuric oxide, we get:

$$\frac{A}{C} = \text{Constant} \quad \text{and} \quad \frac{B}{C} = \text{Constant}$$

Dividing one by the other:

$$\frac{A}{B} = \text{a constant}$$

From this it will be seen that there is a constant ratio between the weights of the oxygen and mercury obtained from mercuric oxide.

This may be stated as follows: when mercury and oxygen combine to form mercuric oxide they do so in a perfectly fixed and definite proportion by weight.

This is simply one example of the law of constant proportions, which is one of the most important of the laws of chemistry, and may be stated as follows: "*Whenever two or more substances combine to form another substance, they do so in a perfectly fixed and invariable ratio by weight.*"

**Elements.**—As we have seen above, mercuric oxide yields two substances, oxygen and mercury, whose combined weights are equal to that of the mercuric oxide, while their individual weights are less. This was spoken of as decomposition, and it is a common characteristic of all decomposition processes that substances are produced whose individual weights are less than the weight of the substance from which they were formed. If we examine all of the chemical transformations which oxygen undergoes, we will find that in no case is there a substance formed whose weight is less than that of the oxygen used up. In one case, that of the formation of ozone (p. 35), the weight of the resulting substance is the same as that of the oxygen consumed; in all other cases it is greater. We must conclude then that oxygen has never been decomposed, that is, changed into something having a smaller weight. The same is true for mercury, and for about 80 other substances. *These substances are called the elements,<sup>1</sup> and in all ordinary chemical transformations they yield substances of either equal or greater, but never less weight than their own.*

#### TABLE OF ELEMENTS

Aluminum	Bismuth	Carbon
Antimony	Boron	Cerium
Argon	Bromine	Cesium
Arsenic	Cadmium	Chlorine
Barium	Calcium	Chromium

<sup>1</sup> The word "ordinary" is introduced here to exclude radio-active transformation, since it is possible that in these cases the above statement may not hold.

TABLE OF ELEMENTS.—(Continued.)

Cobalt	Lutecium	Selenium
Columbium	Magnesium	Silicon
Copper	Manganese	Silver
Dysprosium	Mercury	Sodium
Erbium	Molybdenum	Strontium
Europium	Neodymium	Sulfur
Fluorine	Neon	Tantalum
Gadolinum	Nickel	Tellurium
Gallium	Nitrogen	Terbium
Germanium	Osmium	Thallium
Glucinum	Oxygen	Thorium
Gold	Palladium	Thulium
Helium	Phosphorus	Tin
Hydrogen	Platinum	Titanium
Indium	Potassium	Tungsten
Iodine	Praseodymium	Uranium
Iridium	Radium	Vanadium
Iron	Rhodium	Xenon
Krypton	Rubidium	Ytterbium
Lanthanum	Ruthenium	Yttrium
Lead	Samarium	Zinc
Lithium	Scandium	Zirconium

**Compounds.**—The eighty some elements are capable of entering into combination with one another, thus giving rise to the almost innumerable substances known to chemists as chemical compounds. These chemical compounds show the following characteristics. They have entirely different properties from those of the elements from which they are formed. They are homogeneous. The proportions by weight in which the elements combine is in accord with the law of constant proportions. The weight of the compounds is always greater than that of any one of the elements from which it was formed and is equal to the sum of their weights. Probably the most important of all properties is that described by what is known as the *law of the conservation of the elements*. *No ordinary chemical process (excluding radio-active changes) ever produces from a compound any other elements than those which united for its formation, and these elements are reproduced in precisely the proportion by weight in which they combined for the formation of the compound.* These points may be illustrated by mercuric oxide. It may be formed

by the union of the two elements oxygen and mercury in definite proportion by weight. Its properties are very different from those of mercury and of oxygen, and no elements but mercury and oxygen have been obtained from it. With a proper understanding of the meaning of the term "element" we may now resume the discussion of the element oxygen.

**Occurrence in Nature.**—As we have already seen, oxygen makes up about one-fifth of the volume of the air. That the air is a mixture of gases and not a chemical compound will be shown later. An element which is found in nature uncombined chemically with any other element, although it may be mixed with them, is said to exist in the "free state." Since there is such a great quantity of air, oxygen in the free state is very plentiful. The compounds of oxygen are numerous and exceedingly abundant. More than 40 per cent. of the earth's crust and eight-ninths of the water is oxygen.

Almost every one of the elements is capable of undergoing chemical change with oxygen. The substance so formed differs radically in its properties from either oxygen or the other element. Its weight is equal to the sum of the weights of the other element and of the oxygen, and the two elements unite for the formation of the substance in perfectly definite proportion by weight. Therefore all substances formed in this way are chemical compounds, and since they all have one common component, oxygen, they are called oxides. We have, for example, oxide of mercury, oxide of iron, oxide of lead, etc.

**Preparation of Ozone.**—When oxygen is exposed to the influence of the silent electrical discharge, it undergoes remarkable alterations in its properties, and is partially transformed into a new substance called ozone. With pure dry oxygen something like 18 per cent. of the gas can be converted into ozone. By removing the latter as it is formed, the whole of the oxygen can be changed into ozone.

**Physical Properties of Ozone.**—When oxygen is converted into ozone, the volume of the ozone is only two-thirds that of the oxygen from which it was formed and consequently its density is one and one-half times that of oxygen or 0.002144. It boils at  $-119^{\circ}$  C. and may be obtained as a deep blue liquid by passing ozonized oxygen through a tube cooled with liquid air. The

greater part of the dissolved oxygen may be removed by partial evaporation. Liquid ozone is a very dangerous substance since it explodes with great violence either when brought in contact with oxidizable substances or when its temperature has reached its boiling-point. The gas when compressed is also explosive. Gaseous ozone has a faint blue color and a very strong odor. It is somewhat soluble in water.

**Chemical Properties.**—Gaseous ozone has a very irritating action on the mucous membrane. A piece of bright silver when exposed for some time to ozone becomes blackened. A colorless solution of potassium iodide becomes dark brown from liberated iodine when exposed to the action of ozone although oxygen has no effect on it.

If ozone be heated to a temperature of 250 to 300° C. it is changed back to oxygen again with an increase in volume equal to the contraction which took place when the ozone was formed. The presence of metallic silver and also of several metallic oxides increases the rate at which this transformation of ozone into oxygen takes place at any given temperature. Many coloring substances are destroyed by ozone and hence it is used as a bleaching agent. It rapidly destroys the lower organisms, such as bacteria, and is therefore used as a disinfectant. In general its action is one of oxidation and differs from oxygen chiefly in that it is more vigorous.

**Allotropy.**—Oxygen may be converted into ozone or ozone into oxygen without any alteration in weight. From this the conclusion is drawn that no other substance combines with the oxygen for the formation of the ozone. This conclusion is confirmed by the fact that when phosphorus is acted upon by ozone in one case and oxygen in another, the same substance, phosphorus pentoxide, is formed in each case, and if equal weights of oxygen and ozone are taken the weight of phosphorus pentoxide formed in each experiment will be the same. What then is the difference between oxygen and ozone?

Whenever oxygen is transformed into ozone, energy is taken up; and when the ozone is changed back into oxygen, this energy reappears, generally in the form of heat.

Ozone then is to be regarded as a modification of the element oxygen, possessing more energy than the latter. This property



which oxygen has in common with several of the other elements of existing in two or more distinct forms, each having its own set of properties, even when the physical state of the different forms is the same, is called allotropy.

Allotropy then is the property shown by certain elements of existing in more than one distinct form, each having the same physical state but possessing different physical properties. The different forms are spoken of as allotropic modifications of the element.

The root of the difference between the allotropic modifications of any one element consists of a difference in energy, although in some cases and possibly in all there is a difference in molar weight (see page 83).

**Uses for Ozone.**—As was mentioned before, ozone is used for bleaching of oils, paper, delicate fabric, and flour, sterilization of water, and in addition is used for the purification of air and of starch, resinification of oils, and in the aging of liquors. When ozone acts upon these substances, in general, one-third of the weight of the ozone is used in oxidizing and two-thirds becomes ordinary oxygen.

## CHAPTER IV

### HYDROGEN

Hydrogen was shown to be a distinct substance by Cavendish in 1766. It had been observed as an inflammable gas many years before, but was confused with other inflammable gases. That it is an element is shown by the fact that whenever it undergoes chemical changes the substances produced weigh more than the hydrogen which was transformed. Like oxygen it is a gas at ordinary temperatures.

**Occurrence.**—Hydrogen occurs free in nature in rather small quantities. It is found in the gases given off from some volcanoes and fumaroles and is present in the air to the extent of something like one volume in 30,000 volumes of air. The quantity is so small that it is difficult to determine it with accuracy. In the combined state it is very abundant. Its chief compound is water, of which it forms 11.19 per cent., by weight, the remainder being oxygen. It occurs also in combination in coal, petroleum, natural gas, and in almost all substances of animal or vegetable origin. It is the essential element in a large and important class of substances known as the acids.

**Preparation of Hydrogen.**—Since water is so abundant and contains so much hydrogen it would seem natural to suppose that hydrogen might be obtained from it economically by some such process as was used in the preparation of oxygen.

The preparation of oxygen from its compounds is comparatively simple because there are several fairly abundant and cheap compounds, for example, mercuric oxide and potassium chlorate, which will break up on being heated to a moderate temperature into gaseous oxygen and some other substance which is either liquid (mercury) or solid (potassium chloride) at ordinary temperatures, and can consequently be readily separated from the gaseous oxygen.

In the case of hydrogen, neither water nor any other compound has these properties and, therefore, a different method of preparation is required. At a fairly high temperature, water can be

decomposed, but the products are hydrogen and oxygen, and there is no practical method for the mechanical separation of these two gases. However, if there were present in the heated system something with which the oxygen in the water vapor could combine to form a compound which is either solid or liquid at ordinary temperature, it ought then to be possible to separate this compound from the hydrogen and so get the latter in the pure state.

Metallic iron forms a compound with oxygen which is solid even at very high temperatures, and if steam be passed over finely divided iron, heated in a tube to redness, iron oxide and hydrogen will be formed. The iron oxide will remain in the tube, while the hydrogen, mixed with some unchanged steam, will pass on over. The hydrogen may be collected by the displacement of water, as was done with oxygen, the steam which accompanies it being condensed in the water of the pneumatic trough.

The place of the iron may be taken by several other metals. Magnesium, for example, may be used, in which case the temperature may be very much lower. In fact magnesium will rapidly decompose boiling water if a little of a magnesium salt is dissolved in the water to keep the surface of the magnesium free from the magnesium compound formed.

Metallic calcium in the form of turnings decomposes cold water at a convenient rate, thus furnishing a ready means for the preparation of hydrogen on a small scale.

The metals sodium and potassium act upon water so vigorously, even at ordinary temperatures, that only very small quantities of the metals can be brought in contact with water without giving rise to dangerous explosions.

In each of these cases hydrogen and a non-gaseous substance result from the action, and the non-gaseous substance contains the metal and the oxygen. In addition it sometimes contains some hydrogen as we shall see later.

This method consists essentially in treating the compound of hydrogen, water, with some other element which combines with the rest of the compound other than hydrogen and leaves the hydrogen free. This is an example of one of the most commonly used methods for the preparation of the elements from their compounds.

**Preparation from Acids.**—As has been mentioned above, hydrogen is present in all acids. As examples of acids may be mentioned sulfuric, hydrochloric, acetic acids, etc. When acids are mixed with water and brought in contact with many metals, hydrogen is given off, and the metal forms a compound with the rest of the acid. The hydrogen in this case comes from the acid and not from the water. Although most metals and acids will work in this way, in some cases the action may be violent, in others extremely slow. Metallic zinc with either dilute sulfuric or hydrochloric acid works very regularly and at a convenient rate, so that these substances are largely used in the laboratory for the preparation of hydrogen (Fig. 8).

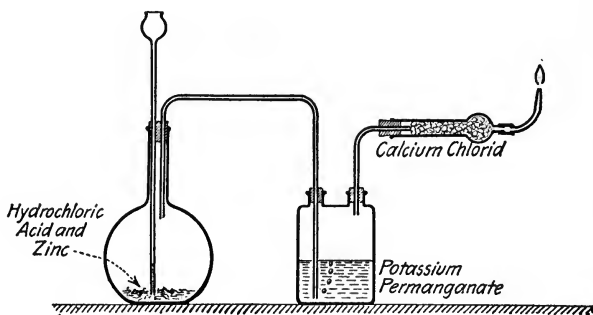


FIG. 8.

Hydrogen is similarly prepared on a commercial scale or for filling balloons by the action of sulfuric acid on iron, but the iron always contains some carbon, and the hydrogen obtained in this manner is contaminated with compounds of hydrogen and carbon.

**Electrolytic Preparation.**—When two pieces of platinum, a metal which is very resistant to chemical action, are placed in water containing a little sulfuric acid, and connected to a suitable source of electricity, a current of electricity passes through the dilute sulfuric acid from one piece of platinum to the other. At the same time, free oxygen appears at one of the platinum plates and free hydrogen at the other. The process is really quite complex, but since the water gradually disappears and hydrogen and oxygen appear in the proportion in which they will form water,

while the quantity of sulfuric acid in the solution is unaltered, it amounts to the decomposition of water at the expense of electrical energy. Here water is decomposed with the absorption of electrical energy very much as mercuric oxide is decomposed at high temperature with the absorption of heat, which it will be remembered is a form of energy. Since the hydrogen and the oxygen are given off at different points, it is an easy matter to collect each separately. One of the methods for the commercial preparation of hydrogen is based upon this principle using, however, plates of lead instead of the very expensive platinum. A solution of sodium hydroxide may be used instead of the sulfuric acid, but in this case the metal plates should be of iron or nickel.

**Purification of the Hydrogen.**—The hydrogen prepared by the methods outlined above always contains water vapor, and usually compounds of hydrogen and carbon from the carbon contained in the metal. The hydrocarbons may be largely removed by passing the gas through a solution of potassium permanganate. To remove the water vapor, advantage is taken of the fact that there are several substances which vigorously retain water while having no action upon hydrogen. One of the most convenient of these is calcium chloride. This is a white, very hygroscopic substance which is formed as a waste product in many chemical operations and is therefore cheap. The calcium chloride is usually placed in a tube through which the gas is passed. The column of calcium chloride should be as long as convenient and held in place by plugs of cotton wool (Fig. 8).

Concentrated sulfuric acid is a far more efficient drying agent than calcium chloride and is largely used. Since this is a liquid it is either placed in a suitable container and the gas bubbled through it, or it is taken up by pumice stone and packed in drying tubes or towers. When the sulfuric acid takes up water from a gas it increases in volume, so space has to be provided for the dilute acid which runs down to the bottom of the containing vessel.

**Physical Properties.**—Hydrogen has no taste or color. The pure gas has no odor, but that prepared by the action of acids upon metals usually has a disagreeable odor due to the compounds of carbon and hydrogen which have been mentioned above. After

the gas has been passed through a solution of potassium permanganate, it is so far purified that it loses the greater part if not all of the odor.

Its density is smaller than that of any other known substance, being .00008986 gram. per cubic centimeter under standard conditions. This is perhaps the most important physical property of hydrogen, since upon it depends its use in balloons. The density of air under standard conditions is .001293 gram. per cubic centimeter or .0012031 gram. per cubic centimeter more than the density of hydrogen, consequently 1 c.c. of hydrogen under standard conditions will have an upward flotation of .0012031 gram. when surrounded by air under the same conditions.

Hydrogen and air both follow closely the gas laws, and a given change in temperature or pressure which would double the volume of the .00008986 gram. of hydrogen would also double the volume of the .001293 gram. of air and leave the difference in their weights and the flotation of the hydrogen unaltered. From this it will be seen that the flotation of a given *mass* of hydrogen is independent of the temperature and pressure upon the hydrogen and amounts to .0012031 gram. per .00008986 gram. of hydrogen or 13.39 gram. per one gram. The lifting power of a fixed *volume* of hydrogen is dependent upon both the temperature and pressure. It would be reduced to one-half for a change in conditions which would tend to double the volume of the hydrogen, because this change in conditions would double the volume of the corresponding *mass* of air, and hence reduce to one-half the *mass* of the air displaced by the fixed volume of hydrogen.

From the above it will follow that if the envelope of the balloon were capable of indefinite extension without increasing the pressure upon the hydrogen inside the balloon, it would rise until it reached the very outer limits of the atmosphere, but since any given balloon can hold only a perfectly definite number of c.c. of gas it can rise only to the point where the difference in the weight of that volume of hydrogen which will just fill the balloon and that of an equal volume of air under the existing conditions is just equal to the weight of the balloon and its equipment.

The extreme levity of hydrogen may be easily shown by filling a small rubber balloon with the gas when it will float in the

air and exert a lifting power of something like a gram per liter. Or soap bubbles may be blown with the gas, and these upon being detached from the pipe will rise rapidly.

Another way to demonstrate this same property is to fill two cylinders with hydrogen and hold one of them mouth upward and the other mouth downward. After a few minutes bring a flame to the mouth of each jar. It will be found that the one with the mouth upward contains only air, while the one with the mouth downward still contains hydrogen since the gas burns.

**Diffusion.**—Because of the very great difference in density between hydrogen and air one would expect that if two cylinders were brought together mouth to mouth, the upper one filled with hydrogen and the lower one with air, that the gases would remain unmixed. But if they are left in this position for a few hours it will be found that both cylinders contain hydrogen and air. If the cylinders are of the same size and have been left in position for a sufficient length of time the upper cylinder will contain as much air as the lower, and the lower will contain as much hydrogen as the upper. This spontaneous mixing of one gas with another, even against the action of gravity, is an example of the phenomenon called diffusion.

All gases diffuse into one another and the process goes on until each gas is uniformly distributed through the entire space. If the pressure of each gas be measured separately, it will be found that diffusion continues until the pressure of any given gas is the same in all parts of the space; and further, it will be found that the pressure exerted by each gas is the same as that which the given mass of the gas would have exerted if it alone were occupying the entire space. This pressure is called its partial pressure.

The total pressure of a gaseous mixture is the sum of all the partial pressures of its component gases. The volume of each gas is the total volume of the space occupied by the entire gaseous mixture.

The law which describes these phenomena is known as Dalton's law of partial pressures, and may be stated as follows: "*Each gas, in a gaseous mixture, fills the entire space occupied by the gaseous mixture and the total pressure of the mixture is the same as the sum of the partial pressures of the component gases.*"

This law may be expressed in symbols by representing the total volume by  $V$ , and that of the separate gases by  $v_1, v_2, v_3 \dots$  and the total pressure by  $P$ , and the partial pressures by  $p_1, p_2, p_3, \dots$  then,

$$v_1 = v_2 = v_3 = V$$

and

$$p_1 + p_2 + p_3 = P$$

While any gas will diffuse into any other gas no matter what the difference in density may be, there is often a great difference in the velocity with which the diffusion takes place. For example, in the case of the hydrogen and air cited above, the hydrogen diffuses downward more rapidly than the air diffuses upward. In fact in all cases the less dense gas will diffuse more rapidly than the denser.

Something very nearly like this may be demonstrated by closing a porous cell, such as is used in electric batteries, with a cork carrying a glass tube, and supporting the whole arrangement in such a way that the glass tube dips into water. If a cylinder containing hydrogen be brought over the porous cell, bubbles will quickly begin to pass out from the glass tube. This action soon ceases and if the jar of hydrogen be removed the water will begin to ascend the tube. Both the effects are due to the fact that the hydrogen will pass through the porous cell more rapidly than the air, producing in the first case, some little pressure within the cell, and after the removal of the cylinder, the hydrogen passes out so much more rapidly than the air can enter that a partial vacuum results and the water rises.

**The Law of Effusion of Graham and Bunsen.**—Graham and Bunsen studied the velocity with which different gases pass out through a single small opening when acted upon by the same pressure. They found that *the velocities of effusion varied inversely as the square roots of the densities of the gases*, or if one gas were four times as dense as another it would take twice as long for a given volume of it to pass out through a certain opening as it would for the same volume of the first gas to pass out through the same opening, both gases being acted upon by the same pressure.



Representing the velocities by  $c_1$  and  $c_2$ , and the densities by  $d_1$  and  $d_2$  this law may be expressed as follows:

$$c_1 : c_2 = \sqrt{d_2} : \sqrt{d_1}$$

**Hydrogen and the Gas Laws.**—The gas laws which were developed under oxygen describe very accurately the behavior of hydrogen under ordinary conditions; in fact, hydrogen follows them more closely than almost any other gas. At very high pressures, however, it is found that hydrogen does not decrease in volume as rapidly as it ought according to Boyle's law. The discrepancy becomes greater as the pressure is increased. This behavior may be represented by saying that the hydrogen behaves as though its total volume were made up of one part which exactly follows Boyle's law and another part which is independent of the pressures. If the total volume be represented by  $V$ , the compressible part by  $v$ , and the incompressible by  $b$ , then

$$V = v + b$$

From Boyle's law

$$pv = \text{constant (at constant temperature)}$$

Replacing  $v$  by its value  $V - b$  as obtained from the first equation we get

$$p(V - b) = \text{constant}$$

For hydrogen under standard conditions,  $b$  amounts to .00062 of the total volume. From this it may be seen that it is only at fairly high pressures that hydrogen differs appreciably from the gas laws. Other gases at ordinary temperatures are usually more compressible at a moderate pressure than they should be from Boyle's law, and then at higher pressures they behave like hydrogen and become less compressible. At higher temperatures many of them act like hydrogen and are less compressible from the start than they should be from Boyle's law. At very low temperatures hydrogen changes its behavior and is first more and then less compressible than it should be, thus behaving like the other gases.

**Liquid Hydrogen.**—Hydrogen cannot be liquefied by any pressure, however great, at ordinary temperatures, but must first be cooled to  $-242^\circ \text{C}$ . when it will liquefy under a pressure of about 15 atmospheres. Its boiling-point under atmos-

pheric pressure is about  $-252.5^{\circ}$  C. or only  $20.5^{\circ}$  C. above absolute zero. By reducing the pressure to 5 cm. of mercury the temperature falls to about  $14^{\circ}$  A. or  $-259^{\circ}$  C. At this temperature hydrogen is a transparent solid. Liquid hydrogen is colorless and has a density at its boiling-point of only .07. It is used to get very low temperatures, since substances placed in it will be very quickly cooled to the boiling-point of hydrogen. At this temperature all other liquids and all other gases except helium become solids.

**Solid Hydrogen.**—Solid hydrogen is a transparent ice-like substance with a melting-point of  $-258^{\circ}$  C. Its density is .076.

**Absorption of Hydrogen by Metals.**—Hydrogen is absorbed in appreciable quantities by many metals, but especially by the rare metal palladium. Under favorable conditions, palladium will take up 900 times its own volume of hydrogen, considerable heat being evolved during the process. This hydrogen will practically all be given up in a vacuum at ordinary temperature or it may be driven off at atmospheric pressure by warming the palladium.

The absorbed hydrogen does not enter into a chemical compound with the palladium but forms a solid solution.

**Spectrum of Hydrogen.**—When an electric discharge is passed through hydrogen under a pressure of a few tenths of a centimeter of mercury, the hydrogen glows and gives out light. This light appears rose red to the eye, but when it is examined with a spectroscope (Fig. 9), a very large number of lines are seen scattered all along from the red to the violet end of the spectrum.

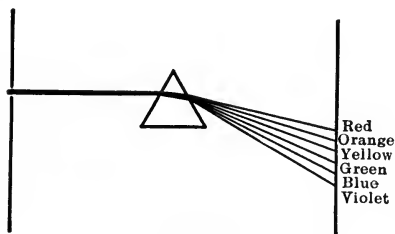


FIG. 9.

There are, however, four lines, a red, a green, and two violet, which are much stronger than the others. Other gases under similar conditions will give spectra but no other gas will give lines in precisely the same position in the spectrum as the hydrogen lines. These same lines will appear when hydrogen is caused to glow in any other way and their appearance is not prevented by the

presence of other substances. Hence an examination of the spectrum is the very surest means for the identification of hydrogen. These same lines are found in the spectra of many of the stars, and we may safely say that hydrogen is present upon them as well as upon the earth (see Frontispiece).

The light from the sun and many of the stars shows dark lines at exactly the points where the hydrogen lines are bright. As will be explained later, these dark lines are due to hydrogen, and prove the presence of this element just as certainly as the bright lines. Therefore the spectroscope shows us that hydrogen is very widely distributed throughout our universe. In much the same way it has been established that a large number of the elements known to us here are also present in the sun and stars.

**Chemical Properties of Hydrogen.**—The most marked property of oxygen is that it will support combustion vigorously. Hydrogen on the other hand will burn but not support the combustion of things which will burn in the air. This may be readily shown by bringing a lighted candle to the mouth of an inverted cylinder filled with hydrogen. The gas will take fire with a slight explosion and burn with an almost invisible flame at the mouth of the cylinder. Pass the candle up into the hydrogen and it will go out. Withdraw the candle slowly, and as the wick passes through the flame of the burning hydrogen it will be relighted.

From what we have learned of combustion in studying oxygen, we would draw the conclusion, correctly, that hydrogen will combine with oxygen. It will also enter into combination with a large number of the other elements—notably with chlorine, sulfur, nitrogen, and carbon. The conditions under which the combination will take place, and the substances formed will be discussed in connection with the several elements.

A small stream of hydrogen issuing from a jet of platinum, or other difficultly fusible metal, burns quietly in the air with an intensely hot flame which is almost invisible. If the jet is made of glass the hydrogen flame will be colored yellow from the sodium of the glass. Water is produced by the burning of hydrogen, as may be shown by holding a glass cylinder over the flame. A dew at once appears on the glass which has all the properties of water and consequently is water. If all the water formed by the burning of

a given quantity of hydrogen be collected and weighed, it will be found to weigh much more than the hydrogen itself, and therefore it follows that water is a compound of hydrogen with one or more of the constituents of the air.

If the air be replaced by pure oxygen it will be found that the hydrogen will burn even more vigorously and water will be produced as before. Hence we must conclude that water is a compound of hydrogen and oxygen and nothing else, a conclusion which is confirmed by the fact that the weight of the water formed is equal to the sum of the weights of the oxygen and hydrogen transformed.

Hydrogen and oxygen may be mixed at ordinary temperature and no perceptible combustion will take place, but if the mixture be brought in contact with a flame or heated at any point to a temperature of about  $500^{\circ}$  to  $600^{\circ}$  C. a combination will take place very rapidly, and a flame will spread throughout the mixture almost instantaneously. The result is a rather powerful explosion due to the sudden expansion of the gases by the heat evolved during the rapid burning of the hydrogen. Because of its explosiveness, a mixture of hydrogen and oxygen in the proportion for the formation of water, *i.e.*, two volumes of hydrogen to one volume of oxygen, is called detonating gas. This detonating gas must be very carefully kept away from flames or incandescent bodies.

Because of the oxygen in the air a mixture of hydrogen and air in proper proportions is decidedly explosive. On this account hydrogen from a gas holder or from a generator should never be lighted until it has been tested and found to be pure. This may be done by collecting the escaping gas in an inverted test tube and bringing it in contact with a flame which is kept at a distance of several feet from the hydrogen apparatus. At first the gas in the tube will behave like air, but soon it will take fire, and the flame will rush up the test tube with a whistling noise. As the trials are repeated and the gas becomes more nearly pure hydrogen, the explosions in the test tube first become stronger and then weaker until at last the hydrogen burns quietly at the mouth of the test tube for a sufficiently long time so that a flame may be carried back in this way from the burner to the hydrogen apparatus and ignite the escaping gas. This method of lighting a jet

of hydrogen is perfectly safe since so long as the gas in the apparatus is explosive the explosions take place the instant the mouth of the test tube is brought to the flame, and no fire is left in the tube to ignite the jet upon the return of the tube.

**Oxy-hydrogen Blowpipe.**—Many important applications have been found for the very high temperature produced by hydrogen burning in oxygen. Because of the dangerously explosive character of a mixture of these gases it is of course out of the question to mix them in one gas holder and burn the mixture. The gases must then be stored separately and burned from a special burner called the oxy-hydrogen blowpipe, which is so arranged that the gases are conveyed to the burner in separate tubes and mixed just before they reach the orifice of the burner. In this way a flame may be produced whose temperature is something like 2500° C. In this flame silver boils, iron burns, and even platinum melts. If the flame be brought in contact with a piece of lime the latter becomes intensely heated and produces an exceedingly bright light known as the calcium light, or lime light, and has often been used as a source of light for the stereopticon, but is now generally replaced by the electric arc. The oxy-hydrogen blowpipe is largely used in the autogenous welding of metals, especially of lead.

**Formation of Water From Hydrogen and Oxygen Compounds.**—If hydrogen be passed over mercuric oxide at ordinary temperature no perceptible action takes place, but if the oxide be gently warmed taking care that the temperature does not rise high enough to bring about its decomposition, water and metallic mercury will be rapidly formed. Hydrogen and iron oxide heated to a somewhat higher temperature will yield water and metallic iron. If tin oxide is used, metallic tin and water will be formed. This last case is especially interesting because at no temperature which can be reached by an ordinary burner will tin oxide give off oxygen and therefore it is shown conclusively that the reaction for the formation of water and tin takes place between the tin oxide and the hydrogen. Many other oxides will react in the same way with hydrogen so that we have here a rather general method for the laboratory preparation of a metal from its oxide.

A very natural inference to draw from these facts given above

is that the hydrogen has a stronger attraction for the oxygen than the metal has, and so robs the latter of its oxygen. This conception has often been used, and the attraction was called chemical affinity. That this conception is inadequate is shown by the following case. Iron oxide and hydrogen will react at a somewhat elevated temperature for the formation of water vapor and metallic iron. And the explanation of this in terms of the above conception would be that the hydrogen had a greater affinity for the oxygen than the iron had. But as was mentioned earlier in the book, if water vapor be passed over metallic iron heated to the same temperature used in the above case, hydrogen and iron oxide will be formed. The explanation of this would be that the iron had a greater affinity for the oxygen than the hydrogen had and so robbed the water of its oxygen. The action in the one case is just the reverse of that in the other and of course it cannot be that the iron has both a greater and a less affinity for oxygen than hydrogen has. Nor can the reversal be due to change in affinity due to the difference in temperature because they will both take place at the same temperature. From this it can be seen at once that the explanation must be either abandoned or modified.

Such actions as this we have just been discussing are called reversed or reversible reactions and are very common in chemistry. In fact they are more commonly met with than the irreversible reactions or those which go only in one direction. A careful study of these reactions is desirable because of their frequent occurrence, and also the ease with which they may be controlled when once understood. The rate at which any given reaction takes place depends upon the nature of the substance undergoing the change, the temperature, and the mass of each of the reacting substances present per cubic centimeter of reaction mixture. As these last two factors are increased the rate increases. The mass of any given substance present per cubic centimeter is called its "active mass" or its concentration.<sup>1</sup>

At constant temperature, the rate at which any given substance

<sup>1</sup> When dealing with a pure substance the concentration of that substance would be the same as the density, but for solutions the concentrations are different from the densities.

reacts is greater, the higher the concentration of the reacting substance is.

Let us choose for example the reaction between iron and water vapor and imagine that we seal up in a strong glass tube some water and some iron and raise the whole to a temperature of say 400° C. The water will react with the iron at a certain rate for the formation of hydrogen and iron oxide. As the water is used up the concentration of course decreases and the rate of reaction will diminish. On the other hand just as soon as some iron oxide and hydrogen have been formed they will begin to react for the re-formation of iron and water. The rate of this reaction will be zero at the start and gradually increase as the concentration of the hydrogen increases from its accumulation as the result of the first reaction. Hence the reaction between the iron and the water will go slower and slower as the water is used up and that between the iron oxide and the hydrogen will go faster and faster as the latter accumulates until finally just as much iron and water will be used up in the first reaction in a given time as is re-formed by the second reaction in the same time. When this state of affairs is reached, no further change in the concentrations will take place and the system is said to be in equilibrium, because equilibrium is a condition which does not change with the passage of time.

In the above discussion no attention has been paid to the concentration of either the iron or the iron oxide because these substances are solids and do not form solutions either with each other or with the water vapor and hydrogen. Therefore so long as any iron is present its concentration is unaltered and is the same as its density at the temperature of the experiment; similarly for the iron oxide. In general the concentrations of gaseous substances or of substances in solution can be altered, while those of pure solids or liquids cannot be appreciably changed.

The rate at which iron and water vapor react is proportional to the concentration of the latter and may be represented as follows:

$$R = K'a$$

where  $R$  is the rate and  $a$  the concentration of the water vapor.

The rate of reaction of iron oxide and hydrogen may be represented by

$$R' = K'b$$

where  $R'$  is the rate and  $b$  the concentration of the hydrogen.

When equilibrium results,

$$R = R'$$

and therefore

$$K_a = K'b$$

and

$$\frac{a}{b} = \frac{K'}{K} = K''$$

or the system will be in equilibrium when the ratio of the concentration of the water vapor to that of the hydrogen has reached a certain definite value. If a mixture of hydrogen and water vapor in the proportions thus found be passed over iron and iron oxide, no action will take place, but if either is deficient action will go on until this deficiency is made good. In the case of the preparation of hydrogen from water and iron the gas after passing over the iron contained both water and hydrogen, but the former was condensed in the water over which the hydrogen was collected and hence the latter seemed the only product. Similarly when hydrogen acted upon iron oxide, the escaping gas contained both hydrogen and water vapor, but the latter condensed and seemed the only product because the hydrogen escaped unobserved. A more detailed discussion of the general law of which this is a special case will be given later under the head of the law of mass action.

**Catalysis.**—At temperatures of 500° to 600° C., oxygen and hydrogen combine with explosive rapidity. As the temperature is lowered the rate rapidly decreases but is still appreciable at 250° C., and there is no temperature at which we can say that the reaction just begins and below which it does not take place. We must conclude then that it is taking place at all temperatures and that even at ordinary temperatures it is still going on, though at an immeasurably slow rate. However, if one introduces into a mixture of hydrogen and oxygen a piece of platinum, the gases combine with appreciable rapidity at the surface of the platinum. Since in this combination a great amount of heat is developed, the temperature of the platinum is raised. This tends to increase the rate of combination and not infrequently the platinum is heated to incandescence and explodes the gases. It must be noticed that the rise in temperature of the platinum is the result of the combination of the gases and not the cause of the combination or combustion. What the platinum does in this case is to increase the rate of the reaction so that from being immeasurably small it goes on with visible rapidity. This effect takes place right at the surface of the platinum and, other things being equal, is proportional to the surface exposed. On this account, finely divided or spongy platinum acts more rapidly than massive platinum, and is almost certain to become so heated



as to explode the gases. By mixing the spongy platinum in the proper proportion with clay and making the whole into pellets and burning them, the mass to be heated may be so increased that the temperature does not rise high enough to explode the gas mixture, and yet the gases will combine rapidly.

An experiment to show this can be readily performed by fastening one of these pellets to a wire and supporting it several inches above the surface of water in a pan or other suitable vessel (Fig. 10) and inverting a cylinder filled with detonating gas over the pellet so that the mouth of the cylinder is below the surface of the water. The gases quickly begin to combine as shown by the rise of the water into the cylinder. This continues until the pellet is covered with water or one or the other of the gases is used up, if one of the gases is in excess.

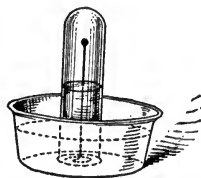


FIG. 10.

If the platinum be examined after such an experiment it will be found to be absolutely unchanged. Here we have another instance of a substance merely by its presence increasing the rate at which a reaction takes place. (See case of manganese dioxide and potassium chlorate, page 19.) Some other metals have the same property although to a smaller degree than platinum and it is very common to find that the rate of a reaction is greatly altered by the presence of a substance which is not changed by the reaction. We call actions of this kind catalytic actions. The substance through whose presence the rate of action is altered is called a catalyzer, and the whole process is spoken of as catalysis.

Some catalyzers act as platinum does in this case and increase the rate of reaction; these are called positive catalyzers. Others decrease the rate of reaction and are known as negative catalyzers.

Catalyzers simply alter the rate at which a reaction is taking place and cannot bring about one which is not already going on.

Cases of catalysis are of very frequent occurrence and will be often mentioned in the course of this work.

## CHAPTER V

### WATER

Water is one of the most important as well as one of the most widely distributed substances in nature. Some idea of its abundance may be gathered from the fact that the ocean contains about 302,000,000 cubic miles of water and each cubic mile weighs 4,205,650,000 tons. Liquid water covers 72 per cent. of the earth's surface; the atmosphere contains enormous quantities of water in the gaseous state, and the polar regions and the tops of lofty mountains are covered with solid water or ice. The crust of the earth is everywhere permeated by water, and all living organisms, both plants and animals, contain water as an absolutely essential portion of their structure. The human body contains about 70 per cent. and the ordinary foods from 35 to 95 per cent. water.

Water is a very good and general solvent and takes up more or less of nearly everything with which it comes in contact. The rivers of the world carry into the sea yearly 2,740,000,000 tons of dissolved substances, to say nothing of the suspended matter or silt. Water is usually purified by the process of distillation which consists in heating the water until it boils and is converted into vapor and then, in a separate vessel, cooling the vapor and reconvertng it into water. Most of the substances present in the water are much less easily vaporized than water and are left behind when the latter is boiled. Some impurities, such as ammonia and carbon dioxide, are more volatile than water and pass over with the first portions of the vapor. By rejecting the first part of the distillate, practically pure water may be obtained. Absolutely pure water cannot be prepared because it must come in contact with a vessel of some kind, and it will inevitably dissolve some of the latter, thus rendering the water impure. Stills and condensers of platinum or pure block tin are least attacked and give the purest water.

For drinking purposes the dissolved impurities in natural fresh waters are not so important as the bacteria which they carry. Since the latter are in suspension and not in solution,

they may be removed by very fine pored filters, and in a sense the water is thereby purified. The same result may be obtained by killing the bacteria by ozone (see page 37), or by bleaching powder (see page 150), or by boiling.

**Physical Properties of Water.**—It is at ordinary temperatures a transparent, almost colorless liquid with a faint bluish tint which first becomes apparent upon looking through a thick layer of water. This color can be seen in clear lakes and in the ocean.

When the metric system was devised the mass of a cubic centimeter of water at its temperature of maximum density was taken as the unit of mass and called the gram. The volume of the unit mass of water at its temperature of maximum density is then unity and the density of water under these conditions is also unity. Most substances increase in volume more or less regularly with rising temperature, but water is a decided exception. If one starts from 0° C. and warms the water its volume will decrease until a temperature of 4° C. is reached, and then with rising temperature the volume increases. The temperature of maximum density of water is then 4° C. From what has just been given it follows that at 0° C. the density of water is less than one, that it increases as the temperature rises until 4° C. is reached, after which it again decreases. The extensity, on the other hand, goes in just the other way and has its minimum value at 4° C.

The table gives some of the values for the density and extensity of water at different temperatures.

Temperature	Density	Extensity
0° C.	0.999868	1.000132
4° C.	1.000000	1.000000
10° C.	0.999727	1.000273
20° C.	0.998230	1.001773
30° C.	0.995673	1.004346
40° C.	0.99224	1.00782
50° C.	0.98807	1.01207
60° C.	0.98324	1.01705
70° C.	0.97781	1.02270
80° C.	0.97183	1.02899
90° C.	0.96534	1.03590
100° C.	0.95838	1.04343

To get values for the extensity or density at temperatures intermediate between those given in the above table, the data may be carefully plotted on cross-section paper and the points connected by a smooth curve. The intermediate points may then be read from the curve.

**Compressibility of Water.**—The extensity of water is altered by changes of pressure as well as changes in temperature. The coefficient of compressibility is the change in the extensity produced by a change in the pressure of one atmosphere. It is small and changes with the temperature, having a minimum value at 62° C. At 0° C. the value of the coefficient is .000052, at 20° it is .000046, at 62° it is .000041, and at 100° it is .000045.

**Ice.**—At a temperature of 0° C. water changes from the liquid to the solid state and is then known as ice. The question as to whether this transformation of water into ice is a chemical or a physical change is an open one. If a chemical change is one which alters all or nearly all of the properties of a substance, this transformation is a chemical one because most of the properties of ice are different from those of water. The ease with which the transformation back and forth from water into ice and ice into water takes place is about the only serious argument in favor of considering this a physical change.

**Properties of Ice.**—Ice is a transparent solid of a faint bluish color which is seen only in large masses such as icebergs or glaciers. It is such a poor conductor of electricity that it becomes electrified when rubbed. Ice is almost twice as good a conductor of heat as water, but even then it is a very poor conductor.

The density of ice at 0° C. is 0.91674, which is much smaller than that of water at the same temperature which is 0.99987. This means that on freezing water increases nearly one-eleventh in volume, and also that ice will float on water. In these respects water is somewhat unusual, since most substances decrease in volume upon solidification, and the solid sinks in the liquid.

In all climates where freezing and thawing take place, the great increase in volume when the water passes into ice has played a very important part in the disintegration of rocks.

When the rain falls upon the rocks it fills even the small cracks. Upon freezing the increase in volume forces the crack to widen. When the ice melts the water runs down in the crack and upon freezing spreads the pieces of rock still farther apart until presently the rock is split up under the repeated action of the freezing and thawing of the water. The bursting of water pipes when the water in them freezes, and the loosening of the soil in the winter time are due to this same cause.

On account of the destructive action of freezing water upon rocks, it is of importance to pay attention to the following points in laying a masonry wall. The stone should either be so close in texture that it is impervious to water or so coarse that the rains may drain away rapidly and leave the openings only partially filled, giving plenty of room for expansion. If sandstone be used care must be taken to see that the cementing material which binds the grains together is strong so that the stone does not crumble easily, for if it be weak, since all sandstones are more or less pervious to water the stone will go to pieces rapidly under the action of frost. Practically every kind of stone breaks easier in one direction than in the other, and should be laid so that this plane of fracture is horizontal.

Ice is a crystalline substance, and crystals may be defined as bodies whose properties vary with the direction in which they are measured. As a result of this variation a crystalline substance tends, when it takes on the solid state, to form bodies whose limiting surfaces meet at perfectly definite angles, and so build up regular polyhedral forms. All other physical properties which can possibly do so vary with the direction in which they are measured. Some of these properties are conductivity for heat and electricity, velocity of light, elasticity, etc.

Those solids which are not crystalline are called amorphous substances, and glass is a good example of such a substance. All the properties of glass are the same in every direction. The property of forming crystals is very common among pure solid substances, while most amorphous substances are mixtures.

Well-formed crystals often grow on the surface of water, but the best are found in the snow because they have been formed in the air with nothing to interfere. The snow crystals usually appear as six-pointed stars.

Water in contact with ice cannot be cooled below  $0^{\circ}$  C. nor warmed above this temperature, but so long as there is present an intimate mixture of ice and water the temperature is  $0^{\circ}$  C. The only conditions which need to be fulfilled are that the ice and water shall be pure and that the pressure upon the ice shall be the standard pressure. When ice separates from impure water the crystals of ice are pure but may inclose some of the impurities which are present in the solution from which it is formed. By allowing such ice to melt and discarding the first of the water that is formed, pure ice in contact with pure water may be obtained. And since the effect of the changes in the melting-point due to changes in the atmospheric pressure are very small indeed, it is very easy to reproduce the temperature of  $0^{\circ}$  C. For this reason the ice point is generally used for a standard temperature.

In the absence of ice, water may be cooled a number of degrees below zero without freezing. In this condition it is said to be **supercooled**. It is interesting to note that while water is cooling down from  $0^{\circ}$  it continues to expand just as it does from  $4^{\circ}$  to  $0^{\circ}$ . In fact there is no sudden change in the properties of water at  $0^{\circ}$  except that at that temperature it becomes possible for ice to exist which it cannot do at higher temperatures. Water which has been cooled to a few degrees below zero is stable toward all kinds of changes except the introduction of ice. Let the very smallest piece of ice come in contact with the water and freezing at once starts and the temperature rises to  $0^{\circ}$  C.

If a test tube partially filled with ordinary distilled water be supported in a freezing mixture of ice and salt in such a manner that the surface of the water in the tube is a centimeter or so above the surface of the freezing mixture, the water will supercool several degrees. By taking elaborate precautions water has been supercooled to  $-15^{\circ}$  C.

**Heat of Fusion.**—Whenever any liquid substance solidifies, heat is evolved; and conversely when a solid melts heat is absorbed. The heat absorbed during the melting of one gram of a solid is called the heat of fusion of that solid. That evolved during the freezing of unit mass of the substance is called the heat of solidification. These heats are of numerical equal value and are both often called the heat of fusion. Ice behaves

like all other solids in these respects and is only noteworthy because its heat of fusion is greater than that of any other substance except ammonia.

**Measurement of Heat.**—Heat is one of the forms of energy and so the most rational unit of heat would be that quantity of heat which can be obtained from one erg, the unit of work. This quantity of heat is so very small that another unit called the joule is commonly used. A joule is 10,000,000 ergs and even this is too small for many purposes and is replaced by the kilojoule which is 1000 joules or  $10^{10}$  ergs. A quantity of heat is measured by determining the change in temperature which it will produce in a known weight of water; the heat capacity of the water, *i. e.*, the number of joules required to raise the temperature of 1 gm. of water  $1^{\circ}$ , having been carefully determined. The heat capacity is also known as the specific heat and varies somewhat with the temperature. Another unit is that quantity of heat which raises the temperature of 1 gm. of water  $1^{\circ}$  Centigrade. This is called the small calorie (abbreviated "cal."). Since the specific heat of water varies with the temperature, it is necessary to specify the temperature of the water. A larger and somewhat more suitable unit is the rational calorie K, which is the quantity of heat which is necessary to raise 1 gm. of water from the melting- to the boiling-point. It is nearly one hundred times the small calorie. A still larger and very generally used unit is the large or kilogram calorie. It is the heat necessary to raise the temperature of 1 kgm. of water  $1^{\circ}$  C. It is abbreviated Cal. and equals 1000 small calories.

The heat of fusion of ice, that is, the heat required to melt 1 gm. of ice, is 334 joules or 80 cal. If, therefore, 80 gm. of water at  $1^{\circ}$  be mixed with 1 gm. of ice, 81 gm. of water at  $0^{\circ}$  will be produced.

In technical work in England and the United States, another unit for the measurement of heat is in use. It is known as the British Thermal Unit and is abbreviated B.T.U. It is the quantity of heat required to raise the temperature of 1 lb. of water  $1^{\circ}$  Fahrenheit.

The relation between the small calorie and the erg has been carefully worked out by Joule and others, and a small calorie at

$15^{\circ}$  is equal to 41,890,000 ergs or 4.189 joules. 1 cal. = 4.189 joules.

The fact that the temperature of a mixture of ice and pure water is always  $0^{\circ}$  finds its explanation in this heat of fusion. If heat is applied to the mixture, instead of raising the temperature some of the ice melts and absorbs the heat. If heat is taken away from the mixture, instead of the temperature's falling some of the water freezes and supplies the heat. Because of the constancy of this temperature ice finds many applications in science. Because of its cheapness, its great heat of fusion, and its rather low melting-point, enormous quantities of ice are used in every day life for the preservation of food since the destructive changes take place much more slowly in the food cooled by ice than at ordinary temperatures. They are like all other chemical changes in that they are slowed down by lowering the temperature.

When ice and common salt are brought together a solution results, the freezing-point of which is much lower than  $0^{\circ}$  C. This is the basis of the use of ice and salt for freezing ice cream, etc. By using three parts of ice to one of salt a temperature of  $-18^{\circ}$  C. can be obtained, and this was taken by Fahrenheit as the zero point for his thermometer. The common salt may be replaced by other soluble substances because the freezing-point of any solution is lower than that of the pure liquid. Most substances will not give as low a temperature as salt, but a few will give even lower. However, on the score of cheapness and convenience salt is the best to use. The use of salt for the removal of ice and snow from sidewalks, etc., depends upon this same phenomenon.

**Gaseous Water.**—Both water and ice are very easily transformed into gaseous water which is commonly known as water vapor at ordinary and as steam at higher temperatures, although there is no real difference between them. To bring about this transformation, all that is necessary is to introduce the water or ice into a vessel which it does not entirely fill. Under these circumstances the formation of the gaseous water will begin at once and the vapor will soon fill all the space unoccupied by the other modification. The transformation of water or ice into water vapor is called evaporation. Water vapor is a gaseous substance and its behavior is fairly well described by



the gas laws. This is particularly the case if the pressure is low. Like all other gaseous substances, it exerts a pressure upon the walls of the containing vessel, and experiment shows that when water is brought into a space which it does not fill, evaporation takes place until either all the water has been converted into vapor or the pressure of the water vapor has reached a certain definite limit. This limit varies with the temperature but is always the same at any given temperature, and is entirely independent of the shape or size of the vessel or the relative volume of the liquid or the solid and the water vapor. We are dealing here then with a state of equilibrium between the water vapor and the liquid water or the ice. This limiting pressure at which the water vapor is in equilibrium with the other modification is called the **vapor pressure** of the water, or of ice as the case may be. It may be measured in the apparatus shown in Fig. 11. The vertical distance from *a* to *b* measures the vapor pressure.

Not only may water be readily converted into vapor, but the latter may as easily be changed back into water, so we are dealing with a reversible reaction, and the conditions of equilibrium may be readily understood by looking at this reaction as we did that between water and iron. When liquid water is introduced into a space it immediately begins to evaporate at a rate which depends upon the temperature and upon the concentration of the liquid water. Since the concentration of a pure liquid is constant, the rate of evaporation at any given temperature is constant but naturally is greater the higher the temperature.

As soon as any water vapor is formed, it begins to pass back into the liquid state at a rate which depends upon the temperature and upon the concentration of the water vapor. Since water vapor is a gaseous substance its concentration is variable,

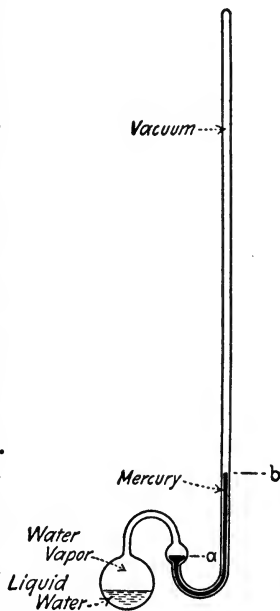


FIG. 11.

and hence the rate of reaction varies. When the water first begins to evaporate, the concentration of the water vapor is very small and the rate of its transformation back into water is very much less than the rate of its formation from the latter. So the concentration of the water vapor continually increases and with it the rate of its transformation until finally as much water vapor is transformed back into liquid water in a given time as is formed from the water in the same time. At this point the two rates are equal and the substances are in equilibrium. It must be noticed that although some liquid water is converted into gaseous water in this process the mass per unit volume of the water that is left is unchanged so the concentration of the water is unaltered.

To express the state of affairs at equilibrium mathematically, let us represent the rate of formation of the vapor by  $R$ , and of the water by  $R'$ , and the concentration of the water by "a," and that of the vapor by "b," then

$$R = ka, \text{ and } R' = k'b$$

At equilibrium

$$R = R'$$

Therefore

$$ka = k'b$$

and

$$b = \frac{ka}{k'} = \text{constant (since "a" is a constant)}.$$

From this it is to be seen that at any given temperature the concentration of the water vapor in equilibrium with water is constant and independent of the relative volume of the vapor and the water. From the definition of concentration (mass divided by volume), and Boyle's law for gases (that the volume of a fixed mass of a gas is inversely proportional to the pressure—the temperature being constant) it follows that the concentration of a gaseous substance is directly proportional to its pressure. Letting "b" stand for concentration,

$$b = m/v \text{ or } v = m/b$$

but from Boyle's law

$$v = k/p \text{ for the fixed mass of gas "m"}$$

therefore

$$m/b = k/p \text{ and } b = mp/k$$

or

$$b = Kp \text{ where } K = m/k$$

("m" is the mass of the gas which is fixed in Boyle's law equation).

Therefore the concentration of a gaseous substance is directly proportional to the pressure. Since the concentration of the vapor in equilibrium with water is constant at any given temperature, its pressure will be constant also and is what we have called the vapor pressure of water.

From Dalton's law of partial pressures and the fact that water vapor is gaseous, it can be readily seen that the vapor pressure of water will be the same whether the evaporation takes place in a vacuum or into a space filled with gases which do not dissolve to any marked degree in water. If the gases are very soluble they will alter the water, and hence the vapor pressure of the water.

When heat is applied to water in an open vessel, the temperature of the water gradually rises and finally small bubbles of gas appear in the liquid, rise to the surface and burst. These small bubbles consist of the gases dissolved in the water and of water vapor. The temperature continues to rise and these small bubbles are replaced by larger ones which consist of water vapor alone. This phenomenon is then called boiling. After the water has begun to boil, the temperature does not rise.

A little reflection will convince one that a bubble of vapor down in the body of the liquid must be under a pressure equal to that of the atmosphere plus that due to the column of liquid above it, and that due to the action of surface tension.

The vapor pressure of the boiling liquid must be equal to these. Neglecting the last two factors which are usually small, we may say that the **boiling-point** of a liquid is the temperature at which the vapor pressure of the liquid is equal to the atmospheric pressure.<sup>1</sup> Since the boiling-point is the temperature at which the vapor pressure of the liquid is equal to the external pressure, the boiling-point will vary as the pressure changes, and will rise as the pressure is increased. The boiling-point of water under a pressure of one atmosphere is 100° C.; at two atmospheres the boiling-point is 121° C.; under ten atmospheres it is 180° C., and continues to rise up to the critical point when the boiling-point of water is 374° C. under a pressure of 200 atmospheres. By lowering the pressure, water may be made to boil at temperatures below 100° C. With the aid of a good water vacuum pump, water may be made to boil at temperatures below 30° C. If the

<sup>1</sup>The following remarks may be in order at this place. The boiling-point is not a point, but is a temperature and is not the temperature at which the liquid begins to evaporate, because all liquids evaporate at all temperatures.

pressure be reduced to less than 0.4 cm. of mercury, the boiling-point will fall below the freezing-point, and the water will freeze and boil at the same time.

Use is often made in the laboratory of the fact that the temperature of water boiling in an open vessel, and also the steam from it is never far from  $100^{\circ}$  C. For example it is often necessary to heat a substance to about  $100^{\circ}$  C. and at the same time absolutely essential that the temperature shall not go higher. This can be easily done by heating it on what is known as a water bath. The simplest form of a water bath consists of a beaker half full of water and loosely covered with an evaporating dish or other suitable vessel containing the substance to be heated. If now the water be boiled, the steam will come in contact with the dish and quickly raise the temperature to about  $100^{\circ}$  C. but never above the boiling-point of water at the pressure of the atmosphere.

**Superheated Water.**—In the entire absence of bubbles of vapor or of gas in the body of the liquid, water can be heated far above its boiling-point. Water in this condition is said to be superheated. A clear picture of the cause of superheating may be obtained if we consider all that the vapor must do before a bubble can form. As was mentioned under the subject of boiling, before the bubble can form the vapor pressure of the liquid must be great enough to equal the external pressure plus the hydrostatic pressure of the liquid plus the pressure due to the surface tension of the liquid. The effect of the surface tension is greater the smaller the bubble is, and while it is insignificant for large bubbles it becomes much larger than either of the other two factors when the bubble is minute as it must necessarily be at the instant of its formation. From this it follows that in the absence of a gaseous substance, any liquid must be heated above its boiling-point before the vapor pressure can overcome this added effect of the surface tension. In the case of water, it is possible to heat the water to  $130^{\circ}$ – $140^{\circ}$  C. by suspending small drops of recently boiled water in linseed oil and carefully heating. The purpose of boiling the water is to expel the dissolved air. When superheated water once starts to boil it does so with extreme violence, and the temperature falls rapidly until the boiling-point is reached. This is due to

the fact that as soon as bubbles are fairly started the effect of surface tension disappears, and all the extra heat stored in the liquid because it is superheated is used up in the sudden transformation of a part of the liquid into vapor. The fraction of the liquid so transformed is evidently equal to the quantity of heat required to raise 1 grm. of the liquid  $1^{\circ}$  in temperature times the number of degrees of superheating divided by the heat of vaporization of the liquid.

In order that considerable superheating shall occur, it is not necessary that the liquid be absolutely out of contact with all gases and vapors, but only that there shall be no bubbles of gas in the body of the liquid. For example, if the water be boiled in a clean glass beaker for some time, it finally begins to "bump," that is, ebullition will cease for a time and then begin again violently. This is due to superheating. At first the water contained air which is less soluble in hot water than in cold water, so separates out upon heating and furnishes starting points for the formation of vapor. So long as this goes on, superheating is impossible. But this air is removed with the bubbles of steam, and soon there is no more air in the water, then the bubbles of water vapor have greater difficulty in getting started, and if a moment comes when there are no bubbles anywhere in the liquid, superheating begins, and the next time it boils it will give a "bump."

Obviously superheating can be avoided by taking care always to have present some bubbles of gas to give the vapor a start. The simplest way to do this is to put in the liquid some porous substance, insoluble in the liquid. Such a substance is pumice stone. This carries down with it little bubbles of air and even when the air has all been removed by boiling, the pores will still be filled with water vapor at all times, provided always that the temperature has never fallen below the boiling point. If the temperature falls below the boiling point, the pores will fill up with the liquid, and the stone will be nearly useless.

**Humidity of the Air.**—From the very wide distribution of liquid water upon the earth's surface, it of course follows that water vapor is always present in the air. One might expect that the partial pressure of water vapor in the air would be equal to

the vapor pressure of the water. However, this is rarely the case because the temperature of a body of water is usually lower than that of the surrounding land area, and even if the partial pressure of the water vapor in the air over the water becomes as great as the vapor pressure of the water at the temperature of the water, as soon as the air moves over the land, its temperature will rise and the partial pressure of the water vapor will then be less than the vapor pressure of the water at the temperature of the air. This is sometimes expressed by saying that the air is only partially saturated, carrying the idea that the air dissolves the water much as water dissolves salt. The notion is only partly correct. The term "relative humidity" is often used in this connection and is the ratio of the partial pressure of the water vapor in the air to the vapor pressure of water at the temperature of the air. This may be determined in several ways, one of the simplest being to note the difference in temperature between two thermometers freely exposed in a rapid current of air, the bulb of one of the thermometers being covered with a layer of fine cloth moistened with distilled water. From the difference in temperature of the wet and dry bulb thermometers and the reading of the dry bulb instrument, the relative humidity may be easily obtained with the aid of an empirical table.

The water vapor in the air is of great consequence in chemistry because of the fact that everything which is exposed to the air takes on more or less water. Some things take on so much water that they pass into a liquid solution or deliquesce, while others simply condense a thin film of water upon their surface. This last is the behavior of glass and other substances that do not dissolve. This water condensed upon the surface often gives a great deal of trouble in making accurate weighings, because of the fact that it will vary markedly with the relative humidity and temperature of the air. Often the best way to overcome the difficulty is to use for a counterpoise a vessel as nearly similar as possible to the one which is being weighed and to treat both vessels for some time with a mixture of concentrated sulfuric acid and potassium bichromate. After washing they are ready for use. The most efficient way to remove this film of liquid water is to heat the object and drive

the water off as vapor. However, it must be noticed that a film of water does not behave exactly like liquid water in that its vapor pressure is very much smaller than that of liquid water at the same temperature, and consequently the temperature has to be very high to remove the water thoroughly. In some cases it is not possible to heat the object to drive off the water, and in this case it must be placed in a closed vessel called a desiccator which contains one of the drying agents already mentioned. Under these conditions, the water will vaporize from the object and slowly diffuse to the desiccating substance. The process is a very slow one and will be greatly hastened by removing the air, since the latter interferes with the diffusion of the vapor.

**Heat of Vaporization of Water.**—Whenever any liquid, water included, passes into the gaseous state heat is absorbed unless the transformation takes place at the critical point. This absorption of heat is not accompanied by a rise in temperature and simply represents the difference in energy between the liquid and the gaseous substance and the work done in the transformation. This absorption of heat is often ascribed to the work done in separating the particles of water from each other, since gaseous water occupies a very much larger volume than the liquid water from which it was formed. However, this cannot be the explanation because there is an increase in volume when water freezes, and yet heat is given out in this case. The heat absorbed in the transformation of 1 grm. of a liquid into its vapor, without rise in temperature, is called its heat of vaporization. In the case of water it is 537 cal. or 2245 joules at 100° C. or 606.5 cal. or 2535 joules at 0° C. So as the temperature rises, the heat of vaporization decreases and becomes zero at the critical temperature.

Steam is extensively used for the heating of buildings, because such large quantities of heat may be transmitted with the movement of only a small amount of substance.

**Definitions of Systems and Phases.**—A little later we shall have occasion to discuss an important law of chemistry known as the phase law. In connection with this and in other cases also, we shall have to use the terms system, phase, and degrees of freedom.

A system may be defined as consisting of one or more substances

isolated from the surroundings and in a state of equilibrium or tending to approach equilibrium. Systems are made up of phases and there are as many phases present in a system as there are different kinds of homogeneous portions of the system. If a system be broken up into a number of parts there need not be as many phases as there are parts, but only as many as there are different kinds of homogeneous parts. Since the phases are homogeneous, they are either pure substances or solutions. A phase is then a homogeneous portion of a system. If more than one is present, they are physically distinct and may be mechanically separated.

As an illustration of all this, we may consider a system consisting of water. This may be obtained by isolating a portion of water from all other substances by which it can be affected. If it consists entirely of liquid water or of water vapor or of ice, it will be homogeneous throughout and will be a system of only one phase. If it contains liquid water and ice, only two phases, water and ice, will be present no matter into how many pieces the ice may be broken because there are only these two kinds of homogeneous parts to the system. Water and water vapor, or water vapor and ice constitute the other possible two-phase combinations of this system. Water vapor, liquid water and ice existing together would make a three-phase system.

**Volume Relation.**—The volume of a given mass of water is so affected by temperature and pressure that given these two magnitudes the volume may be calculated. The relationship, however, is not so simple as with gases where it is described by " $p_v = rT$ ," but it still is a relation for any given mass which may be expressed by an equation containing the three variables  $T$ ,  $p$ , and  $v$ . Now of course in an equation containing three variables, if the value of two be fixed, that of the third becomes fixed and determined. We may then in the case of liquid water make two simultaneous and independent choices between the three variables  $T$ ,  $p$ , and  $v$ , but cannot choose all three because the third is fixed by the other two. The number of simultaneous and independent choices which we may make at any one time between the variables temperature, pressure and volume we call the **degree of freedom** with respect to thermal and spacial variability. Every pure substance which exists in



one phase—solid, liquid, or gaseous—has then two degrees of freedom.

In connection with the discussion of the transformation of water into gaseous water, it was pointed out that the vapor pressure of any given liquid depended upon the nature of the substance and the temperature and not at all upon the relative volume of the gaseous and liquid phases. From this it follows that the state of the system, water vapor and water, will be fixed by the two variables, temperature and pressure. Since when one of these is chosen the other becomes fixed, this system has only one degree of freedom. The same thing is true for a system of water vapor and ice as may readily be seen. From these instances we might guess that as the number of phases increases the degrees of freedom decrease and that for each added phase a degree of freedom is lost.

**Effect of Pressure on the Melting-point of Ice.**—A system consisting of liquid water alone has two degrees of freedom. If ice be added, the number of phases is increased to two, and from what has been said above, the degrees of freedom should be reduced to one. This means that ice and water should exist in equilibrium over a certain range of temperature and pressure, and that for each temperature there should be a perfectly definite pressure of equilibrium. Experiment has confirmed these conclusions and shown that the melting-point of ice is lowered by  $0.0072^{\circ}$  for each atmosphere by which the pressure is increased. An increase in the pressure of 139 atmospheres is required to lower the temperature  $1^{\circ}$ . A mixture of ice and water then, can have a temperature of  $0^{\circ}$  C. only when under a certain pressure. By definition of  $0^{\circ}$  C. this is the standard pressure. Change in the barometric pressure should then affect the melting-point of ice and the alteration should amount to about  $0.0001^{\circ}$  C. for a change in the barometric pressure of 1 cm.

Although the lowering of the temperature for each atmosphere increase of pressure is very small, it is possible by pressure alone to keep water in the liquid state at  $-24^{\circ}$  C. The pressure necessary for this may be most readily obtained by freezing a part of the water contained in a very strong steel vessel. The freezing of only a small part of the water will produce an enormous pressure because of the marked increase in the volume of

water when it is changed into ice. The fact that some of the water is still liquid at  $-24^{\circ}\text{C}$ . may be shown by the rattling of a steel ball enclosed with the water.

If two pieces of ice at their temperature of melting be pressed firmly together, they will melt at their points of contact and the water so formed will of course be below zero. When the pressure is taken off, this water will at once freeze and the two pieces of ice will become one. The loose snow of the mountains is finally welded into the firm ice of the glacier largely through this same process. The glaciers themselves in their movement down the mountains are constantly being cracked and then healing their wounds under the influence of the varying pressure.

**Triple Point.**—From the fact that a system of water and ice has one degree of freedom and that an increase of the number of phases of a system by one seems to be accompanied by a

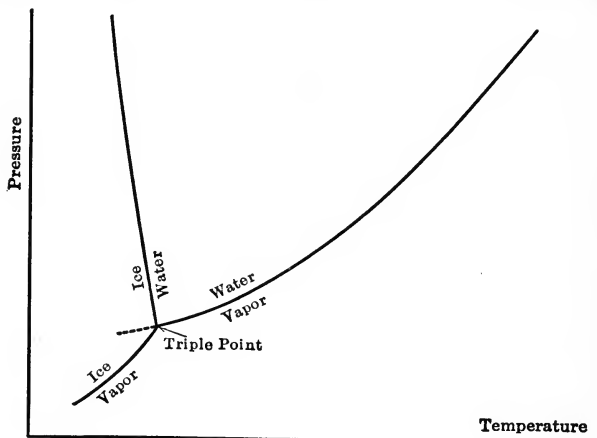


FIG. 12.

decrease of one in the degrees of freedom, we would be led to expect that a system of ice, water, and water vapor would have no degrees of freedom, *i.e.*, these three phases would exist side by side only at one temperature and pressure. This is exactly what turns out to be the case. Ice, water and water vapor exist in equilibrium only under a pressure of 0.4 cm. of mercury; the vapor pressure of water at its freezing-point and at a temperature of  $+0.0072^{\circ}\text{C}$ ., the melting-point of ice under this

pressure, which is practically one atmosphere less than the standard pressure at which the melting-point is zero. If the pressure is raised, the water vapor will disappear; if lowered, the water disappears. Raise the temperature and all the ice will melt, lower it and water will freeze. Only at  $+0.0072^{\circ}$  and at 0.4 cm. can all three phases of water exist together (Fig. 12). These are called the triple point for water. In general every substance which will melt has a triple point in the neighborhood of its melting-point. These triple points have this in common—that they are invariable conditions of temperature and pressure under which three phases of the substances can exist together, but they are scattered over practically the whole range of temperature and pressure. The name triple point is given to them because they are the meeting-point of three curves—usually the vapor pressure for the liquid, that for the solid, and the melting-point curve for the solid. It is, of course, only at the triple point that the three phases can be in equilibrium.

**The Law of Mobile Equilibrium.**—The melting-point of practically every solid is altered to some extent by a change in pressure. An increase in pressure lowers the melting-point of some few but raises that of most substances. In every case an increase of pressure is followed by the formation of the phase which occupies the smaller volume per unit mass. This contraction would tend to relieve the pressure. Usually the solid is more dense than the liquid, and the tendency is for it to form when the pressure is increased. So the melting-point of most substances is raised. The case is just the other way around with water for the ice is less dense than the water and the melting-point is lowered. In every instance we are dealing with an equilibrium between a solid and a liquid, and the shifting of this equilibrium under the action of a constraint in the form of pressure. The equilibrium is always shifted in such a way that the pressure tends to be relieved. These are special cases of a very general law which applies to all kinds of equilibria both physical and chemical. This law may be stated as follows: *If a constraint is put upon a system in equilibrium whereby the equilibrium is altered, that reaction will follow which tends to decrease the constraint.*

**Solutions.**—It is a matter of every-day experience that many

substances will dissolve in water. We call these water or aqueous solutions of the substances. A solution, it will be recalled, is a homogeneous mixture of two or more substances, the relative proportions of which may vary continuously within certain limits and whose properties vary with the proportions of the components. Solutions may exist in all three of the physical states and it is simply the circumstance that we are so familiar with water solutions that makes us tend to think of a solution as a liquid.

In connection with solutions two terms, solute and solvent, are in constant use, and their meaning should be understood. The substance which is dissolved is called the solute, while that in which the solute is dissolved is called the solvent. A solution of salt in water is obtained by dissolving the solute salt in the solvent water. The solute may be solid, liquid, or gaseous, and so may the solvent. As an example of a liquid dissolving in a gas, we may take the vaporization of water into air.

Aqueous solutions are of great importance in chemistry because of the fact that many chemical processes take place very readily in them; one reason for this being apparently that the water will bring together into one liquid phase, solid, liquid or gaseous solutes in the very most intimate mixture.

In general, solutions have properties which are a sort of mean between the properties of the two components, so these aqueous solutions will have in the main the properties of water. One very important circumstance to note about solutions is that a solute always lowers the vapor pressure of its solvent upon passing into solution. From this it follows that if the solute is non-volatile, the vapor pressure of the solution will always be less at any given temperature than the vapor pressure of the pure solvent. In case the solute is volatile, the partial pressure of the solvent is lowered as before, but the vapor pressure, which is the sum of the partial pressures of the solvent and of the solute, may or may not be lower than that of the solvent in the pure state. For solutions which are dilute, the lowering of the vapor pressure is proportional to the mass of the solute dissolved in a given fixed mass of the solvent, at constant temperature. If the temperature varies, everything else being constant, the ratio of the decrease of the vapor pressure to the vapor pressure

of the pure solvent, at that temperature, is constant or,

$$(p - p')/p = \text{constant}$$

where "p" is the vapor pressure of the pure solvent and "p'" that of the solution.

In Fig. 13, the curve AOB is the vapor pressure curve for the pure solvent, and the curve CO'D that for the solution. It will be noticed that the curve for the solution lies below that for the solvent, and that they are not parallel. This last is due to the constancy of the ratio  $(p - p')/p$ . The curve EO'O is the vapor pressure curve for the ice. The line MN represents the atmospheric pressure. From the definition of boiling-point it will be seen that the temperature corresponding to the points B and D represent the boiling-points of the pure solvent and of the solution respectively. This also shows that owing to the decrease in the vapor pressure caused by the solute, the boiling-point of the solution is higher than that of the solvent. This is true in every case where the solute is non-volatile. If the solute is volatile, the boiling-point of the solution may be higher or lower than that of the pure solvent depending upon whether the partial pressure of the solute is less than or greater than the lowering of the vapor pressure of the solvent.

The freezing-point of all solutions from which the solvent separates as a pure solid is lower than that of the pure solvent. In order to understand this, it will be necessary to consider the relations between the vapor pressure of the solid and of the liquid. It seems very natural to assume that ice has no vapor pressure, but this is a mistake for ice has a measurable vapor pressure even when cooled to many degrees below zero. This pressure is 0.4 cm. at zero degrees, and becomes smaller as the temperature falls. As may be seen by reference to Fig. 13, page 74, the vapor pressure curve for ice is not a continuation of that for water, but lies below the water curve except at point O, where the curves meet. It is only at this point, O, then that the solid and liquid have the same vapor pressure and can be in equilibrium with each other. At temperatures below this point the vapor pressure of the water is higher than that of the ice and a little thought will convince anyone that the two could not continue to exist side by side because the water would evaporate and condense on the ice as the solid, and this would

go on until all the water had disappeared. A little reflection will show that a system must be in equilibrium in every way to be in equilibrium in any way. Therefore it follows that since at the freezing-point the solid and the liquid are in equilibrium, the vapor pressure of the two must be the same. We may then frame a definition of freezing-point so that it shall be similar to that for the boiling-point. The freezing-point for a substance is the temperature at which the vapor pressure of the solid is the same as that of the liquid modification. In Fig. 13 this is at the point *O*, where the two curves *AOB* and *EO'O* cut. Correspondingly the freezing-point of the solution will be the temperature

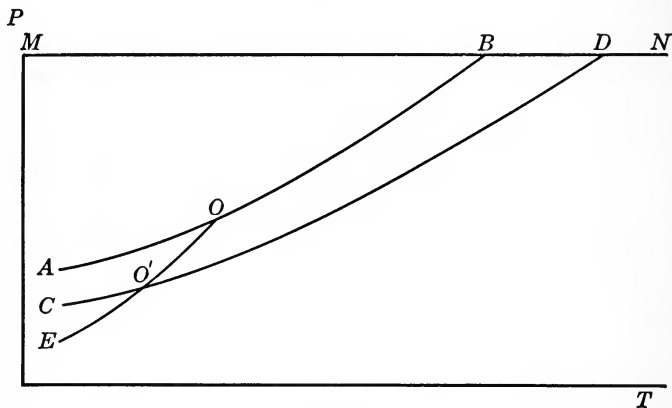


FIG. 13.

at which the vapor pressure of the solution equals that of the ice, and this will be at the point, *O'*, on the curves and will always be at a lower temperature than that of the pure solvent. From these considerations it will be seen that the solute lowers the vapor pressure of the solvent and that this results in the solutions boiling at a higher, and freezing at a lower temperature than the pure solvent. No real explanation for the lowering of the vapor pressure can be given, but we can picture it to ourselves by assuming that things dissolve because they have an attraction for each other, and that, because of this attraction the solvent finds it more difficult to pass over into the gaseous state from a solution than when it is pure.

When a solid salt is brought in contact with water, some of it, at any rate, dissolves. If the salt is difficultly soluble, like silver chloride, the amount of the salt which a given quantity of water, say 100 gm., can take up is very small indeed; but in the case of an easily soluble compound like calcium chloride, the amount which can be dissolved by the same weight of water is very large. However, there is at each temperature a definite limit to the weight of a salt which a given weight of water will dissolve. A solution in which this limit has been reached, and which is in equilibrium with some of the solid solute, is called a saturated solution. The ratio between the weights of the solute and the solvent in a saturated solution is called the solubility of the solute. It is usually expressed in terms of parts by weight of solute in 100 parts by weight of solvent.

If less of the salt be added to the solvent than it is capable of dissolving, all will be taken up. The solution is said to be unsaturated because it can still take up more of the salt. If more of the salt be added than the solvent can dissolve, that quantity which corresponds to the solubility will pass into solution and the excess will be left undissolved. The concentration of the salt in solution is absolutely independent of whether this excess be large or small. The solubility of a solid salt is an expression of the equilibrium between solid and liquid phases and like all other equilibria between phases is independent of the absolute amounts of each phase.

Just as a liquid may be supercooled if the solid modification be excluded, so a solution may be prepared which contains more of the solute than corresponds to its solubility if the solid solute is not present. Such solutions are called supersaturated. In the absence of the solid solute, they are stable toward most changes; but when brought in contact with even a very small piece of the solid, all the excess of solute over that corresponding to the solubility quickly separates out in the solid form.

All these relationships are indicated by the phase law (page 119). A system composed of a solid salt and water is one of two components and hence the sum of the phases and the degrees of freedom is four. If the system has only one phase, say solution, there are three degrees of freedom and we may make three simultaneous choices of the values of the variables—concentration

of salt, temperature and pressure. So, even after fixing the temperature and pressure, we can still choose the concentration of the salt within certain limits. But if two phases, solid salt and solution, are present one of these degrees of freedom disappears and there is left for simultaneous choice only any two of the three variables—temperature, pressure, and concentration. At any given pressure then, say atmospheric, there is at each temperature a certain definite concentration of the salt in the solution, corresponding to its solubility. As a rule the solubility of a salt is markedly altered by changes of temperature. Generally, but by no means always, the solubility increases with rising temperature.

The other variable which affects the concentration of the salt in the system, solid salt and solution is the pressure. The solubility of a salt is very much less sensitive to changes in pressure than to changes in temperature, in fact it requires a change in the pressure of hundreds of atmospheres to make a measurable change in the solubility. So small is the influence of pressure that for all practical purposes it may be neglected.

**Application of the Law of Mobile Equilibrium.**—The phase law tells us that the solubility of a salt will change with the temperature and pressure, but for information as to the direction of the change we must go to the law of mobile equilibrium. This law says that if a system in equilibrium is subjected to a constraint whereby the equilibrium is altered, that reaction will follow which tends to relieve the constraint. If the constraint consists in the addition of heat whereby the temperature of the system is raised, the change which will follow will be accompanied by the absorption of heat. If a salt dissolves in its almost saturated solution with the absorption of heat, more salt will pass into solution when the system is heated. In other words, the solubility of the salt increases with rising temperature. On the other hand, if a salt dissolves in its almost saturated solution with the evolution of heat, it will pass out of solution into the solid state with the absorption of heat. So if such a solution be heated, solid salt will separate as the temperature rises, or the solubility will decrease with rising temperature. A salt which dissolves without any heat effect will not change its solubility with the temperature. This is very nearly true of sodium chlo-



ride. The heat of solution of a salt in its saturated solution is often very different, not only in magnitude but also in sign, from its heat of solution in the pure solvent. It is only the former heat effect which is of significance in this connection.

If the pressure be increased, that change will take place which is accompanied by a decrease in volume, since this will tend to relieve the pressure. The solubility of the salt will increase with the pressure in case the more concentrated solution has a smaller volume than the saturated solution together with the solid salt. But if the volume of the system would be decreased by the separation of the solid salt, the solubility of the salt will decrease with increasing pressure.

**The Chemical Properties of Water.**—Water can react chemically in essentially two different ways, that is, it may combine directly, in which case only one new substance is formed, or it may react because of its being a compound of hydrogen and oxygen. In this case two or more new substances are formed. As examples of direct combination, we might cite the union of water with lime (calcium oxide) to form calcium hydroxide; with anhydrous copper sulfate to form crystallized copper sulfate or blue vitriol; with anhydrous calcium chloride to form crystallized calcium chloride. These compounds of water and the salts such as the copper sulfate and the calcium chloride are called hydrates or salts with water of crystallization. The hydrates differ greatly in their stability, and some are so easily decomposed into water and the rest of the compound that many have been led to believe that they are essentially different from other chemical compounds, and that the water exists in them in some peculiar way as water. They have, however, all the characteristics of chemical compounds, that is, follow the law of definite proportions, differ radically in their properties from their components, etc., so there is no reason for setting up a special class for these substances.

As cases of the behavior of water as a compound of hydrogen and oxygen, we may call to mind the reactions between water and iron, or magnesium, calcium or sodium whereby hydrogen and a compound of the metal with oxygen or with oxygen and hydrogen is formed.

**The Reaction of Sodium and Water.**—The action of sodium

upon water is so very vigorous that only very small quantities of sodium, a piece not larger than a pea, should be used at a time. Larger quantities are very likely to produce explosions which are as violent as those due to an equal weight of dynamite. By the action of sodium upon water, hydrogen and some substance which evidently dissolves in the water are produced, because after the evolution of the hydrogen has ceased only a homogeneous liquid remains. This liquid has some properties which are very different from those of water and which evidently belong to the solute. For example it has a soapy feeling, a peculiar taste known as alkaline, turns red litmus blue, etc. When this solution is boiled, nothing passes off but water, and a white substance, solid at ordinary temperatures, is left behind. This is known as caustic soda or sodium hydroxide. That it contains sodium and oxygen is evident from the circumstances of its formation. When this solid is mixed with aluminum and heated, hydrogen is evolved, and indeed as much hydrogen as was obtained by the action of the sodium on the water. Hence the sodium hydroxide contains sodium, oxygen and hydrogen, and contains as much hydrogen as was liberated by the sodium; therefore when sodium acts upon water, half of the hydrogen of the water which is transformed is changed into hydrogen gas, and half goes into the sodium hydroxide. When this sodium hydroxide is exposed to the air, it becomes moist and finally passes back into a liquid which is identical in its properties with a strong water solution of the substance and hence is such a solution. The water necessary for the formation of this solution comes from the air. Sodium hydroxide and things like it which take up water vapor from the air and form solutions, are called **deliquescent substances**. All such substances are very freely soluble and have the common characteristic that their saturated solutions give a smaller vapor pressure of water than the partial pressure of the water vapor in the air. If this were not so the substance could not deliquesce. Many of the salts containing water of crystallization decompose readily into their components and give an easily measurable vapor pressure of water. If the partial pressure of the water vapor in the air is less than the vapor pressure of the water from the salt, the latter will decompose and

the crystals will fall to powder. The substance is then said to **effloresce**. At any given temperature the vapor pressure of a saturated solution of a substance or that of water from a hydrate is constant, but the partial pressure of the water vapor in the air varies from time to time, so a substance may deliquesce one day, be stable the next, and even effloresce on the day after; its behavior being determined by the partial pressure of the water vapor in the air and the vapor pressure of the water from the substance.

In ordinary weather calcium chloride will deliquesce, and even after the salt has all dissolved, the solution will continue to take up water from the air until the partial pressure of the water vapor in the air is equal to the vapor pressure of the solution. If such a solution be allowed to stand in the laboratory until winter comes on, it will be found that the water will gradually evaporate and finally crystals of calcium chloride with water of crystallization will form. In the depth of winter these crystals sometimes fall to a powder or effloresce. So calcium chloride is both a deliquescent and an efflorescent substance. The explanation being of course that in the summer the partial pressure of the water vapor in the air is high, while in the winter it is low indoors on account of the low temperatures prevailing outside.

**The Composition of Water.**—Water is, of course, a chemical compound of hydrogen and oxygen and hence from the law of definite proportions the relative proportions by weight in which these elements combine to form water will be fixed and invariable. These proportions are very important properties, not only of hydrogen and oxygen, but also of water.

There are two general methods of procedure for determining the composition of a substance. We may decompose the substance into its elements and determine the proportions by weight in which each is present. This is called analysis. Or we may bring together the elements which go to make up the substance and make the conditions such that they will combine to form the desired compound. By carefully noting just what weight of each element disappears in the formation of a given weight of the compound, the quantitative composition of the substance may be determined. This is called synthesis.

For the analysis of water, advantage may be taken of the fact mentioned under the discussion of the methods for the preparation of hydrogen, that when a current of electricity is passed through water between two plates of platinum, hydrogen appears at one of the platinum plates and oxygen at the other. In this process the platinum plates are unaffected, and the weight of the hydrogen plus the weight of the oxygen equals the weight of the water which disappears, thus showing that

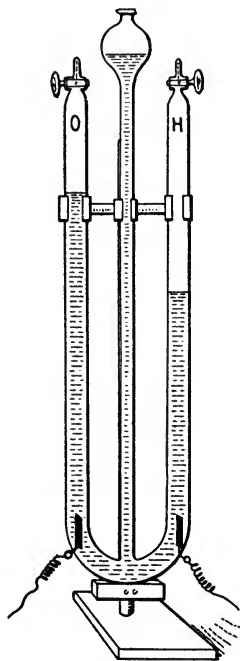


FIG. 14.

these substances are the only ones formed in the process. By collecting the gases separately and determining their weights, a quantitative analysis of the water may be made. Since the densities of the gases are known, it is not necessary to weigh them; all that is required is that their volume be measured under known conditions of temperature and pressure (Fig. 14), and from these data the volumes under standard conditions may be readily calculated. The volumes under standard conditions times the densities of the gases will, of course, give the weights of the gases, and therefore the proportions by weight in which they combine to form water which is the result desired.

When this operation is performed it turns out that if the gases be measured under the same conditions of temperature and pressure, that the volume of hydrogen is almost exactly twice that of the oxygen. The ratio according to the best determinations being 2.0025 volumes of hydrogen to 1.0000 volume of oxygen. The density of hydrogen is .00008986 and of oxygen .0014293 and therefore the ratio by weight is  $2.0025 \times .00008986$  divided by  $1.0000 \times .0014293$ , or 1.000 of hydrogen to 7.943 of oxygen or roughly 1 to 8. The percentage composition of water is then 11.19 per cent. hydrogen and 88.81 per cent. oxygen.

The electrical conductivity of pure water is very low so that

it is a difficult matter to pass through water, in a reasonable time, a sufficient quantity of electricity to decompose enough water so that the gases may be accurately measured. A dilute solution of sulfuric acid is a good conductor of electricity and at the platinum plates oxygen and hydrogen are given off as from pure water. After the operation is finished, as much sulfuric acid is found as in the beginning, and therefore it is not used up. It turns out, in fact, that the net result of all the chemical changes taking place during the passage of the current through dilute sulfuric acid is the decomposition of water and therefore dilute sulfuric acid is what is actually used in the analysis of water.

One of the standard methods which has been much used for the quantitative synthesis of water is based upon the reaction taking

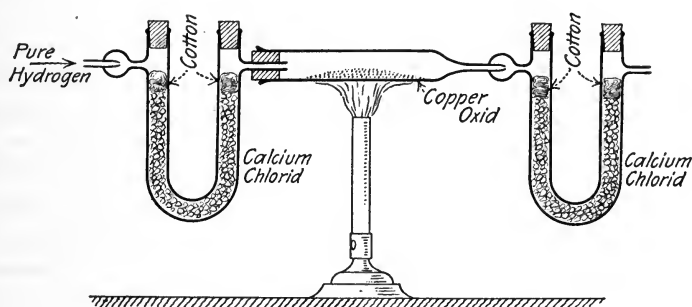


FIG. 15.

place between copper oxide and hydrogen at a somewhat elevated temperature whereby water and copper are produced. The process may be briefly outlined as follows: Pure dry hydrogen (Fig. 15), is passed over a weighed quantity of copper oxide at a little below the temperature of redness. The water formed is collected by absorption in a weighed quantity of calcium chloride. The increase in weight of the calcium chloride at the end of the experiment over that at the beginning gives the weight of the water formed. The difference between the weight of the copper oxide and of the copper formed from it gives the weight of the oxygen which was transformed into the water. The difference between the weight of the water and that of the

oxygen is, of course, the weight of the hydrogen. The composition of water from data obtained in this way checks very closely with that given above.

Another method for the quantitative synthesis of water consists in determining the proportions by volume in which hydrogen and oxygen unite to form water. From these data and the densities of the gases, the proportions by weight may be easily obtained as was shown above. Since

a mixture of hydrogen and oxygen may be caused to explode by passing an electric spark through the mixture at any point this synthesis is very easily carried out. The apparatus necessary consists of a thick-walled glass vessel (Fig. 16), strong enough to stand the explosion of the gases and having two platinum wires sealed through its walls. Carefully measured volumes of hydrogen and of oxygen are introduced into the vessel, mixed and exploded. The residual gas is then measured and examined to see whether it is hydrogen or oxygen. The results show as before that the gases combine in the proportions of very nearly two volumes of hydrogen to one of oxygen. If the gases are mixed in just these proportions no residue is left; but if an excess of either one is used, the excess of that gas is left unchanged. If this

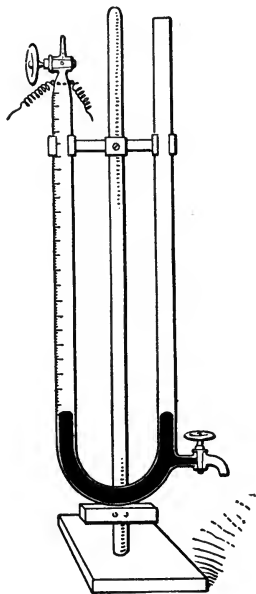


Fig. 16.

synthesis is carried out at temperatures above the boiling-point of water and at pressures somewhat below that of the atmosphere so that the water formed shall stay in the gaseous state, as water vapor, the volume of this water vapor is very nearly the same as that of the hydrogen from which it was formed, both measured at the same temperature and pressure. So the following very simple relation exists between the volumes of the gaseous substances involved in this reaction: two parts by volume of hydrogen will combine with one part by volume of oxygen to form two parts by volume of water

vapor, all being measured under the same conditions of temperature and pressure.

When other gases enter into reaction with one another, relations between the combining volumes are always very simple, often even simpler than in the case given above. This behavior of gases is described by the law known as **Gay Lussac's law of the combining volumes of gases**. *Whenever in any chemical reaction two or more gases appear or disappear, they do so in the ratio of small whole numbers by volume. In the case given above, the ratios are 2 : 1 : 2.*

When we come to compare the proportions by volume in which solids or liquids react, we find no suggestion of the existence of a simple relation, nor is there any simple proportion by weight in which substances react. We find here another instance of the great simplicity of the behavior of gases.

It will be recalled that the general gas law  $p v = r T$  does not exactly describe the behavior of any gas, but that they all vary somewhat from this. Similarly Gay Lussac's law of combining volumes is not an exact law as may be seen from the fact that hydrogen and oxygen do not combine in the ratio of 2 : 1 as called for by the law, but in the ratio of 2.0025 : 1. The deviations, however, are not large, in most cases, and the law is very useful and important.

**Molar Weight.**—The conception of molar weights which is about to be developed is highly useful since with its aid the interpretation of many apparently complicated chemical phenomena becomes simple.

Specific gravity of a substance, it will be recalled, is the ratio of the weights of equal volumes of the substance in question and of some other substance taken as a standard. To make it definite it is necessary to state the conditions of temperature, etc., under which the volumes shall be taken. As the standard substance for liquids and solids, water is commonly used. Air has often been taken for the standard substance for the specific gravity of gases, but for reasons which will be evident later, oxygen is more suitable. In the case of the specific gravity of liquids and solids it is necessary to give the conditions under which both substances are measured. For gases, however, since they all follow the one general gas law,

$pV = rT$ , it is only necessary to state that the gas in question and the standard gas shall be measured under the same conditions of temperature and pressure, whatever these may be. The specific gravity of any given gas referred to oxygen as the standard will then be always the same number no matter what the temperature and pressure of comparison. These specific gravities may be readily calculated by dividing the densities of the various gases by the density of oxygen, all under the standard conditions. These magnitudes are well known, or,

$$\text{sp. g.} = D / .001429$$

where .001429 is the density of oxygen and D that of the gas in question.

The molar weight of a gaseous substance is conceived of as being proportional to the density of the gas. For reasons which cannot be brought out until later, the molar weight of oxygen is taken as 32. At the proper point the reasons for this choice will be given. If then the molar weight of a gas is proportional to its density the following relation will hold:

The molar weight of the gas : the molar weight of oxygen =  
the density of the gas : the density of oxygen, or

$$\frac{\text{The molar weight of the gas}}{\text{The molar weight of oxygen}} = \frac{\text{The density of the gas}}{\text{The density of oxygen}}$$

Substituting for the molar weight of oxygen its value 32, and solving for the molar weight, we have

$$\text{Molar weight} = 32 \times \frac{\text{The density of the gas}}{\text{The density of oxygen}} = 32 \times \frac{D}{.001429}$$

but  $\frac{D}{.001429}$  is the specific gravity of the gas referred to oxygen, and therefore for a gaseous substance the *molar weight may be defined as thirty-two times the specific gravity of the gas referred to oxygen as the standard.*

For the sake of illustration, let us calculate the molar weight of hydrogen. The density of hydrogen is .00008986, and letting M represent the molar weight,

$$M = 32 \times .00008986 / .001429 = 2.012$$

Therefore the molar weight of hydrogen is 2.012.



Water vapor of course cannot exist under standard conditions, but could exist at  $0^{\circ}$  C. if the pressure were less than 0.4 cm. of mercury or at atmospheric pressure if the temperature were higher than  $100^{\circ}$  C. Since water vapor follows the gas laws, if the weight of a given volume be found under any conditions of temperature and pressure, the density which it would have under standard conditions, if it did not liquefy, can be readily calculated. The density of water vapor obtained in this way is .0008063.

Molar weight of water =  $32 \times .0008063 / .001429 = 18.05$ . If one did not feel satisfied with this method of calculation, all that would be necessary would be to divide the density of the water vapor at the temperature and pressure under which it was measured by the density of oxygen at the same temperature and pressure, and this specific gravity times thirty-two would give the molar weight of the water, 18.05, as before.

By a slight extension of the conception of molar weight we can get another very useful conception, that of a gram mole. A gram mole of a substance is nothing more or less than the molar weight of the substance expressed in grams. Or it is a weight in grams of the substance numerically equal to its molar weight. For example, the molar weight of hydrogen is 2.012 and a gram mole of hydrogen is 2.012 gm. of hydrogen. The molar weight of water vapor is 18.05, so a gram mole of water vapor is 18.05 gm. of water vapor. The molar weight of oxygen is 32, and a gram mole of oxygen then is 32 gm. of oxygen.

The volume occupied by a gram mole of a gaseous substance under standard conditions can be easily calculated by dividing its molar weight by its density under standard conditions. The volume of a gram mole of oxygen under standard conditions is then  $32 / .00143$  or 22,400 c.c. The volume of a gram mole of hydrogen is  $2.012 / .00008986 = 22,400$  c.c. These and other examples which may be worked out, together with a few moments thought on the definition of molar weight should soon convince one that the volume of a gram mole of all gases under standard conditions is the same and is 22,400 c.c.

Turning now to our general gas law  $pV = rT$  or  $pV/T = r$ , if the temperature and pressure are those for standard conditions,

then these two factors will be the same for all gases, and if we are dealing with gram moles of the different gases the volume will be the same for all, viz., 22,400 c.c. Therefore, since all these magnitudes are the same for all gases when gram moles are taken, the "r" is the same for all gases. When gram moles are referred to, "r" is usually written as "R" and p and v as P and V, so that for gram molar quantities the general gas law becomes  $PV/T=R$ , in which R has the same value for a gram mole of any gas. The numerical value of R depends, of course, upon the units in terms of which P, V, and T are measured. If the pressure is measured by atmospheres, and the volume in c.c. and the temperature in Centigrade degrees,

$$\begin{aligned} R &= 1 \times 22,400 / 273 \\ &= 82.05 \text{ atmosphere cubic centimeters} \end{aligned}$$

The pressure is often expressed in dynes per square centimeter which may be calculated as follows: A pressure of one atmosphere upon a sq. cm. is equal to the weight of a column of mercury 76 cm. in height and 1 sq. cm. in cross-section. This would be the weight of 76 c.c. of mercury, and since the density of mercury is 13.595 at 0° C. the mass of this mercury is  $76 \times 13.595$  and its weight 980 times this; the weight of 1 grm. being 980 dynes. If the dyne is used as the unit of pressure, and the cubic centimeter as the unit of volume, then

$$\begin{aligned} R &= 76 \times 13.595 \times 980 \times 22,400 / 273 \\ &= 8.31 \times 10^7 \text{ ergs per degree.} \end{aligned}$$

A part of the usefulness of the conception of molar weights and especially of gram moles is due to the fact that gram moles of the different substances are really those quantities which are physically equivalent in many ways, and not infrequently also are chemically equivalent. To illustrate let us recall that, as is given above, gram moles of different gaseous substances occupy the same volume under the same conditions. As we shall soon see, a gram mole of most substances when in solution will lower the vapor pressure, raise the boiling-point and lower the freezing-point of a fixed mass of the given solvent by constant amounts irrespective of the nature of the substance making up the gram mole. In these and many other ways, gram moles are equivalent.

## CHAPTER VI

### THE LAW OF COMBINING WEIGHTS

There can be no question but that the law of combining weights is the most important generalization of chemistry, and we must now turn our attention to the formation of this conception. The starting point for the development of this law is Gay Lussac's law of combining volumes which was discussed in the preceding chapter. But in connection with this, it seems advisable to consider briefly the deviations of gases from the general gas laws.

Mention has been made several times of the fact that the behavior of gases with regard to temperature and pressure is not accurately described by the laws of Boyle and Gay Lussac. The variations are not large, and for most purposes may be neglected. These deviations have been carefully studied for many years by a number of men, and it is now possible to say from purely experimental data, how much the more common gases deviate from the gas laws. The correction of oxygen for the deviation from Boyle's Law,  $pV=K$ , may be taken as an illustration of this. The law seems to be the more correct the lower the pressure; and if it were experimentally possible to determine  $pV$  at very low pressure, the result would be its true value. Since this cannot be done, we reach what must be very nearly the same end by determining  $pV$  for 32 gms. of oxygen at  $0^{\circ}$  C. under a pressure of 1 atm., and again under a pressure of 2 atms. The value at 1 atm. is 22,400; at 2 atms. it is 22,395.  $PV$  then has decreased 5 units for an increase in pressure of 1 atm. For the corresponding decrease in pressure, we may reasonably expect it to increase by 5 units; and therefore the value of  $pV$  at very small pressure may be taken at 22,405. From this, the conclusion is drawn that the volume of a gram mole of oxygen under standard conditions would be 22,405 c.c., if it followed the gas laws. With the aid of the corrections determined in this manner, the densities which these gases would have, under standard conditions, if they exactly followed the gas laws, may be ascertained. The numbers so obtained are just as

experimental as the densities gotten by the direct weighing of the gases, since they are these numbers plus or minus a small experimentally determined correction. The following table gives in the first column the densities of a number of gases just as they are determined; in the second, these densities corrected for the deviations of the gases; in the third, the experimental specific gravities referred to oxygen; in the fourth, the uncorrected molar weights obtained by multiplying the numbers in column three by 32 and lastly, the molar weights corrected for the deviations.

TABLE

Name	Density as determined	Density corrected	Sp. gr. oxy. stan.	Molar wt. uncorr.	Molar wt. correct
Oxygen.....	.0014293	.0014282	1.0000	32.000	32.000
Hydrogen.....	.00008986	.00008991	.06287	2.0119	2.015
Nitrogen.....	.0012507	.0012501	.87508	28.005	28.012
Chlorine.....	.0032215	.0031650	2.254	72.13	70.926
Water.....	.0008063	.0008041	.5642	18.05	18.015
Nitric oxide.....	.0013405	.0013390	.9379	30.013	30.004
Nitrous oxide.....	.0019788	.0019641	1.3845	44.31	44.009
Hydrogen chloride....	.0016398	.0016270	1.1473	36.72	36.46
Ammonia.....	.0007709	.0007599	.5394	17.26	17.027

In most cases it will be noticed that the corrected densities and molar weights are not very different from the uncorrected values; the greatest difference being found in the case of chlorine.

In the discussion of Gay Lussac's law of combining volumes as given in the chapter on water, it was pointed out that the statement of the law that "whenever in any chemical reaction two or more gases appear or disappear, they do so in the ratio of small whole numbers by volume," was not quite exactly followed in any case. A simple calculation will show that we may get the proportions by weight in which hydrogen and oxygen combine to form water, either by multiplying the ratio of the exact combining volumes 2.0025/1, by the ratio of the determined densities .00008986/.0014293, or by taking the approximate ratio of the volumes 2/1 and multiplying by the ratio of the corrected densi-

ties .00008991/.0014282. Either set of figures gives the same result, 1: 7.943. This and similar cases show that Gay Lussac's Law of Combining Volumes would be exact if the gases followed the other laws exactly; and that the corrected densities have taken into account all necessary corrections and that the precise proportions by weight in which gases combine may be obtained by taking the law of combining volumes as exact and multiplying the ratio of the volumes by the ratio of the *corrected* densities. Having reached this conclusion, we are in a position to proceed at once to the law of combining weights. We shall need for this the proportions by volume in which the gases combine, their corrected densities, and molar weights. It is a little unfortunate that in this connection we shall have to make use of some substances which we have not as yet studied, but there is no reason why we should not learn a few of their properties now, since this will simplify the study of the substances later.

In the table given below, the proportions by volume are shown in which the gases hydrogen, oxygen, nitrogen and chlorine will combine, together with the volumes of the resulting compounds. Just below the name of each gas is given the density of the substance. This when multiplied by the proportion by volume gives the proportion by weight in which the gas unites with the other gas or in which it is formed.

#### THE PROPORTIONS BY VOLUME AND BY WEIGHT IN WHICH GASES COMBINE <sup>1</sup>

2 vol. hydrogen	+ 1 vol. oxygen	= 2 vol. water vapor
2 × .00008991 gm.	+ .0014282 gm.	= 2 × .0008041 gm.
1 vol. hydrogen	+ 1 vol. chlorine	= 2 vol. hydrogen chloride
1 × .00008991 gm.	+ 1 × .003165 gm.	= 2 × .001627 gm.
1 vol. nitrogen	+ 1 vol. oxygen	= 2 vol. nitric oxide
1 × .0012501 gm.	+ 1 × .0014282 gm.	= 2 × .0013390 gm.
2 vol. nitrogen	+ 1 vol. oxygen	= 2 vol. nitrous oxide
2 × .0012501 gm.	+ 1 × .0014282 gm.	= 2 × .0019641 gm.
1 vol. nitrogen	+ 3 vol. hydrogen	= 2 vol. ammonia
1 × .0012501 gm.	+ 3 × .00008991 gm.	= 2 × .0007599 gm.

<sup>1</sup> The values given in this and the succeeding tables are experimental numbers and the difference between the sums of those on the left and those on the right of the equality sign is due to experimental error.

By inspecting this table, it will be seen that the proportions by weight in which hydrogen will combine with the other elements may be represented by its density .00008991 or by some rational multiple of this. The multiple is 2 in case it combines with oxygen and 3 if with nitrogen. Nitrogen combines with the other elements in proportions which may be represented by its density or a rational multiple of this, and so on for the others. In fact, we can now state the law that gaseous elements combine with each other in proportions by weight which may be represented by the corrected densities of the gases or by some rational multiple of these.

These densities are somewhat awkward to work with and molar weights are more convenient. Of course, there is no reason why we should always use a cubic centimeter as the unit of volume. The relations would be just the same if some other unit were used, say the liter, or better still the volume of a gram mole under standard conditions. The volume of 32 gm. of oxygen under standard conditions, it will be recalled, is 22,400 c.c. and this is what we have been using as the volume of the gram mole. If we take into account the correction for oxygen, the corrected volume of oxygen becomes 22,405 c.c. and since we are dealing with corrected magnitudes we should use this as the volume of a gram mole and also as our unit of volume. The following table gives again the proportions by volume and by weight for the gases, calling one volume equal to 22,405 c.c.

2 vol. hydrogen	+1 vol. oxygen	=2 vol. water vapor
2×2.0146	+1×32	=2×18.015
1 vol. hydrogen	+1 vol. chlorine	=2 vol. hydrogen chloride
1×2.0146	+1×70.926	=2×36.46
1 vol. nitrogen	+1 vol. oxygen	=2 vol. nitric oxide
1×28.012	+1×32	=2×30.004
2 vol. nitrogen	+1 vol. oxygen	=2 vol. nitrous oxide
2×28.012	+1×32	=2×44.009
1 vol. nitrogen	+3 vol. hydrogen	=2 vol. ammonia
1×28.012	+3×2.0146	=2×17.027

We see from these figures for the weights that the proportions by weight in which these elements enter into combination with one another may be represented by their molar weights or by some rational multiple of these. Now this is exactly what combining weights do. They are numbers whose ratio or else

the ratio of some rational multiples of them represents the proportions by weight in which the elements combine with one another. Therefore these molar weights might be called combining weights. If this were done, the combining weight of hydrogen would be 2.0146 and of oxygen 32. But now in one mole of water vapor there are 2.0146 parts by weight of hydrogen and 16 parts of oxygen, then using the above numbers for the combining weights there would be per mole of water one combining weight of hydrogen, but only half a combining weight of oxygen. In other cases the number of combining weights per mole of compound would often turn out fractional. To avoid this we have adopted the principle that we shall take as the combining weight of an element the smallest number of parts by weight of that element which shall occur per mole of any compound of the element.

In the following table is shown the number of parts by weight of the different elements per mole of the compounds given above.

TABLE OF PARTS BY WEIGHT OF THE ELEMENTS PER MOLE OF COMPOUND

Name of compound	Molar wt.	Oxygen	Hydrogen	Nitrogen	Chlorine
Water .....	18.015	16.000	2.0146	.....	.....
Hydrogen chloride ...	36.46	.....	1.0073	.....	35.463
Nitric oxide .....	30.004	16.000	.....	14.006	.....
Nitrous oxide .....	44.009	16.000	.....	28.012	.....
Ammonia .....	17.027	.....	3.0219	14.006	.....

From these figures it follows that the smallest number of parts by weight in which hydrogen is found per mole of compound is 1.0073, for oxygen 16.000, nitrogen 14.006, and chlorine 35.463, and since there are no other compounds known which contain a smaller number of parts by weight of these elements per mole, these numbers are the combining weights of the elements. It will be noticed that in the cases given the combining weights are just half the molar weights of the elements, so that for these substances there are two combining weights per mole of the

elements. One must not jump to the conclusion that there are always two combining weights per mole of an element, for in a number of cases there is only one per mole, and in others more than two.

We can now state the law of combining weights: *To each gaseous element a number can be assigned, called its combining weight, which has the property that the proportions by weight in which the element enters into combination with other elements can be represented by this number or some rational multiple of it. This combining weight is simply related to the molar weight of the element and is so chosen that it is the smallest number of parts by weight of the element found per mole of any of its compounds.*

This law need not be confined to elements gaseous at ordinary temperatures, since all solid or liquid elements may be converted into gaseous substances at high enough temperatures and low enough pressures, and under these conditions they follow the gas laws. We can then extend the law to all elements and put it in this form: *To each element a number can be assigned which has the property that the proportions by weight in which that element enters into combination with other elements can be represented by this number or by some rational multiple of it. This number is its combining weight and is so chosen that it is the smallest number of parts by weight of the element found per mole of any of its compounds.* To illustrate this, we may take the element carbon. This element is a solid, and it is exceedingly difficult to vaporize it, but a number of gaseous compounds are known; one of these is called carbon monoxide. Its molar weight is 28.00 corrected, and there are 16.00 parts by weight of oxygen and 12.00 parts of carbon per mole. No other compound of carbon is known which contains less than 12.00 parts by weight of carbon per mole, so this number is the combining weight of the element. In some cases, neither the element itself nor any of its compounds are gaseous, so that the determination of its molar weight is difficult. Under such conditions, the combining weight is figured from the proportions by weight in which the element will combine with 16 parts by weight of oxygen. In fact until recently when it became possible to correct the molar weights of gases for



the deviation from the gas laws, only approximate combining weights could be figured from the molar weights, and the more accurate ones were obtained by carefully determining the number of parts by weight of the elements which would combine with 16 parts by weight of oxygen, or with a combining weight of some other element whose combining weight was accurately known. This number was either the combining weight or so simply related to it that it could easily be obtained from the approximate molar weights. That is, it would be the combining weight or twice it, or half of it, or some other simple fraction of the combining weight. There are several principles in addition to the one based on the molar weights which govern the choice of combining weight into which we cannot go until a later point, but given these and the proportions in which the substance will combine with oxygen, it is not difficult to decide upon the combining weight. With our present knowledge of some of the gases, many of the combining weights can be as accurately determined from the molar weights as by analysis.

**Standards of Combining Weights.**—It doubtless seems strange that the combining weight of hydrogen is so near 1, and yet is not 1, while oxygen has a combining weight of exactly 16. There is a good deal of history back of this. In the early days, hydrogen was taken as having a combining weight of 1, since it was the element which combined with other elements in the smallest proportions by weight. Quantitative methods were not very well worked out in those days, and according to their best experiments, if the combining weight of hydrogen was 1, that of oxygen was 16. Since hydrogen will not combine with very many elements to make stable compounds, most of the combining weights of the elements were obtained from the proportions in which they combined with oxygen, taking the latter as 16. Later experiments showed that if the combining weight of hydrogen is 1, that of oxygen is not 16, but is something less than this. It then became necessary to change all the combining weights which had been referred to oxygen. The ratio of the weight of hydrogen to that of oxygen has been carefully determined a great many times by a large number of men, and in most cases somewhat different results have been obtained. So long as we stuck to the standard hydrogen=1,

every time this ratio was redetermined, practically all the combining weights had to be changed, because they really referred to oxygen; and if this was changed, they were altered to correspond. Finally we grew tired of this, and decided to take oxygen as the standard, since most things were referred to it anyway, and say that oxygen has a combining weight of 16, and let hydrogen do the varying. Now, when a new determination shows that the old ratio is in error, all that we do is to change the combining weight of hydrogen and leave all the others untouched. Since on any basis there are two combining weights of oxygen per mole, it follows that the molar weight of oxygen is 32, and nothing is more natural than to take this for the standard for molar weights, as has been done: We have here then the reason, which was promised you, for that apparently arbitrary number 32 which was taken as the molar weight of oxygen.

**Symbols and Formulæ.**—In order to save time and also for the sake of securing a convenient method for the representation of the composition of substances, a system of symbols has been devised which shall at the same time represent the elements and the combining weights of the elements, and which by combining the symbols of the elements shall represent the compounds and the molar weights of the compounds and their composition. This system was devised by the celebrated Swedish chemist Berzelius. The symbols for the elements are derived from the names of the elements using the Latin or Greek word where there is a difference in the name as we pass from language to language. In most cases the symbol is the first letter of the name, for example, the symbols of oxygen and hydrogen are O and H respectively. In case the names of more than one element begin with the same letter, the symbol of the element is formed from this initial letter and a characteristic letter from the name. Take for example chlorine with the symbol Cl. The first letter of the symbol is *always* a capital and the *second* is *always* a small letter. In addition to representing the element one of these symbols also stands for a combining weight of the element, and so represents a certain number of parts by weight of the element. O stands for oxygen, and 16 parts by weight of the oxygen; H for hydrogen, and 1.0073

parts by weight of hydrogen; Cl stands for chlorine, and 35.46 parts by weight of chlorine.

Hydrogen and chlorine combine to form hydrogen chloride in the proportions of 1.0073 parts by weight of hydrogen to 35.46 parts by weight of chlorine, or of one combining weight of the one element to one of the other. This is the composition of hydrogen chloride and both hydrogen chloride and its composition can be represented by writing the symbol of the elements close together, viz., HCl. This stands first for hydrogen chloride, second for a mole of hydrogen chloride, that is, 36.47 parts by weight of the substance, third it shows that a mole of hydrogen chloride is formed by the combination of one combining weight of each of the elements, or of 1.0073 parts by weight of hydrogen to 35.46 of chlorine. The sum of these combining weights gives the molar weight or the parts by weight of the hydrogen chloride represented by the formula HCl.

Water is formed by the union of 2.0146 parts by weight of hydrogen with 16.000 of oxygen to form 18.0146 parts by weight of water. The 2.0146 parts by weight of hydrogen is two combining weights of this element, while the 16 is of course only one combining weight of oxygen. To represent the composition of water, then we must build up a formula which shall stand for two combining weights of hydrogen and one of oxygen. We might write it HHO or HOH, and it is sometimes written the latter way. The almost universal method of writing it though is  $H_2O$ . The subscript figure 2 being used to show the number of combining weights of hydrogen per mole, the O or any symbol used without the subscript being understood to represent one combining weight of the element. The formula  $H_2O$  then stands for water, 18.0146 parts by weight of water, or a mole of water, and shows that two combining weights of hydrogen unite with one combining weight of oxygen to form a mole of water.

Great care must be taken by the student to avoid getting the notion that the subscripts represent the proportions by volume in which the elements combine. It so happens in the instances cited above that this is the case, but it is by no means always true, and one should never permit himself to think of it in this way.

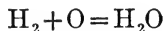
As an exercise the student should write the formulas for the rest of the compounds with which we have been dealing in this chapter up to this point, and also write out in words just what each represents.

The following table gives the latest values for the combining  
COMBINING OR ATOMIC WEIGHTS, 1912

	Symbol	Combining weight		Symbol	Combining weight
Aluminum.....	Al	27.1	Molybdenum.....	Mo	96.0
Antimony.....	Sb	120.2	Neodymium.....	Nd	144.3
Argon.....	A	39.88	Neon.....	Ne	20.2
Arsenic.....	As	74.96	Nickel.....	Ni	58.68
Barium.....	Ba	137.37	Niton (radium emanation).	Nt	222.4
Bismuth.....	Bi	208.0	Nitrogen.....	N	14.01
Boron.....	B	11.0	Osmium.....	Os	190.9
Bromine.....	Br	79.92	Oxygen.....	O	16.00
Cadmium.....	Cd	112.40	Palladium.....	Pd	106.7
Calcium.....	Ca	40.07	Phosphorus.....	P	31.04
Carbon.....	C	12.00	Platinum.....	Pt	195.2
Cerium.....	Ce	140.25	Potassium.....	K	39.10
Cesium.....	Cs	132.81	Praseodymium.....	Pr	140.6
Chlorine.....	Cl	35.46	Radium.....	Ra	226.4
Chromium.....	Cr	52.0	Rhodium.....	Rh	102.9
Cobalt.....	Co	58.97	Rubidium.....	Rb	85.45
Columbium.....	Cb	93.5	Ruthenium.....	Ru	101.7
Copper.....	Cu	63.57	Samarium.....	Sa	150.4
Dysprosium.....	Dy	162.5	Scandium.....	Sc	44.1
Erbium.....	Er	167.7	Selenium.....	Se	79.2
Europium.....	Eu	152.0	Silicon.....	Si	28.3
Fluorine.....	F	19.0	Silver.....	Ag	107.88
Gadolinium.....	Gd	157.3	Sodium.....	Na	23.00
Gallium.....	Ga	69.9	Strontium.....	Sr	87.63
Germanium.....	Ge	72.5	Sulfur.....	S	32.07
Glucinum.....	Gl	9.1	Tantalum.....	Ta	181.5
Gold.....	Au	197.2	Tellurium.....	Te	127.5
Helium.....	He	3.99	Terbium.....	Tb	159.2
Hydrogen.....	H	1.008	Thallium.....	Tl	204.0
Indium.....	In	114.8	Thorium.....	Th	232.4
Iodine.....	I	126.92	Thulium.....	Tm	168.5
Iridium.....	Ir	193.1	Tin.....	Sn	119.0
Iron.....	Fe	55.84	Titanium.....	Ti	48.1
Krypton.....	Kr	82.92	Tungsten.....	W	184.0
Lanthanum.....	La	139.0	Uranium.....	U	238.5
Lead.....	Pb	207.10	Vanadium.....	V	51.0
Lithium.....	Li	6.94	Xenon.....	Xe	130.2
Lutecium.....	Lu	174.0	Ytterbium.....	Yb	172.0
Magnesium.....	Mg	24.32	Yttrium.....	Yt	89.0
Manganese.....	Mn	54.93	Zinc.....	Zn	65.37
Mercury.....	Hg	200.6	Zirconium.....	Zr	90.6

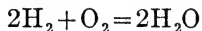
weights of the elements. These are the mean values for all the determinations made up to the beginning of the year 1912. You will notice that they differ only slightly from those we have worked out from the gaseous densities.

**Chemical Equations.**—As we said above, two combining weights of hydrogen unite with one of oxygen to form a mole of water; this can be very well shown with the aid of symbols as follows,



and this is an example of a chemical equation. A chemical equation is a very simple shorthand method for representing chemical reactions quantitatively. For example the above equation shows that 2.016 parts by weight of hydrogen will combine with 16 parts by weight of oxygen to form 18.016 parts by weight of water. The unit of weight may be the gram, pound or any other weight unit, and the equation will hold just the same.

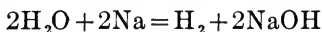
In the earlier part of this chapter, we learned that two volumes of hydrogen will combine with one volume of oxygen to form two volumes of water vapor, or two moles of hydrogen and one mole of oxygen will give two moles of water vapor. In representing this we shall have to use the molar formulas for everything. Now the molar weights of hydrogen and of oxygen are twice their combining weights, so their molar formulas are  $\text{H}_2$  and  $\text{O}_2$  respectively. We may show that two moles of hydrogen combine with one of oxygen thus,



This is read "two moles of hydrogen combine with one mole of oxygen to give two moles of water vapor." The coefficients or numbers before the symbols show the number of moles taking part in the reaction, while the subscripts show the number of combining weights of that element per mole. The coefficients therefore multiply every symbol in the formula which they stand before, as for example,  $2\text{H}_2\text{O}$  represents 2 moles of water or  $2 \times 2$  combining weights of hydrogen and  $2 \times 1$  combining weights of oxygen. On either side of the above equation there are represented then, four combining weights of hydrogen and

two of oxygen. This is the test to see that the equation is properly "balanced." There are two main principles involved in writing these equations. First, the formulas separated by + should be molar formulas, and second, there must be the same number of combining weights of any given element on either side of the equation, since otherwise we would be indicating a deviation from the law of the conservation of weight. The advantage of writing molar formulas lies in the fact that since gram moles of gases occupy the same volumes under like conditions we can tell at once their proportion by volume, from a simple inspection of the number of moles of the one that reacts with the other. The proportion by volume in which gases react are given by the coefficients in the molar equation for the reaction.

When one of these equations is first worked out, it must be found by experiment just what things are formed by the substances which react and the proportions by weight of everything involved in the process. There is no other way of doing it. We must know what is brought together and what is formed before we can represent it by symbols. Students often think that they failed to grasp the idea of equations because they cannot write down symbols and formulas for a number of substances on one side of the equation and then tell by some rule what to put on the other, or else they jump to the other extreme and think that the symbols can be combined in any way at the fancy of the writer. But the truth of the matter is that only certain substances are formed from certain other ones, and one must know what these are and then represent them. Every equation then represents the results of actual experiment. It will be recalled that water and sodium react and form sodium hydroxide and hydrogen. The sodium hydroxide contains per mole 23 parts by weight of sodium, 16 of oxygen, and 1.008 of hydrogen. Its formula then is NaOH and the molar weight is a little over 40. We find by experiment that when 36.032 grm. of water react on 46 grm. of sodium that 2.016 grm. of hydrogen and 80.016 grm. of sodium hydroxide are formed. We may represent this by the following equation,



In studying the properties of substances it is very essential to learn with what other substances they will react and the substances formed. It is not necessary to learn in what proportions they react as, given the other information, the proportions can be reasoned out from the rules for balancing which were given above.

Knowing the substances and their weights we can write the equation, or given the equation we can work out the weights from the combining weights.

**Atomic Theory.**—We seem to feel instinctively that there is a cause for everything, and if of an inquiring turn of mind try to discover this cause. We ask, why is sulfur yellow? For an answer we can say that it is yellow because it absorbs violet light. But why does it absorb violet light. No *real* explanation for this can be offered. The only answer is: because it does. And even if we could give some reason it would be of the form of because it does something or other, and we should be just as puzzled by the question, but why does it do that? So there is no such thing as a real explanation of what are called phenomena. What are called explanations in science are nothing more than somewhat elaborate descriptions of the phenomena illustrated by mental pictures intended to point out resemblances of the phenomena described, to things which are more familiar to us. At the present day people in general are quite familiar with mechanical things, so that most of these scientific pictures are mechanical. They often really are working models which upon turning the crank will perform in a way similar to the phenomena which they represent. These scientific pictures are hypotheses, and are intended as an aid to the representation of facts and in the sense given above to serve as an explanation for the facts. Because of our mechanical tendencies, it often happens that we have mechanical hypotheses concerning things which are in all probability not mechanical.

Many people feel that the simple relationship described by the laws of the definiteness of properties, of definite proportions, of the conservation of the elements, of combining weights, and also by the law of multiple proportions, which will be discussed in the next chapter, call for some kind of an "explanation." A possible "explanation" is furnished by a picture devised more

than one hundred years ago by Dalton. This is known as the **Atomic Hypothesis**, or as it is often called the **Atomic Theory**. This theory makes a rather large number of assumptions and then goes ahead to show that if things were as it is assumed they are, and if they worked as it is thought that they work, the results would be as we observe them.

The **assumptions** are that all substances are composed of very small particles called *atoms*, that the atoms of each elementary substance are alike among themselves, and are different from those of other elements, that chemical compounds are built up by the union of the atoms of the elements of which they are composed in such a way that the smallest particles of a compound are identical in the number and kind of atoms which they contain. It is further assumed that the atoms of any given element preserve their identity in passing from compound to compound. These assumptions furnish easy explanation for the laws of chemical combination. If they did not it would merely be necessary to make other and farther assumptions until they did. The assumed identity of the atoms or groups of atoms going to make up a substance "explains" the law of definiteness of properties and of proportions. The assumption that the atoms of an element are different from those of the others gives a reason for the observation that one element is not changed into another in our ordinary chemical transformations. Evidence is accumulating that in the radio-active transformations of radium and kindred substances some of the elements are really changed into other elements, so we may soon have to make new assumptions. The assumption that the atoms of the elements preserve their identity in passing from compound to compound "explains" the law of the conservation of the elements. In terms of this atomic hypothesis the combining weights become the relative weights of the atoms of the elements, that is to say, it is assumed that the weights of the atoms of hydrogen, oxygen, chlorine, etc., stand to each other as 1.008 :16 :35.46 . . . , and the combining weights then become identical with the atomic weights.

The proportion by weight in which the elements enter into combination with each other are supposed to be determined by



the number and weights of the atoms going to make up the smallest particle of the compound.

This theory then fits the facts described in the above mentioned laws very well indeed, as of course it should, since the facts were well known and the theory built to fit them.

**The Relation Between Fact and Theory.**—The facts upon which the atomic theory is built are the results of experiment and observation. They are *true*. The theory is a speculation and is not a statement of anything found by experiment. About the strongest statement we can safely make in its favor is that it may be true. However, it is a good representation of the facts, and has been of great value in suggesting methods of work, and has contributed largely to the advance of chemistry. Any theory that will do such things is of value even if it should finally prove to be false. The history of science shows a great pile of discarded theories, each of which was good in its day. Each represented facts, predicted new facts, and so led to their discovery, and each in turn proved to be false and had to be discarded. There can be but little question but that this will be the ultimate fate of most if not all of our present theories. This need cause us no uneasiness were it not for the fact that no matter how useful a false theory may be at first it finally becomes a serious drag to science, through causing facts to be misunderstood or even ignored. There is no way of telling but that this will some day be the case with the atomic theory.

The way to use a theory is to keep constantly in mind that it is not a fact and possibly is not true, but to follow up all the lines of investigation which it suggests, always being ready to find that the facts do not agree with the theory. In particular, one should never hesitate to try a thing which upon other grounds promises success simply because a theory predicts failure.

**Molecular Theory.**—The molecular theory has been built up as an explanation for a number of facts the chief of which is described by Gay Lussac's law of combining volumes. Like the atomic theory it is not an experimental fact, but simply an imagined cause. Some of the assumptions involved are as follows: that there are smallest particles of substances which can exist by themselves. These smallest particles are called mole-

cules. These imagined molecules are assumed to be made up of one or more atoms, and even in the case of most elements it is assumed that there are more than one atom per molecule. The molecules of the compounds are of course assumed to be made up of the atoms of the elements forming the compound. The molar weight of a substance bears the same relationship to the molecule that the combining weight bears to the atom, that is, it is the relative weight of the molecule, and is often called the molecular weight. A further very important assumption is made, that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. This is called *Avogadro's hypothesis*, and furnishes a very easily understood picture for the fact that a gram mole of every gas under standard conditions occupies 22,400 c.c. since it follows from the conception of molecular weight that there shall be the same number of molecules per gram mole of different substances. The explanation of Gay Lussac's law of combining volumes in terms of this hypothesis, and the molecular theory is almost self-evident, and will be left to the student.

## CHAPTER VII

### HYDROGEN PEROXIDE

Hydrogen and oxygen will combine in the ratio of one part by weight of hydrogen to 7.943 parts by weight of oxygen, and in no other ratio when they unite to form water. However, they will combine in a different proportion for the formation of an entirely distinct substance known as hydrogen peroxide. The ratio in this case is one part by weight of hydrogen to 15,886 parts by weight of oxygen. If we now compare the parts by weight of the oxygen in the two compounds which will combine with one part of hydrogen we see that they stand to each other as 1 : 2

$$7.943 : 15.886 = 1 : 2$$

This is the first time that we have found a really simple weight relationship and this you will notice is the ratio between the weights of the one element which will combine with unit weight of the other element in the two compounds. This sort of a simple weight relation has been found to be so common that a law has been formulated to describe it.

**The Law of Multiple Proportions.**—*If two or more elements combine to form more than one compound, the masses of the one which combine with unit mass of the other in each of the several compounds, stand to one another in the ratio of small whole numbers.*

Hydrogen and oxygen always combine in one fixed ratio for the formation of water, and in another equally fixed for the formation of hydrogen peroxide, so the law of definite proportions describes the composition of each of these compounds and the law of multiple proportions applies to the two taken together.

**Preparation and Properties of Hydrogen Peroxide.**—Hydrogen peroxide is prepared in a number of ways, but the greater part of that used is made by the action of dilute sulfuric acid upon hydrated barium peroxide, barium sulfate being formed at the same time. It is not practical to prepare it directly from the elements although minute quantities are formed by allowing the

flame of an oxy-hydrogen blowpipe to play upon ice. The hydrogen peroxide prepared by the interaction of barium peroxide and sulfuric acid is present in a dilute solution with water. To prepare pure hydrogen peroxide is not easy, but the method usually adopted depends upon the fact that hydrogen peroxide is less volatile than water, so that if a mixture of the two be distilled, relatively more of the water than of the hydrogen peroxide will pass off, and the residue will contain more and more hydrogen peroxide per cubic centimeter. By repeating the process, practically pure hydrogen peroxide may be obtained. Hydrogen peroxide is rather unstable and decomposes into water and oxygen. This reaction like nearly all others goes more rapidly at high temperatures than at lower ones, therefore the process of distillation is carried out under diminished pressure because this lowers the boiling-point.

Hydrogen peroxide is a rather thick, syrupy liquid which has a very faint greenish-blue color somewhat more intense than that of water. Its density at 0° C. is 1.4584. It melts at -2° and boils at 69° under a pressure of 2.6 cm. of mercury. Its boiling-point under atmospheric pressure is not known as it decomposes with explosion before it boils. It is odorless and has an astringent bitter taste. It is soluble in water in all proportions and the solution looks like water. This solution slowly decomposes into water and oxygen and keeps best in the dark, in a cool place, and when it contains a little acid. This transformation seems especially sensitive to the presence of foreign substances which after the completion of the process are found unchanged. These substances are therefore catalyzers. The following is a partial list of the catalyzers of hydrogen peroxide; charcoal, silver, gold, platinum, manganese dioxide, potassium and sodium hydroxides, saliva, and blood. The solid substances mentioned act the more vigorously the more finely powdered they are. In fact, it seems that any fine powder will hasten the decomposition of hydrogen peroxide. But since there is often a very great difference in the rate of decomposition in the presence of different substances of equal fineness of division, it is evident that there is a specific catalytic effect due to the nature of the substances.

A 3 per cent. solution is a standard article of commerce. It is often called a 10 volume solution from the fact that it will

evolve, when all the hydrogen peroxide is decomposed, about ten times its volume of oxygen. This solution will rapidly destroy bacteria, and hence is much used as a disinfectant.

**Oxidizing Action of Hydrogen Peroxide.**—Since hydrogen peroxide gives up part of its oxygen so easily that it will do it even at ordinary temperatures, it seems very natural to expect that it will be able to give it up to other things which can combine with oxygen and thus oxidize them. Upon trial this is found to be the case, and this action is exhibited the more strongly, the more concentrated the hydrogen peroxide; that is, the greater the weight of this substance per cubic centimeter. If the pure hydrogen peroxide be brought in contact with many inflammable substances, the latter are oxidized so rapidly that they ignite spontaneously. The solutions are much less intense in their action and decrease in activity as the dilution is increased.

Substances which will give up oxygen to other substances in the way that hydrogen peroxide does are called oxidizing agents. As we shall see later, oxidizing agents can do many things besides give up oxygen to other substances, but this is one of the things which they may do, and must be kept in mind until finally we come to a definition of an oxidizing agent which will cover all cases. Other oxidizing agents are like hydrogen peroxide, in that they act more vigorously as their concentration increases. Oxygen itself is an oxidizing agent, and like the others it is more active the higher the concentration. The higher the pressure, the greater its concentration and oxidizing power. So the pressure of the oxygen is a measure of the oxidizing power of the gas. Hydrogen peroxide is able to oxidize many things which oxygen under atmospheric pressure cannot do. Therefore, the pressure of oxygen must be increased to equal it. Because of its action as an oxidizing agent, hydrogen peroxide is able to change many organic coloring matters into colorless substances, and it is therefore used for bleaching hair, feathers, ivory, silk, wool, bones, leather, etc. For this purpose fairly dilute solutions are used.

**Reducing Action of Hydrogen Peroxide.**—When hydrogen peroxide acts upon many oxides such as those of silver, gold and mercury, the metals, water and *oxygen* are produced. The oxides are unquestionably reduced and to this extent hydrogen

peroxide acts as a reducing agent; but it differs from what are generally regarded as reducing agents in that elementary oxygen is evolved, while when ordinary reducing agents act upon oxides, the oxygen of the latter enters into combination with the reducing agent. Potassium permanganate is also reduced by hydrogen peroxide and in this case again oxygen is evolved.

**Composition and Formula of Hydrogen Peroxide.**—Before the formula of any compound can be worked out the substance must be analyzed or synthesized and its molar weight determined. From the data the formula is then made up in a way which may be well illustrated by hydrogen peroxide.

The analysis of hydrogen peroxide shows that it consists of 5.93 per cent. hydrogen and 94.07 per cent. oxygen. The next step is to calculate the relative number of combining weights of the elements. To do this, we divide the percentage of each element by the combining weight of the element. This will give the number of combining weights of each element per hundred parts by weight of the compound. Applying this to hydrogen peroxide we get the following results:

$$\frac{5.93}{1.008} = 5.88$$

$$\frac{94.07}{16.0} = 5.88$$

From this it is easily seen that there are the same number of combining weights of each element per mole of the compound, and that the formula must be  $\text{HO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_3\text{O}_3$  or  $\text{H}_n\text{O}_n$ , where  $n$  is some whole number.

It is impossible to decide between these formulas without a molar weight determination, but it is very easy after this has been made. The molar weight of hydrogen peroxide is about 34, and therefore the formula must be  $\text{H}_2\text{O}_2$ , representing a molar weight of 34.016, because the formula  $\text{HO}$  corresponds to a molar weight of 17.008, while  $\text{H}_3\text{O}_3$  represents a molar weight of 51.024.

**Determination of the Molar Weight of Hydrogen Peroxide.**—Hydrogen peroxide is so unstable that it is not possible to determine its molar weight from its gaseous density, but recourse must be had to an entirely different method called the "Freezing-point Method."

It will be recalled that mention has been made of the fact that any dissolved substance will lower the freezing-point of water, and also that gram moles of the various substances were such quantities of the different things as would produce equal physical effects. Experiment has shown that if a gram mole of substance be dissolved in 1000 grm. of water, the freezing-point of the water is lowered 1.85° C. This then furnishes a ready method for the determination of the molar weight of such substances as hydrogen peroxide which cannot be vaporized without decomposition. The molar weight of a substance, with a few exceptions, is identical with the number of grams of the substance required to lower the freezing-point of 1000 grm. of water 1.85° C.

The lowering of the freezing-point "L" is proportional to the number of gram moles of solute, which in turn is equal to the weight of the solute "w," divided by the molar weight "M," or

$$L = K \frac{w}{M}$$

and the lowering of the freezing-point is also inversely proportional to the mass of the solvent, "W" or,

$$L = \frac{K'}{W}$$

and therefore

$$L = \frac{K''w}{MW}$$

or

$$M = \frac{K''w}{LW} = 1850 \frac{w}{LW}$$

in which "M" represents the molar weight of the solute, "w" the weight of the solute, "W" the weight of the solvent, "L" the lowering of the freezing-point, and 1850 is the numerical value of "K" when w and W are measured in grams and L in degrees Centigrade.

The molar weight of hydrogen peroxide determined in this way comes out a little over 34, showing that the formula is H<sub>2</sub>O<sub>2</sub>.

Under the discussion of water it was pointed out that solutes lowered the vapor pressure of their solvents and that there was a connection between this fact and the fact that the solutions

froze at lower and boiled at higher temperature than their pure solvents. From these facts, one would be led to expect that there would be a constant rise in the boiling-point of water per gram mole of solute per 1000 grm. of water, because gram moles are in the main, physically equivalent. This is found to be the case. One gram mole of most substances will raise the boiling-point of 1000 grm. of water .52° C., and a method for the determination of molar weights is based upon this. The formula is

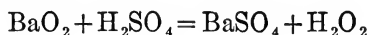
$$M = \frac{520 w}{rW}$$

in which M, w, and W have the same significance as before, and "r" is the rise in the boiling-point, and 520 the proportionality constant.

Of course all other solvents are affected as water is, that is to say, their freezing-points are lowered and their boiling-points raised by solutes, and molar weights may be determined from these changes as well as from the corresponding changes for water. The formulas used are the same except for the constants 1850 and 520 which are different as one passes from solvent to solvent.

As has been implied above, there are some exceptions to the rule that a gram mole will lower the freezing-point of 1000 grm. of water 1.85° C. We will find later that these exceptions lead to very interesting and important conclusions. All these exceptional substances yield solutions which are conductors of electricity. Hydrogen peroxide in solution is a non-conductor, so we may feel confident that the molar weight given above is correct.

**Equation for the Preparation of Hydrogen Peroxide.**—As has been already mentioned, hydrogen peroxide may be prepared by the action of dilute sulfuric acid upon barium peroxide, barium sulfate being formed at the same time. The equation for the reaction is as follows:



in which BaO<sub>2</sub> stands for 169.37 parts by weight of barium peroxide, H<sub>2</sub>SO<sub>4</sub> for 98.086 parts by weight of sulfuric acid, BaSO<sub>4</sub>



for 233.44 parts by weight of barium sulfate, and  $H_2O_2$  for 34.016 parts by weight of hydrogen peroxide.

**Explosive Properties of Hydrogen Peroxide.**—Pure or nearly pure hydrogen peroxide is decidedly explosive. The explanation for this is that the peroxide passes into water and oxygen with the evolution of a great amount of heat, so that if decomposition gets started, the heat evolved raises the temperature of the remaining peroxide and this makes it break up more rapidly, evolving still more heat and raising the temperature yet higher, thus making it decompose even faster until the reaction takes place so violently that it is explosive. All other explosives are like hydrogen peroxide in that they give off heat during their transformation, and in fact they owe their explosiveness to this property.

Explosives are rather unusual substances because most things decompose with the absorption of heat, and hence if they once get started to splitting up they cool themselves off and so tend to stop the transformation. So pronounced is the heat of decomposition of hydrogen peroxide that even the dilute solution of commerce will experience a rise in temperature of  $15^\circ$  to  $20^\circ$  C. upon the addition of manganese dioxide which will catalytically bring about a rapid destruction of the peroxide.

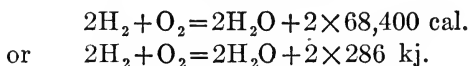
**Thermochemistry.**—Practically every chemical change is accompanied by either the absorption or evolution of heat. These heat effects are of importance because, if the conditions are made such that no work is done, they represent the difference in energy between the substance before and after the reaction. These differences in energy are of vital importance to us because it is really the difference in energy between the coal and oxygen on the one hand and the products of combustion on the other which drives the steam engine, cooks our food, and keeps us warm.

These heat effects are measured in very much the same way as the heat of fusion of ice or the heat of evaporation of water, and are expressed in calories or kilojoules per gram, or better still per gram mole of substance transformed.

By a very slight addition to our scheme for representing chemical reactions we can indicate at the same time the chemical and energy changes. In doing this the chemical formulas stand

for gram moles of the various substances, and at the end of the equation is written the number of kilojoules "Kj" or calories evolved or absorbed, evolution being indicated by a plus (+) sign and absorption by a minus (-).

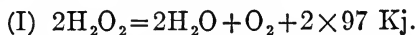
To illustrate this, let us consider the heat effect accompanying the burning of hydrogen to form water. For every gram mole of water produced 68,400 calories or 286 kilojoules of heat are evolved. This is represented as follows:



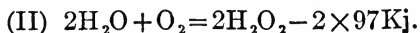
The heat effect accompanying the formation of a gram mole of a substance is called its **heat of formation**, so the heat of formation of water is 286 Kj. or 68,400 cal. per mole.

There are two points in connection with thermochemical equations such as those just given, which must be carefully kept in mind. The first one is—that if a certain quantity of heat is evolved during the formation of a gram mole of a substance, precisely the same quantity of heat will be taken up during its decomposition. The second is that the heat effect accompanying a given transformation depends only upon the initial and final states of the substances and not at all upon the intermediate stages through which they pass.

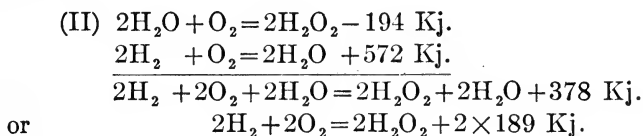
**The Heat of Formation of Hydrogen Peroxide.**—Since hydrogen and oxygen combine with such difficulty to produce hydrogen peroxide it is not possible to determine the heat of formation of this substance by direct measurement. This magnitude may, however, be calculated by taking advantage of the facts pointed out above. Hydrogen peroxide spontaneously decomposes into water and oxygen, and the heat effect belonging with this change may be easily measured. It is 97 Kj. or 23,100 cal. per mole of peroxide transformed. The equation is



From what has been said above and the law of the conservation of energy, it follows that if oxygen and water should unite for the formation of hydrogen peroxide that 97 Kj. of heat would be absorbed for each gram mole of peroxide formed, the equation being



The heat of formation of the peroxide from oxygen and water therefore is  $-97$  Kj. To obtain the heat of formation from the elements, all that is necessary is to add to the above number the heat of formation of the water. In fact these thermochemical equations may be handled like ordinary algebraical equations. To equation (II) may be added the equation for the formation of water and the result will be the equation for the formation of the peroxide from its elements.



So the heat of formation of hydrogen peroxide is  $189$  Kj. or  $45,300$  cal. per gram mole. Of course the thermochemical equations expressed in cal. may be substituted for those in Kj. and the figure  $45,300$  will then be obtained directly.

The method applied here is a general one for calculating the heat effects which cannot be directly measured.

## CHAPTER VIII

### CHLORINE

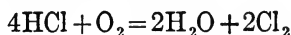
The third element which we will discuss is chlorine. This element does not occur free in nature but is found in very large quantities in compounds, such as sodium, potassium, and magnesium chlorides. The element itself and many of its compounds are of very great importance not only in the chemical industries, but also in every day life. The sodium chloride, for example, is our common salt, and we all know how indispensable this is. This common salt or sodium chloride is found in enormous quantities in beds of rock salt at many places on the earth's surface and is present in still larger quantities in the ocean. It has been estimated that the ocean contains, in solution, salts, principally sodium chloride, which if they could be obtained in a solid state would have a volume of 4,800,000 cubic miles, and something like 60 per cent. of this by weight would be chlorine. So it is very evident that this element is abundant.

Chlorine was first prepared by Scheele in 1774, but that it was an element was first shown by Sir Humphrey Davy in 1810.

**Preparation of the Element.**—There are a few chlorides, such as those of gold and platinum, which will decompose into chlorine and the metals upon being raised to a high temperature, but these chlorides are so expensive and difficult to make that chlorine is practically never prepared in this way. The preparation of chlorine then resembles that of hydrogen more nearly than that of oxygen in that a compound of chlorine is treated with some substance which will convert the rest of the chlorine compound into a substance which will readily take on a different physical state from that of the gaseous chlorine and hence may be easily separated from this element. Chlorine may also be prepared by electrolysis of solutions of soluble chlorides very much as hydrogen and oxygen may be prepared. In the case of the electrolysis of the chlorides, chlorine is given off at one electrode,

and either hydrogen or the metal of the chloride is deposited at the other.

The most suitable substance for the chemical preparation of chlorine seems to be hydrochloric acid, a compound of chlorine and hydrogen whose formula is  $\text{HCl}$ . This substance may be easily prepared by treating common salt with sulfuric acid and gently heating. Under these conditions gaseous hydrogen chloride comes off which is very soluble in water, the solution being known as hydrochloric acid. Solid sodium sulfate is formed at the same time, but remains behind in the reaction vessel. The details of this process will be given later. From this hydrogen chloride or hydrochloric acid, we can easily prepare chlorine by converting the hydrogen into water. This may be done in several ways. Gaseous hydrogen chloride mixed with oxygen or air may be passed through a tube containing clay balls or pieces of pumice stone coated with copper chloride or sulfate, heated to  $370^\circ$  to  $400^\circ$  C. Under these conditions water and chlorine are produced according to the equation,



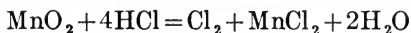
The copper salt acts as a catalyser.

When air is used the product is of course greatly contaminated with nitrogen as well as unchanged hydrogen chloride and oxygen, so that the method is not suitable for laboratory purposes, but has been largely used for the commercial preparation of chlorine, and is known as the Deacon Process.

**Other Methods.**—The preparation of chlorine from hydrogen chloride belongs to the processes which we call oxidation, and oxygen here is the oxidizing agent. Other oxidizing agents, if sufficiently powerful, may be used in the place of oxygen. Among those which are convenient may be mentioned manganese dioxide,  $\text{MnO}_2$ , potassium chlorate,  $\text{KClO}_3$ , potassium permanganate,  $\text{KMnO}_4$ , and bleaching powder,  $\text{CaCl}_2\text{O}$ . Each of these substances treated with hydrochloric acid will oxidize the latter to water and chlorine.

A very commonly used laboratory method for the preparation of chlorine is to gently heat a mixture of manganese dioxide with four times its weight of commercial hydrochloric acid (Fig. 17). The liquid first turns brown and then gives off greenish-

yellow gaseous chlorine. After the reaction is finished, the solution contains manganous chloride,  $\text{MnCl}_2$ . The equation is



It seems to be very probable that the reaction goes in two stages, first forming water and manganese tetrachloride,  $\text{MnCl}_4$ , which is dark colored, and then this tetrachloride decomposes into

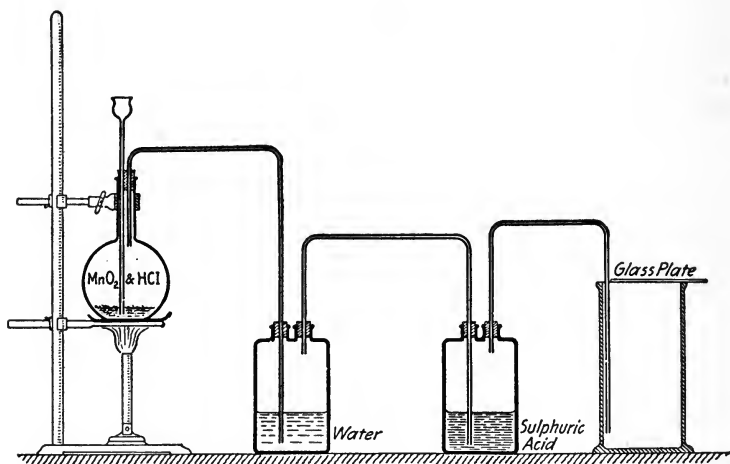
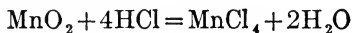


FIG. 17.

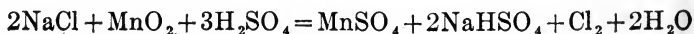
the lighter colored manganous chloride,  $\text{MnCl}_2$ , and chlorine,  $\text{Cl}_2$ . The equations representing this would be



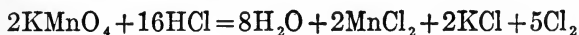
and



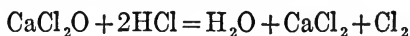
Instead of starting with hydrochloric acid and manganese dioxide one may form the hydrochloric acid from salt and sulphuric acid and oxidize it with manganese dioxide right in the same vessel. To do this one warms a mixture of commercial salt and manganese dioxide with moderately dilute sulphuric acid. The chlorine comes off very regularly, and at a convenient rate, so that this modification of the first method is often used. The equation is



Perhaps the most convenient laboratory method for the preparation of chlorine is to allow hydrochloric acid to fall drop by drop upon solid potassium permanganate,  $\text{KMnO}_4$ . The action takes place promptly and at ordinary temperatures. Water, manganous chloride, potassium chloride, and chlorine are the products. The equation is



A very important method which is much used both in the laboratory and technically is to treat bleaching powder,  $\text{CaCl}_2\text{O}$ , with hydrochloric acid. Water, calcium chloride,  $\text{CaCl}_2$ , and chlorine are the products. The equation is



It should be noted that in each of the above cases liquid water, a non-volatile salt or salts, and gaseous chlorine are formed. This difference of state makes it easy to isolate the chlorine.

**Technical Preparation.**—Each of the above-mentioned methods for the preparation of chlorine, together with many others, has been used on a manufacturing scale, but at the present time the greater part of the chlorine of commerce is produced by the electrolysis of solutions of sodium or potassium chloride. The anode or positive electrode where the chlorine appears is usually made of graphite because almost everything else is attacked by the chlorine. At the cathode or negative electrode hydrogen is given off and sodium or potassium hydroxide is formed in solution. The process takes place as though metallic sodium or potassium were liberated at the cathode and then at once reacted with the water for the formation of hydrogen and sodium or potassium hydroxide. That there is another way of looking at it will be pointed out later. The process is carried out chiefly for the preparation of the hydroxides, and the chlorine is rather a by-product, and since there is more demand for the hydroxides than for chlorine, the latter is comparatively cheap.

**Physical Properties.**—At ordinary temperatures chlorine is a greenish-yellow gaseous substance whose density is 0.0032215 and whose uncorrected molar weight is 72.13. Chlorine does not follow the gas laws very closely, a fact which is connected with the circumstance that it is very easily converted into a liquid

either by cooling it to  $-33.6^{\circ}$  C. under a pressure of one atmosphere, or by putting it under a pressure of 3.66 atmospheres at  $0^{\circ}$  C. or of 6.62 atmospheres at  $20^{\circ}$  C. The critical temperature is  $146^{\circ}$  and the critical pressure 94 atmospheres.

Liquid chlorine has a greenish-yellow color, a density of 1.56, and is of an oily consistency. At  $-102^{\circ}$  the liquid freezes to yellow crystals of solid chlorine.

After correcting for its deviations from the gas laws the molar weight of chlorine is found to be 70.92.

Gaseous chlorine is soluble in about half its volume of cold water but is much less soluble in hot. Because of its solubility in cold water and the fact that it attacks mercury with great vigor, chlorine must be collected over hot water or by displacement of air. The latter is the more convenient, and since chlorine is nearly 2.5 times as heavy as air, it is easily carried out.

Chlorine has a very disagreeable odor, is exceedingly irritating to the mucous membrane of the throat and nose and has often produced death.

**Chemical Properties.**—The combining weight of chlorine is 35.46 and its corrected molar weight is twice this, so there are two combining weights per mole and the molar formula is  $\text{Cl}_2$ . Chlorine is a rather more active element than oxygen and combines with almost all the other elements to form compounds called chlorides. In many cases the combination takes place with the production of light and heat, and closely resembles the combustion of substances in oxygen. So striking is the resemblance that we call the phenomena combustion in chlorine. In fact chlorine reacts so vigorously with a number of other substances that they will take fire spontaneously when introduced in the gas at ordinary temperatures. Among these may be mentioned thin copper foil, phosphorus, and powdered antimony. In each case a chloride is formed.

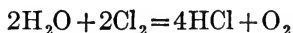
The greater intensity of action of chlorine over that of oxygen is due rather to a higher velocity of reaction than to a greater energy change as is shown by the fact that in general the heat of formation of a chloride is just about the same as the heat of formation of the corresponding oxide. When completely dry, chlorine is much less active than when moist, and carefully dried liquid chlorine is now an article of commerce, being sold



in strong steel cylinders lined with lead or bronze. One of the most important chemical properties of chlorine is that it is able to destroy many coloring substances, and it is therefore extensively used as a bleaching agent in the cotton and paper industries. It bleaches only in the presence of water, and is not able to destroy many of the mineral dyes nor black tints due to carbon in the form of lamp black. Chlorine makes all animal fibers brittle and therefore cannot be used to bleach wool or silk.

It is a very powerful disinfectant and is much used to destroy bacteria.

**Chlorine Water.**—As has been mentioned, chlorine is fairly soluble in water. The solution, which has the greenish-yellow color, the odor, taste, and bleaching qualities of the gas is called chlorine water. A portion of the gas undergoes a chemical change with the water, forming compounds which can best be discussed later. When exposed to sunlight, the chlorine disappears, oxygen is given off, and hydrochloric acid is left. The equation is



This reaction appears to be just the reverse of that taking place in the Deacon Process, but there is this difference that the Deacon Process takes place in the gaseous state, while this goes on in dilute solution; a circumstance which reverses the stability relationship.

The light acts in this case almost like a catalyzer for the action takes place slowly in the dark but much more rapidly in the light, and the more rapidly the stronger the light. The different kinds of light act quite differently; the red rays are almost without effect while the blue, violet and ultra-violet rays are especially active.

**Chlorine Hydrate and the Phase Law.**—When chlorine is passed into ice-cold water, there soon separates out a greenish crystalline substance which is a compound of water and chlorine having the formula  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  and is called chlorine hydrate. Chlorine hydrate is a rather unstable compound breaking down into chlorine and water. At each temperature there is a certain definite pressure of chlorine at which the compound

becomes stable. A few of these pressures are given in the following table:

0° C.	4° C.	8° C.	9° C.	9.6° C.	14° C.	28.7° C.
24.9 cm.	39.8 cm.	62.0 cm.	70.1 cm.	76.0 cm.	124.0 cm.	456.0 cm.

From this it can be seen that in an open vessel the substance cannot exist above 9.6° C. while under a pressure of 6 atmospheres it is stable up to 28.7° C. Above this temperature it melts and changes into water and chlorine no matter how great the pressure may be. The conditions of equilibrium in this case are strikingly like those for a pure liquid and its vapor, that is, for every temperature there is a definite equilibrium pressure, or in other words the system has one degree of freedom.

Let us recall for the moment the relation between the number of phases and the degrees of freedom as it was brought out in connection with the discussion of water. When a system composed of water, existed in only one phase—solid, liquid, or gaseous—it had two degrees of freedom, while if it contained two phases, liquid and solid or liquid and gaseous, or gaseous and solid, there was only one degree of freedom; and if it contained three phases, there were no degrees of freedom and the system could exist only at one certain temperature and pressure. From this we derived the rule that an increase of one in the number of phases is followed by a decrease of one in the degrees of freedom, and the sum of the degrees of freedom and the phases of a system of one pure substance is always three.

In the case of the system, chlorine and water, the system has one degree of freedom as shown above when there is present in equilibrium the three phases chlorine water, chlorine hydrate and gaseous chlorine. It has two degrees of freedom when any two of these are present and none when to the three phases mentioned above ice is added. The temperature at which these four phases can exist side by side in equilibrium is  $- .24^{\circ}$  C. and the pressure of the chlorine is 24 cm. These conditions are called the quadruple point of the system chlorine and water. In this case as with water, for each phase added to the system, the degrees of freedom decrease by one. There is this difference though, that the number of phases plus the degrees of freedom is always four instead of three.

There is this point to be noticed, however, that the system of water is composed of one substance, while the other system is made up of two substances, water and chlorine. If we compare the number of phases plus the degrees of freedom with the number of substances which must be brought together to form the system, we will find that this number of substances plus two is equal to the number of degrees of freedom plus the phases. This turns out to be the universal case so that we have what is known as the Phase Law of Gibbs, which is as follows: *When a system is in equilibrium the number of phases plus the degrees of freedom equals the number of the components of the system plus two.* In symbols this is

$$P + F = C + 2$$

in which "P" stands for the number of phases, "F" for the degrees of freedom, and "C" for the components. The components may be defined as the smallest number of substances of independent variable concentration which must be brought together to form the system. The Phase Law has many important applications as will be seen later.

Chlorine hydrate is now being prepared on a large scale as one of the steps in the process of manufacturing liquid chlorine from the impure gas obtained by the electrolysis of sodium or potassium chlorides. The chlorine is cooled to a low temperature and exposed to the action of a spray of cold water. The hydrate is formed and thus removes the greater part of the chlorine from the gaseous mixture. The hydrate decomposes at higher temperature into water and chlorine, the latter is dried and is then practically pure and is ready for liquefaction.

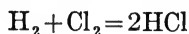
**The Naming of Chlorides.**—As has been mentioned, the compounds of other elements with chlorine are usually called chlorides, prefixing the name of the other element to form the name of the compound, as for example—sodium chloride, potassium chloride, etc. If, as is not infrequently the case, the same element will form more than one compound with chlorine, it becomes necessary to distinguish between these substances. Where there are only two of these compounds, they are commonly distinguished by adding to the name of the element other than the chlorine the terminations -ous and -ic. The -ous being used for the compound containing the smaller and the -ic for that containing the larger

amount of chlorine per combining weight of the other element. There are two chlorides of iron, the one  $\text{FeCl}_2$  is called ferrous chloride, and the other  $\text{FeCl}_3$  is called ferric chloride. Similarly we have mercurous chloride  $\text{HgCl}$  and mercuric chloride  $\text{HgCl}_2$ . In some cases, particularly where there are more than two compounds of an element with chlorine, the necessary distinction is made by prefixing to the chloride the Greek word signifying the number of combining weights of chlorine to a combining weight of the other element. For example we have phosphorus trichloride,  $\text{PCl}_3$  and phosphorus pentachloride,  $\text{PCl}_5$ .

**Hydrogen Chloride.**—Hydrogen chloride which we have already discussed somewhat in connection with the preparation of hydrogen and of chlorine is an exceedingly important compounds of chlorine. It may be formed by the direct combination of the two elements, which can be brought about in a number of ways most of which closely resemble those which will induce the combination of hydrogen and oxygen. For example, a stream of hydrogen will burn in an atmosphere of chlorine much as in air except that the color of the flame will be a peculiar green instead of the blue of the ordinary flame. A colorless gaseous compound is formed which fumes when brought in contact with the air and which is hydrogen chloride. It is much more readily soluble in water than chlorine, does not bleach as chlorine does, but turns blue litmus red. Its solution in water does not in any way resemble chlorine water, but is highly acid and is identical with hydrochloric acid, of which we have had much to say. It has an odor which is disagreeable, but entirely different from that of chlorine. It has a very sour taste, like all other acids, and in this respect also it differs materially from chlorine. In fact hydrogen chloride is unlike chlorine in color, odor, taste, solubility, action on colors, and in every other property, both physical and chemical.

Another method for bringing about the combination of hydrogen and chlorine is to mix the gases and pass an electric spark through a portion of the mixture. As was the case when this was done with a mixture of hydrogen and oxygen, the gases at once combine, with a violent explosion. If equal volumes of hydrogen and chlorine are used, both of the gases entirely disappear, and the volume of the hydrogen chloride produced is equal to the

sum of the volumes of the separate gases. This shows that the combination follows Gay Lussac's law of combining volumes. If an excess of either gas is used, that excess is left uncombined. The equation for the reaction is



which shows that one mole of hydrogen, 2.016 parts by weight of hydrogen, will combine with one mole of chlorine, 70.92 parts by weight of chlorine to form two moles of hydrogen chloride, or  $2 \times 36.468$  parts by weight of hydrogen chloride. The composition of hydrogen chloride is 1.008 parts by weight of hydrogen to 35.46 parts by weight of chlorine, or 2.76 per cent. hydrogen and 97.24 per cent. chlorine.

Of course the action of the electric spark in bringing about the combination of the gases is due simply to the fact that it produces heat locally, and thus accelerates the reaction sufficiently so that the heat produced at that spot will start a flame which will be propagated throughout the mixture. The spark does nothing but furnish the initial high temperature to start the action. If the mixed gases be heated to a temperature of between  $240^\circ$  and  $270^\circ$  C. explosion takes place. Hydrogen and oxygen, it will be recalled, behave in much the same way except that the combination takes place at a higher temperature.

There is one method for bringing about the combination of hydrogen and chlorine which entirely fails in the case of hydrogen and oxygen. This is with light. A mixture of hydrogen and chlorine combines so slowly in absolute darkness that apparently the action does not take place. If the mixture be exposed to light, the combination takes place at a rate which can be measured and which is proportional to the intensity of the light. In ordinary diffused daylight the reaction is complete in a few days, while if the mixture be exposed to full sunlight or to the light of burning magnesium, explosion almost instantly results. This effect may be easily shown, with perfect safety, by filling thin glass bulbs about the size of a hen egg, blown in the middle of a piece of small glass tubing, with a mixture of equal volumes of chlorine and hydrogen. The glass tube on either side of the bulb should be very small and thin so that it may be sealed off after the bulb has been filled, without exploding the mixture. The

glass of the tube must of course be heated far above  $270^{\circ}$  C. at which the mixture will explode, and without question cause the gases to combine at the spot where the seal is made, but the walls of the very narrow tube so cool the gases that the flame does not pass to the bulb.

The mixture of the gases in the proper proportions may be most easily obtained by the electrolysis of strong hydrochloric acid, using electrodes of carbon or platinum and continuing the action for several hours before the bulbs are filled. This is necessary because of the fact that on account of the solubility of chlorine, at first only hydrogen comes off, and the proper proportion of chlorine appears only when the liquid has become thoroughly saturated with this substance. The bulbs must be filled in very weak light. If carefully protected from the light they will keep for years, and be ready to explode instantly upon exposure to strong light. Properly made bulbs are so thin that there is practically no danger from flying pieces of glass, but as a matter of precaution the eyes of the operator should be protected.

**Photochemical Action.**—The action of light in accelerating the union of hydrogen and chlorine is another example of photochemical action. In this case the light certainly does not have to impart energy to the system, because the combination takes place with a very great decrease in the energy so that a large amount of heat, 92 KJ. or 22,000 cal. per mole, is evolved. A completely dry mixture of chlorine and hydrogen is insensitive to light, so water plays an important part in the process.

**Action of Chlorine on Hydrogen Compounds.**—Oxygen, it will be recalled, was able to act upon many compounds of hydrogen in such a way as to produce water. After much the same fashion, chlorine will react with hydrogen compounds for the formation of HCl. We have had an example of this in the case of chlorine and water. A still more striking case is that of chlorine and turpentine. Turpentine is a compound of hydrogen and carbon. If a piece of filter paper be dipped into some slightly warmed turpentine and then introduced into a cylinder of chlorine, the latter will combine with the hydrogen of the turpentine with the production of so much heat that after a moment the turpentine bursts into a dark red flame which deposits all the carbon in the form of soot, and forms hydrogen chloride which may be identified by its

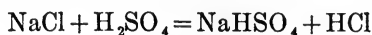
properties. Paraffine is composed of compounds of hydrogen and carbon, and when a burning paraffine candle is introduced into chlorine, it continues to burn, but with a darkened flame and the formation of hydrogen chloride and of soot, because under these circumstances chlorine does not combine with carbon.

When natural gas is mixed with chlorine and exposed to sunlight, the methane,  $\text{CH}_4$ , which is the chief constituent of the gas, is attacked and hydrogen chloride, together with a number of chlorine substitution products of methane are formed. The first of these products is methyl chloride,  $\text{CH}_3\text{Cl}$ , and the final one is carbon tetrachloride,  $\text{CCl}_4$ . These actions take place slowly and at ordinary temperatures.

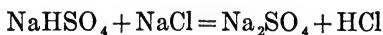
#### Laboratory and Technical Preparation of Hydrogen Chloride.—

While a knowledge of the methods given above for the preparation of this chloride is very necessary in the development of our conception of chlorine, they are not methods in actual use for the preparation of the substance on a laboratory or a commercial scale. For such a purpose the hydrogen chloride is almost always prepared by acting upon common salt, sodium chloride, with concentrated sulfuric acid at a slightly elevated temperature. In the laboratory this is usually carried out in a glass flask heated by a Bunsen burner. The gaseous hydrogen chloride given off is absorbed in water in which it is extremely soluble, forming what is known as hydrochloric acid. So soluble is the hydrogen chloride that care must be taken that the delivery tube from the flask does not extend below the surface of the water in the receiving vessel, or otherwise the absorption will often be more rapid than the evolution of the hydrogen chloride and the water will rush back into the flask. On a manufacturing scale the process is carried out as the first step in the manufacture of sodium carbonate, and the hydrochloric acid is a by-product. The operation is carried through the first stage in a large iron pan, A, heated from below (Fig. 18), covered with a brickwork dome, and finished in a fire clay muffle, B. Both dome and muffle are connected by a flue with brick towers filled with coke over which a small stream of water is kept trickling. The hydrochloric acid vapors pass up through the towers against the stream of water and are absorbed. Almost saturated hydrochloric acid runs out from the bottom of the first tower.

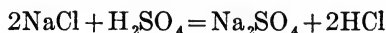
As the operation is carried out in the laboratory, acid sodium sulfate,  $\text{NaHSO}_4$ , is formed in addition to hydrogen chloride as shown in the equation



At the higher temperature which may be reached on the manufacturing scale, acid sodium sulfate will react with salt for the formation of neutral sodium sulfate,  $\text{Na}_2\text{SO}_4$ , and hydrogen chloride



or the two equations may be combined into one



These reactions are reversible and would be incomplete were it not for the fact that the hydrogen chloride is very volatile and hence readily distilled from the mixture. This, of course, de-

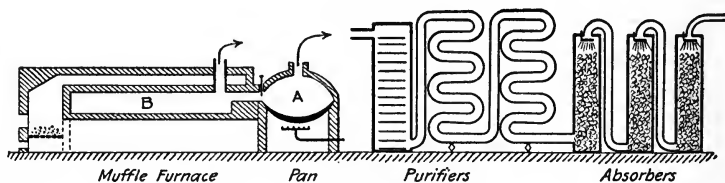


FIG. 18.

creases the concentration of the hydrogen chloride, and more is at once formed to take its place. This will continue until the salt and sulfuric acid have been completely transformed, provided that the hydrogen chloride is carried off as it is formed.

The action takes place not because the hydrochloric acid is a weaker acid than sulfuric acid—it is much stronger, but because the hydrochloric acid is much more volatile than sulfuric acid. In fact sulfuric acid may be replaced by any acid, however weak, which is much less volatile than hydrochloric acid and which is not a strong enough oxidizing agent to attack the latter. Phosphoric acid will do very well.

**First General Method for the Preparation of Acids.**—In the cases given above we are dealing with examples of a general



method for the preparation of acids from their salts. This may be called the first general method for the preparation of acids and may be stated as follows. *Treat a salt of the acid desired with a less volatile acid and distil. It is applicable to such acids as will stand distillation without decomposition, and of course the added acid must not only be less volatile than the acid desired but must also be without action upon this acid.*

**Properties of Hydrogen Chloride.**—A number of properties of hydrogen chloride have already been given; in addition we may say that its density is .00164 and its molar weight is 36.47. Its critical temperature is  $51.4^{\circ}$  C. and its critical pressure  $81.6^{\circ}$  atmospheres. It can then be converted into a liquid by pressure alone at ordinary temperatures. At  $22^{\circ}$  C. the pressure necessary is 46 atmospheres. The boiling-point of the liquid hydrogen chloride is  $-83^{\circ}$  C. and the freezing-point is  $-112^{\circ}$  C. The liquid hydrogen chloride is a colorless almost inactive substance which is without action upon metals or blue litmus, and in general exhibits very little of the great chemical activity which is shown by its solution in water. This difference is of great import as we shall soon see.

As has been mentioned hydrogen chloride is very soluble in water. At its freezing point one volume of water will absorb about 525 volumes of hydrogen chloride. At the same time a great amount of heat is developed which points to the formation of a compound with the water. This is indicated too by the fact that hydrogen chloride does not follow Henry's law of solubility of gases which states that *provided no chemical combination takes place between the gas and the solvent, the mass of the gas dissolved by a given mass of the solvent is directly proportional to the pressure.* In the case of hydrogen chloride and water, Henry's law is far from describing the case. In fact the mass of the hydrogen chloride dissolved is but slightly altered by large changes in pressure. This would indicate that the hydrogen chloride underwent some sort of a change upon passing into solution in water. As a matter of fact by cooling very concentrated solutions of hydrogen chloride to low temperatures, three crystalline compounds of hydrogen chloride and water can be obtained. These are the mono-, di- and tri-hydrates, and have the formulas  $\text{HCl}\cdot\text{H}_2\text{O}$ ,  $\text{HCl}\cdot 2\text{H}_2\text{O}$ , and  $\text{HCl}\cdot 3\text{H}_2\text{O}$ . The first of

these can exist only under pressure. The others can be prepared in an open vessel at a sufficiently low temperature. Whether any of these exist in solution at ordinary temperatures is an open question.

**Constant Boiling Hydrochloric Acid.**—Hydrogen chloride boils at  $-83^{\circ}$  C. and water at  $100^{\circ}$  C. so one would naturally expect that a solution of hydrogen chloride would boil at temperatures between these two points. This is only true, however, of solutions containing more than 40 per cent. of hydrogen chloride. Weaker solutions boil at temperatures above  $100^{\circ}$  C. and a 20 per cent. solution boils at  $110^{\circ}$  C. and is the highest boiling and consequently the least volatile mixture of hydrogen chloride and water. Of course when a mixture of two volatile substances is boiled, the substance which is the more volatile under the existing conditions passes off in the greater quantity, although some of each goes into the vapor. Now hydrogen chloride like every other solute lowers the vapor pressure of water, and the water in turn lowers the vapor pressure of the hydrogen chloride. The vapor pressure of the solution is the sum of the partial pressure of the water and the hydrogen chloride. Up to about 40 per cent. hydrogen chloride, the vapor pressure of the mixture is less than that of water at the same temperature, so it boils at a higher temperature than the latter. Up to 20 per cent. hydrogen chloride, the vapor pressure of hydrogen chloride has been so lowered by the water that the latter is relatively the more volatile, while for higher percentages of hydrogen chloride this substance is the one which tends to distil in the greater quantity. For these reasons if one distils a hydrochloric acid solution of less than 20 per cent. both water and hydrogen chloride come off, but relatively more of the former, and the residue becomes richer and richer in hydrogen chloride. This makes the residue in the flask less volatile and consequently higher boiling. After this process has gone on for some time, the residue finally reaches 20 per cent. hydrogen chloride which is the least volatile of the hydrogen chloride-water mixtures, and boils at  $110^{\circ}$  C. After this has been reached, the mixture distils unchanged in composition and boiling-point.

If on the other hand we start to distil a hydrochloric acid solution containing more than 20 per cent. hydrogen chloride,

this substance will come off with the water but in such quantities that the distillate contains a higher percentage of hydrogen chloride than the original mixture, leaving a residue which contains a smaller percentage of hydrogen chloride and boils at a higher and higher temperature until its boiling-point becomes  $110^{\circ}$  C. and its composition 20 per cent. hydrogen chloride. After this it boils constantly with unchanged composition. From the above it follows that no matter what the original composition of the hydrochloric acid, after it has boiled for sufficient time the residue will be a 20 per cent. acid boiling at  $110^{\circ}$  C.

The relationship between the composition and boiling-point for hydrochloric acid is shown in Fig. 19.

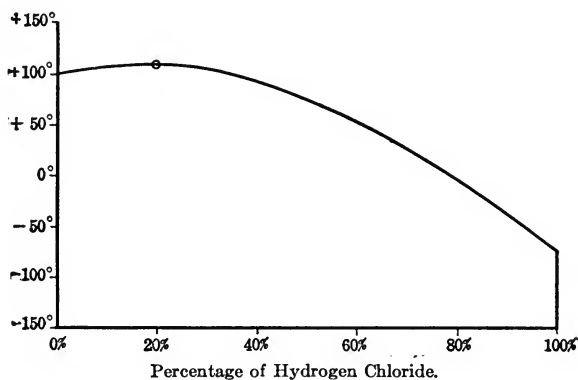


FIG. 19.

This constant boiling hydrochloric acid has often been mistaken for a chemical compound, but that this is not the case is shown by the fact that its composition changes with the pressure. When the boiling is carried out under a pressure of 2.5 atmospheres, the composition is 18 per cent. hydrogen chloride, while at .066 atmospheres it is 23 per cent. hydrogen chloride. Any pair of substances which can yield a certain mixture having a minimum vapor pressure, will upon distillation give a residue of this composition which will boil unchanged. Similarly a pair of substances which give a mixture having a maximum vapor pressure will also yield a constant boiling mixture. The difference between this case and the other lies in the fact that here the

constant boiling mixture will be found in the distillate instead of the residue.

Hydrochloric acid weaker than 20 per cent. does not fume when in contact with moist air while the stronger acid gives rise to dense white fumes which consist of droplets of hydrochloric acid. The reason for this is that the hydrogen chloride given off from the strong solution is capable of uniting with water vapor of the air to form a solution having a smaller vapor pressure than the original solution, and therefore droplets of this solution are formed and constitute the fumes. Any substance which is capable of forming a maximum boiling mixture with water will fume in contact with moist air when it has a strength greater than that of the constant boiling mixture.

## CHAPTER IX.

### IONIC THEORY.

The Ionic Theory, or the Theory of Electrolytic Dissociation as it is often called, is one of the most important tools of modern chemistry, and this chapter will be devoted to its development. As should always be the case, the facts which it was devised to explain will be given first and should be fully appreciated by the student, and then the theory learned not as a fact, but as a possible explanation for the facts.

**Acids.**—Mention has been frequently made in what has gone before of acids, and hydrochloric, sulfuric and phosphoric acids are typical examples of this very important class of compounds. The acids comprise a large group of substances of very different compositions which have certain well marked properties in common. For example, they all taste sour, redden litmus, and contain hydrogen as one of their essential constituents, which hydrogen they will evolve as hydrogen gas when brought in contact with magnesium or zinc. All acids are hydrogen compounds, but many hydrogen compounds are not acids. Water, turpentine, sugar, olive oil, and many other substances contain hydrogen but will not evolve hydrogen when brought in contact with magnesium or zinc at ordinary temperatures, neither do they taste sour, nor redden litmus, and so are not acids. The hydrogen then of acids must be in some kind of a special condition, different from that of the hydrogen of other compounds, and since this is the only constituent which acids have in common, as is shown by the appended list of acids and their formulas, the common properties of acids must be ascribed to the hydrogen in this special condition.

#### SHORT LIST OF THE MORE COMMON ACIDS

Hydrochloric acid, HCl	Nitric acid, HNO <sub>3</sub>
Hydrobromic acid, HBr	Phosphoric acid, H <sub>3</sub> PO <sub>4</sub>
Hydriodic acid, HI	Oxalic acid, H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
Sulfuric acid, H <sub>2</sub> SO <sub>4</sub>	Acetic acid, HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>

The acids show their peculiar properties only when dissolved in water and a few other solvents. When in a perfectly pure state or dissolved in most solvents, they are as indifferent as pure hydrogen chloride and neither redden litmus nor evolve hydrogen with magnesium. Of course, their taste in the entire absence of water cannot be determined. The water has then something to do with the transformation of the hydrogen of the acids into its special state. In this connection it will be recalled that the evidence was that hydrogen chloride underwent a chemical change when it passed into solution in water.

**Bases.**—Bases are another rather large class of substances of varied composition which like acids, have, when dissolved in water, certain properties in common. Their solutions all have a peculiar alkaline taste, a soapy feeling, and turn red litmus blue. As will be seen from the partial list of bases given below, they all contain hydrogen and oxygen in the proportion of one combining weight of the one to a combining weight of the other. We express this by saying that they contain the hydroxyl group, OH, and ascribe their common properties to this group.

#### LIST OF BASES

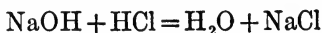
Sodium hydroxide,	NaOH	Calcium hydroxide,	Ca(OH) <sub>2</sub>
Potassium hydroxide,	KOH	Barium hydroxide,	Ba(OH) <sub>2</sub>
Ammonium hydroxide,	NH <sub>4</sub> OH	Strontium hydroxide,	Sr(OH) <sub>2</sub>

Like the acids these bases show their common properties only when dissolved in water and a few other solvents, and since there are many compounds known which contain hydroxyl and yet are not bases, we ascribe the characteristic properties of bases in water solution to the hydroxyl in a peculiar condition, similar to that of the hydrogen from acids in such solutions.

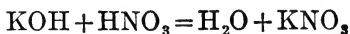
**Neutralization.**—When a solution of hydrochloric acid is added to a solution of sodium hydroxide in just the proper proportions, both the characteristic properties of the acid and those of the base completely disappear, and the solution which is left behind neither reddens blue litmus nor blues red. It has neither a sour nor an alkaline taste, has no soapy feeling and does not evolve hydrogen at ordinary temperatures with zinc or magnesium. Its taste is a pure salty taste and in fact it is in every way identical with a solution of common salt, sodium chloride,

in water. If the solution be evaporated, nothing but water passes off, and nothing but sodium chloride is left behind. What then has become of the hydroxyl of the base and the hydrogen of the acid? Obviously they must have combined to form water, leaving the sodium and chlorine to form sodium chloride.

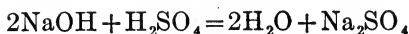
The reaction may be represented by the equation



We say that the hydrochloric acid and sodium hydroxide have neutralized each other and that water and a solution of sodium chloride have been formed. Other acids and bases behave in much the same way. They neutralize each other and leave solutions of the corresponding salts. For example potassium hydroxide and nitric acid give water and a neutral solution of potassium nitrate,  $\text{KNO}_3$



Sulfuric acid gives sulfates and water



**Reacting Ratio in Neutralization.**—By inspection of the above equations and writing others, it is very easy to satisfy one's self that a quantity of a base which contains 17.008 gm. of hydroxyl will just neutralize a quantity of an acid which contains 1.008 gm. of hydrogen in the peculiar acid condition. Since it is a very easy matter to tell with the aid of litmus just when a solution is neutral, the fact mentioned above is made the basis of a simple and much used method for the quantitative determination of acids and bases. The essentials of the method are as follows: Such a quantity of a base, say sodium hydroxide, as will contain 17.008 gm. of hydroxyl is dissolved in water and the solution made up to just a liter. Each cubic centimeter will then contain .017008 gm. of hydroxyl and will neutralize that quantity of an acid which will contain .001008 gm. of hydrogen, that is to say, .03647 gm. of hydrogen chloride for example. Such a solution is called a **normal solution** of a base. To use this in determining the amount of an acid, say hydrogen chloride, in a solution of unknown strength one would weigh out a few grams of the acid, add a drop of litmus solution and

then run in from a graduated vessel called a burette (Fig. 20), enough of the normal hydroxide solution so that the litmus is just on the point of turning blue, and in fact is neither blue nor red. The number of cubic centimeters used multiplied by .03647 gives the weight of hydrogen chloride in the acid solution taken. Say we weighed out 10 gram. of the acid and it required 20 c.c. of the normal base to neutralize it. The acid contained in this 10 gram. is

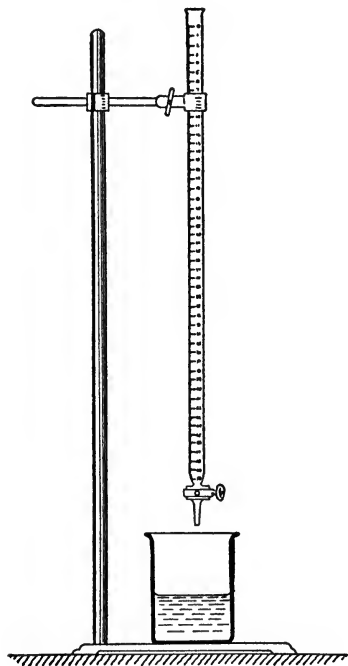


FIG. 20.

$$20 \times .03647 = .7294 \text{ or } 7.294 \text{ per cent.}$$

Similarly with the aid of a **normal acid**, *i.e.*, one containing 1.008 gram. of hydrogen in the acid condition per liter, one may determine very easily the quantity of base in a solution of unknown strength.

Methods like the above are in very frequent use in quantitative chemical analysis, and are called volumetric methods.

**Acids, Bases, and Salts have two Sets of Properties.**—Every acid has when in solution in water, two independent sets of properties, one common to all acids and evidently belonging to the hydrogen of the acid, and the other peculiar to that acid, being shown by no other acid,

and evidently belonging to the rest of the acid other than the hydrogen. For example, hydrochloric acid is like all other acids in that it is sour, reddens litmus and gives hydrogen with zinc, but differs from all other acids in that it will give sodium chloride with sodium hydroxide, and also will yield a white curdy precipitate with silver nitrate which precipitate is silver chloride. A few other acids give somewhat similar precipitates with silver salts, but these all differ sufficiently in their



properties from the silver chloride so that they may be positively distinguished from the latter.

Bases too have two independent sets of properties in water solutions, the one common to all bases and evidently due to the hydroxyl, and the other peculiar to the particular base that is being worked with and belonging to the rest of the base other than the hydroxyl. For example, barium hydroxide shows all the characteristic properties of bases, turning litmus blue, etc., and also gives with sulfuric acid and all sulfates a white precipitate of barium sulfate,  $\text{BaSO}_4$ , which is different in its properties from all other substances. No other base has just this property. When one of these acids with its two sets of properties is neutralized by a base with its two sets, the properties common to all acids together with those common to all bases completely disappear leaving behind that set of properties of the acid which was peculiar to that particular acid, and the set of properties of the base which was peculiar to that base. So the salt solution remaining after the neutralization of an acid by a base has two sets of properties.

It follows from what has just been said that solutions of hydrochloric acid and all soluble salts of hydrochloric acid should give the white curdy precipitate of silver chloride upon the addition of silver nitrate. This is exactly what has been found to be the case. Similarly barium salts formed by the neutralization of this base by acids should and do give a precipitate of barium sulfate upon the addition of sulfuric acid or sulfates.

When these same bases, acids, and salts are in the pure state or even in solution in most solvents other than water, they do not exhibit these two sets of independent properties, but each has only one. An explanation for these and for the succeeding sets of facts will soon be given as the theory of electrolytic dissociation.

**Abnormal Lowering of the Freezing-point.**—In connection with the discussion of hydrogen peroxide it was brought out that a gram mole of most substances lowers the freezing-point of 1000 grm. of water  $1.85^\circ \text{C}$ . and that this fact may be made the basis of a method for the determination of molar weight. In fact we got at the molar weight of hydrogen peroxide in this way.

The acids, bases and salts are the exceptional substances

which do not lower the freezing-point of 1000 grm. of water  $1.85^{\circ}$  C. per gram mole, but always produce a greater lowering. In many cases the lowering is nearly twice what we would expect, in others something like three times, and sometimes even more than three times the  $1.85^{\circ}$  C. per gram mole dissolved in 1000 grm. of water.

For example, hydrogen chloride is a gaseous substance and its molar weight can be readily found from its gaseous density to be 36.47. If one dissolves 36.47 grm. of hydrogen chloride in 1000 grm. of water, the freezing-point of the water is lowered  $3.61^{\circ}$  C. or nearly twice  $1.85^{\circ}$  C. A gram mole of sodium or potassium chloride or of any other salt formed by the union of one combining weight of a metal with one combining weight of chlorine produces about the same lowering as a gram mole of hydrogen chloride when dissolved in 1000 grm. of water or nearly twice  $1.85^{\circ}$ . Such salts as calcium or barium chlorides,  $\text{CaCl}_2$  or  $\text{BaCl}_2$ , which contain two combining weights of chlorine to one combining weight of the metal, lower the freezing-point nearly three times  $1.85^{\circ}$  per mole of salt per 1000 grm. of water. From these facts it looks as though the lowering for salts were  $1.85^{\circ}$  C. per gram combining weight instead of per gram mole. That this is not the case is shown by the fact that nitric acid,  $\text{HNO}_3$ , potassium nitrate,  $\text{KNO}_3$ , and sodium nitrate,  $\text{NaNO}_3$ , only lower the freezing-point of 1000 grm. of water twice  $1.85^{\circ}$  per gram mole of acid or salt. Further, sulfuric acid,  $\text{H}_2\text{SO}_4$ , with its seven combining weights per mole, lowers the freezing-point of 1000 grm. of water only something less than three times  $1.85^{\circ}$  C. per gram mole of acid dissolved. These facts are very significant and important in connection with the theory soon to be developed.

**Electrolytes.**—Metals are called conductors of the first class. As is well known, they are not altered in any way by the current except that their temperature is more or less raised. Some solutions are also conductors of electricity and are called conductors of the second class because they not only become heated, but also are invariably decomposed during the passage of the current provided the circuit consists in part of conductors of the first class as is usually the case. Such solutions are called electrolytes and are formed only when acids, bases, and salts

are dissolved in water or in the few other solvents in which they each show their two independent sets of properties. The decomposition takes place at points where the electric current enters and leaves the salt solution. The terminals of the metallic portion of the circuit are called electrodes and are distinguished from each other by calling that electrode where the electricity enters the solution the anode and that where it leaves it for the metal, the cathode. During the passage of the current, one kind of substance appears at the cathode and an entirely different substance at the anode. When hydrogen chloride solution is electrolyzed, hydrogen appears at the cathode and chlorine at the anode. The two substances appearing at the electrodes are in general the two substances which seem to give to the salt solutions their two sets of independent properties.

A fact which is closely connected with those given above, and which is still more significant is that, when a current of electricity is passed through a salt solution, the two components of the salt which act chemically independently of one another may actually be seen to move slowly in opposite directions, the one toward the cathode and the other toward the anode, and at quite different rates. Especial precautions must be taken to bring this out, but the experiments are rather easily performed and are quite definite in their results.

In the case of hydrochloric acid solutions, the chlorine moves toward the anode while the hydrogen travels toward the cathode, and moves nearly five times as rapidly as the chlorine.

**The Laws of Faraday.**—The English scientist Faraday in the year 1833 carefully investigated the phenomena occurring at the electrodes and devised the names which we have been using such as electrolysis, electrolyte, electrode, anode, cathode, and in addition he called the substances which travel toward the electrodes ions. Those which move toward the cathode being the cations and those which move toward the anode being the anions. He also discovered facts which are described by the following laws known as the First and Second Laws of Faraday.

**The First Law.**—*The mass of any given substance deposited at an electrode is strictly proportional to the quantity of electricity which passes through the solution.*

Electrical energy like all other forms of energy is the product

of two factors, a quantity factor, which is the quantity of electricity, and the other, the intensity factor, which is the potential or voltage. The unit of quantity of electricity is the coulomb which is the quantity of electricity which will deposit .001118 gm. of silver. A steady current of electricity which will transfer one coulomb per second is said to have a strength of one ampere. The unit of potential is the volt, a magnitude with which we need not concern ourselves at the present time further than to say that the product of unit potential by unit quantity of electricity, the volt-coulomb, which is the unit of electrical energy, is equal to  $10^7$  ergs or one joule.

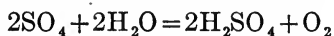
From Faraday's first law, if one coulomb deposits a certain quantity of a substance, two coulombs will deposit twice as much, etc.

**The Second Law.**—The second law of Faraday's says that *the quantity of different substances liberated at the electrodes by the passage of the same quantity of electricity is proportional to the combining weights of the substances.* That is to say, the quantity of electricity which will liberate 1.008 gm. of hydrogen will set free 35.46 gm. of chlorine. In each of the cases, the quantity of electricity required to liberate a gram combining weight of the ion, 1.008 gm. of hydrogen or 35.46 gm. of chlorine, is 96,500 coulombs. To liberate a gram combining weight of calcium, barium, or oxygen requires two times 96,500 coulombs, and in some cases three or more times this number is required.

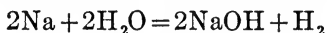
We may sum up all that has been said upon this subject in the statement: *the electricity moves in electrolytes only with the simultaneous movement of their chemically independent components, and is accompanied by the deposition of two different substances upon the electrodes, the quantity of electricity required to liberate a gram combining weight of any substance being 96,500 coulombs or some rational multiple of this.*

**Primary and Secondary Electrolysis.**—Sometimes the substances which are liberated at the electrodes are stable and continue to exist in that form, for example, the hydrogen and chlorine from hydrogen chloride. In such cases they are said to be the primary products of electrolysis. In other cases the substances liberated react with the water to form substances which are called secondary products of electrolysis. As an example, we

may mention the sulfate group,  $\text{SO}_4$ , which is probably liberated at the anode during the electrolysis of sulfuric acid and reacts with water for the formation of oxygen and sulfuric acid,



or sodium which if liberated at the cathode will react for the production of hydrogen and sodium hydroxide,



**Summary.**—We have now discussed the principal groups of facts which the theory of electrolytic dissociation was devised to explain, but before proceeding to the theory itself a brief summary of these facts may be of use.

**First.**—Salts in solution in water show independent sets of chemical properties, and all salts having a common component have one set of properties in common. The term salt as used here includes acids and bases as well as salts in the ordinary sense.

**Second.**—Salts in solution in water lower the freezing-point of the water more than  $1.85^\circ \text{C}$ . per gram mole per 1000 grm. of water; some nearly twice, some three times, and some even more than three times the regular lowering.

**Third.**—Salts in solution are electrolytes and the electricity passes through the solution only with the simultaneous movement of the components of the salts in opposite directions and at quite different rates. In addition two different substances are liberated at the electrodes. One gram combining weight of each substance is liberated by the passage of 96,500 coulombs or some rational multiple of this.

All these are well established facts. The theory which is about to be given is simply an imagined cause or explanation for these facts and is in many respects on a par with the atomic theory. It is very useful in correlating a great many facts of chemistry and has been very successful in predicting the discovery of new facts, and hence is worthy of considerable attention.

**The Theory of Electrolytic Dissociation.**—To explain the facts outlined above, certain **assumptions** are made concerning the nature of salts in solution. The first one is that when salts are dissolved in water, they are decomposed or dissociated into at least two different substances which are chemically separate and distinct from each other and from the original salt. These

new substances are assumed to be the chemically independently acting components of the salts and are called **ions**, from the Greek word *ἰών* meaning wander, because they move in opposite directions toward the electrodes. That which goes toward the anode is known as the **anion** and that toward the cathode as the **cation**.

Each gram mole of salt which dissociates is assumed to give rise to at least 2 gram moles of these new substances, the ions, and each gram mole of an ion, or shortly "gram ion," is assumed to act in lowering the freezing-point of water like a gram mole of any other substance.

To account for the electrical properties of salt solutions, it is assumed that these new substances, the ions, are charged with electricity, the cations with positive and the anions with negative electricity; the charges amounting to 96,500 coulombs or a rational multiple per gram ion. Since salt solutions are electrically neutral, it must be assumed that the + charges upon the cations just equal the - charges upon the anions.

The **explanation** of the first fact in terms of the theory is very simple. We have only to say that each of the two independent sets of properties belongs to one of the new substances or ions formed by the dissociation of the salt, and since these ions are assumed to be uncombined, each set of properties is of course independent of the other component of the salt. The chlorine ion is assumed to be identical whether it came from hydrochloric acid, HCl, sodium chloride, NaCl, potassium chloride, KCl, or any other chloride, and hence all chlorides in solution show the properties of chlorine as ion no matter what the other ion may be. The acid properties are ascribed to hydrogen as ion and since this is assumed to be present in all acids in solution they all show the common properties of acids irrespective of the nature of the other ion.

The abnormal lowering of the freezing-point is explained by the assumption that each gram mole of salt when it dissociates produces two or more gram moles of ions, or gram ions as they are called. A gram mole of hydrogen chloride, it will be recalled, lowers the freezing-point of 1000 gm. of water practically twice 1.85° C. This gram mole of hydrogen chloride is supposed, by the theory, to decompose into a gram mole of *hydrogen as ion*

which lowers the freezing-point of the 1000 grm. of water  $1.85^{\circ}$  and a gram mole of *chlorine as ion* which also lowers the freezing-point another  $1.85^{\circ}$  or  $3.70^{\circ}$  for the two together. The actual observed lowering is  $3.61^{\circ}$ . The difference between this and  $3.70^{\circ}$  is explained by assuming that a small part of the hydrogen chloride remains undissociated.

It must be noted that a gram mole of hydrogen as ion is assumed to differ from a gram mole of hydrogen in that it carries 96,500 coulombs of electricity and has only *one* combining weight of the element instead of two per mole; similarly for chlorine.

The fact that a gram mole of calcium chloride,  $\text{CaCl}_2$ , lowers the freezing-point of 1000 grm. of water nearly three times  $1.85^{\circ}$  is easily explained because the theory requires that it shall break up into a gram mole of calcium as ion and two gram moles of chlorine as ion. Each lowers the freezing-point  $1.85^{\circ}$  or three times this for the three of them. Sulfuric acid acts as though it broke up into two gram moles of hydrogen as ion and a gram mole of sulfate,  $\text{SO}_4$ , and lowers the freezing-point of the standard 1000 grm. of water nearly  $3 \times 1.85^{\circ}$  as would be expected.

The movement of the components of the salts, the one toward the anode and the other toward the cathode and at quite different rates can be easily explained with the aid of the assumptions made above. The ions are supposed to be charged with electricity, the cations positively and the anions negatively. The anode is charged positively and the cathode negatively, just the opposite from the ions. Now from the well-known fact that electricities of opposite signs attract each other, it is easy to see why the cations should go toward the cathode and the anions toward the anode. Since the water is supposed to have broken up the salt before it was electrolyzed, no further explanation is necessary, for the components traveling in opposite directions and at different rates, since there is nothing to hinder them from doing so because they are no longer chemically combined with each other. The laws of Faraday are easily explained by assuming that each gram ion carries 96,500 coulombs or some rational multiple of this which must be neutralized by electricity from the electrode before the ion is deposited at the electrode and hence each gram ion will require 96,500 coulombs or some rational multiple of this before it can be liberated.

The fact that only solutions of salts are conductors of electricity is accounted for by saying that it is only in such solution that ions exist to carry the current. This is checked up by the fact that non-conducting solutions give normal lowerings of the freezing-point and show only one set of properties.

Even these salts, of which we have had so much to say, when dissolved in some solvents other than water are non-conductors and then they do not show the two sets of properties and act normally with respect to the freezing-point lowering. So there must be something of a connection between these three sets of facts, and the theory of electrolytic dissociation is the best guess concerning this which has been made.

In terms of the atomic theory the ions become charged atoms or groups of atoms, but perhaps the better way to look at them is to regard them as substances which are charged with electricity and in a peculiarly reactive condition.

The ions are represented by the symbols of the element or elements going to make them up, together with as many + or - signs as they seem to carry multiples of 96,500 coulombs of + or - electricity. The following list gives the names and symbols of a few of the more common ions.

CATIONS	ANIONS
Hydrogen.....H <sup>+</sup>	Chlorine.....Cl <sup>-</sup>
Sodium.....Na <sup>+</sup>	Bromine.....Br <sup>-</sup>
Potassium.....K <sup>+</sup>	Hydroxyl.....OH <sup>-</sup>
Silver.....Ag <sup>+</sup>	Nitrate.....NO <sub>3</sub> <sup>-</sup>
Calcium.....Ca <sup>++</sup>	Sulfate.....SO <sub>4</sub> <sup>--</sup>
Barium.....Ba <sup>++</sup>	Phosphate.....PO <sub>4</sub> <sup>--</sup>
Ammonium.....NH <sub>4</sub> <sup>+</sup>	

In terms of this theory a **salt** is any substance which when dissolved in water yields ions.

An **acid** is a salt which when dissolved in water gives hydrogen as one of its ions.

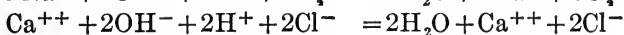
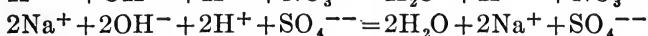
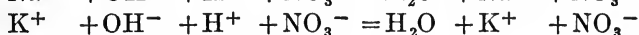
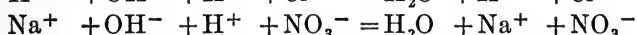
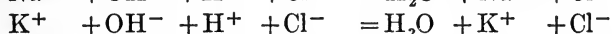
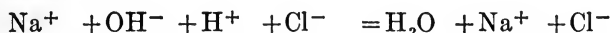
A **base** is a salt which when dissolved in water gives hydroxyl as one of its ions.

**Neutralization of Acids and Bases.**—When we come to consider the neutralization of acids and bases in the light of the theory, we reach the rather surprising conclusion that in the process only



water is formed. The salt in the narrow sense, is not formed since its cation and anion existed as such in the solution of the base and acid before they were brought together and continued to do so after the process was finished.

To illustrate, let us give the equations for a few reactions of this kind.



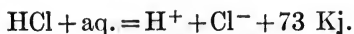
In every case water is formed and water only. The cation of the base and the anion of the acid are left unaltered. This explains why these salt solutions show the properties which were peculiar to the particular base and acid from which they were formed.

**Heat of Neutralization.**—Whenever any of the acids and bases given in the above list neutralize each other there is always 57 KJ. of heat evolved per mole of water produced, and this is true of all other strong acids and bases as well. This fact is very easy to explain on the basis of the electrolytic dissociation theory. In the light of this theory, water is the sole product of these reactions and is always formed from the same substances, hydrogen as ion and hydroxyl as ion, and therefore each reaction should show the same heat effect and thus 57 KJ. or 13,600 cal. is the heat of formation of water from hydrogen and hydroxyl as ions. If the salts had really been formed, the heat effect should have been different in each case.

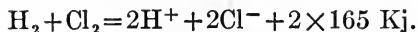
**Heat of Formation of Certain Ions.**—When hydrogen combines with chlorine for the formation of hydrogen chloride, 92 KJ. or 22,000 cal. of heat are given out per gram mole of gaseous hydrogen chloride formed.



When a gram mole of hydrogen chloride is dissolved in a great deal of water so that it is practically completely converted into its ions, a further quantity of heat amounting to 73 KJ. is developed.



aq. represents a great deal of water, or



Now it seems probable for reasons which cannot be gone into here that the heat effect accompanying the transformation of hydrogen into hydrogen as ion is very small, in fact may even be considered zero. Then the whole of the 165 Kj. which is the heat of formation of hydrogen as ion and of chlorine as ion from their gases is the heat of formation of the chlorine ion from chlorine gas.

When zinc dissolves in dilute acids, hydrogen is evolved and a solution of the zinc salt corresponding to the acid is formed. In each case, heat is evolved and experience has shown that the amount is always not far from 146 Kj. or 35,000 cal. When magnesium is used with the same acids hydrogen and solutions of magnesium salts are formed and the heat effect is 452 Kj. or 108,000 cal.

These are simply examples of the general experience, and the statement may be made that when metals act upon dilute acids for the formation of hydrogen and solutions of the salts of the metals that the heat of reaction depends upon the metal and is independent of the acid used. In terms of the theory of electrolytic dissociation, the reaction is between the metal and the hydrogen as ion for the formation of gaseous hydrogen and the ion of the metal. The anion of the acid being the same before and after the reaction has no influence upon the heat effect. Since hydrogen as ion changes into hydrogen gas with practically no heat effect, the heat of reaction of a metal with a dilute acid gives the heat of formation of the metal as ion.

The transformation of a metal into its ion or into salts formed by the union of this cation with an anion is called oxidation and, as will be seen above, hydrogen as ion is the substance which brings about the change and hence is the oxidizing agent. This is another type of oxidation which must be kept in mind in forming our conception of the process.

**Action of Acids.**—In our previous discussion of acids, certain points of similarity, their taste, action on litmus, metals, etc., were made much of and ascribed to their common constituent hydrogen, in what we termed the ionic state. In other respects

acids show great similarity. Quantities of different acids which contain equal amounts of ionizable hydrogen are equivalent to each other in several ways. They will, for example, neutralize the same quantity of any given base, say sodium hydroxide, and also when brought in contact with an excess of metal, like zinc, evolve equal quantities of hydrogen. Such quantities of acid as contain equal weights of ionizable hydrogen are appropriately called equivalent quantities, and that weight of any given acid which contains 1.008 gm. of ionizable hydrogen is called a gram equivalent of that acid. It will be recalled that a gram equivalent of an acid in 1000 c.c. of solution is called a normal solution of the acid.

In some respects acids show striking points of dissimilarity. If pieces of zinc of equal area are introduced into equivalent solutions of hydrochloric, sulfuric, and acetic acids, hydrogen will be evolved in each case, but at very different rates in the different acids. If normal acids are used, less than 1 c.c. of hydrogen will be liberated from the acetic acid, and 65 c.c. from the sulfuric acid during the time required for the liberation of 100 c.c. from the hydrochloric acid. If equivalent quantities of the acids and an excess of zinc are used, ultimately equal quantities of hydrogen will be liberated from each. In order to insure the success of the experiment indicated above, the pieces of zinc, before use should be treated with a dilute solution of copper sulfate. Copper will be deposited on the zinc and will tend to overcome the disturbing influence of local impurities in the zinc and secure a uniform evolution of hydrogen.

In other cases where acids act characteristically at measurable rates these acids stand in practically the same position relative to each other.

Much the same relationship exists between the lowering of the freezing points of these acids. One gram mole of hydrochloric acid, it will be recalled, lowered the freezing-point of 1000 gm. of water  $3.61^{\circ}$  or nearly twice the normal lowering of  $1.85^{\circ}$  per gram mole; while a gram mole of acetic acid per 1000 gm. of water lowers it only a trifle more than  $1.85^{\circ}$ .

Equivalent solution of these acids show very much these same differences in their power to conduct electricity. The solution of hydrochloric acid is a good conductor; sulfuric acid something

like two-thirds as good; while acetic acid, although still a conductor, is a very poor one indeed.

Because of these peculiarities in their actions, everyone calls hydrochloric and sulfuric acids strong acids, and acetic acid a weak acid. The hydrochloric acid is considered to be somewhat stronger than sulfuric.

**Explanation.**—It is a very simple matter to explain the facts outlined above with the aid of the ionic theory. We have only to add to our previous assumptions, that all acids break up or ionize so as to give hydrogen as ion, and that this hydrogen as ion has the characteristic acid properties, the further assumption that the various acids differ among themselves in the extent to which they break up, or in their degree of ionization. Hydrochloric acid is assumed to break up or ionize so far that in normal solution the greater part of the substance has been changed into hydrogen and chlorine as ions, while under the same conditions only a very small part of the acetic acid is supposed to be ionized; while sulfuric acid stands between the other two. Naturally, if hydrogen as ion is the acid acting hydrogen, that solution which contains the greatest concentration of hydrogen actually present as ion will be the most intensely acid. This, from what has been said above, would be the hydrochloric, then would come sulfuric, and last the acetic far behind the other two.

We have learned that the rate at which any given substance will react, other things being equal, depends upon the concentration, and further that in terms of the ionic theory the reaction between an acid and zinc is between hydrogen as ion and the zinc. From all that has been said above, then, it follows that the rate of evolution of hydrogen gas from these three acids should stand in the order, hydrochloric, sulfuric, and acetic acids. This was the order found by experiment.

But if the acids differ so much in their degree of dissociation or ionization, how does it come that equivalent quantities will neutralize the same amount of sodium hydroxide or any other base, and also ultimately evolve the same quantity of hydrogen when acted upon by an excess of a metal? To explain this we have only to assume that the ionization of an acid is a reversible process, and that as the hydrogen as ion is used up by combining with hydroxyl or reacting with the metal, more of the undisso-

ciated acid will break up into ions, and that this process will continue until the undissociated acid is completely used up.

The total acid hydrogen of an acid is called the ionizable hydrogen and that fraction of it which is present at any one instant in the state of the free ion, is called the actual ion, while that which is undissociated, but capable of becoming ionized, is called the potential ion. The ionizable hydrogen is the sum of the actual and the potential ions. Equivalent quantities of these three acids then contain the same amount of ionizable hydrogen, but differ in the relative proportion of the actual and potential ions; hydrogen chloride having the most actual and acetic the least.

The explanation of the difference in the lowering of the freezing-point is so obvious that it need not be gone into here.

The differences in the conductivities of the acids can be easily understood from the previous assumptions. The specific conductivity of a solution is the number of amperes of electricity which will flow through a cube of the solution 1 cm. on an edge under a difference of potential of one volt. Such a cube will, of course, have a volume of 1 c.c. The molar conductivity of a salt solution will be equal to the specific conductivity multiplied by the volume in cubic centimeters which contains one gram mole. The conception may perhaps be best obtained as follows: Imagine two electrodes placed 1 cm. apart and large enough to contain between them the whole of the solution in which one gram mole of the solute is dissolved. There will then be as many of these little cubes 1 cm. on a side as there are cubic centimeters of solution, and the molar conductivity will evidently be the sum of all these specific conductivities, and hence the specific conductivity multiplied by the volume of the solution.

As a rule the molar conductivity of a salt increases as the volume of the solution in which one gram mole is dissolved is increased, *i.e.*, as the solution is diluted. With the great majority of electrolytes, the molar conductivity increases with the dilution up to a certain point, and then runs along without any material increase as far as the measurements can be carried—in other words, it reaches a maximum.

A natural explanation for this is that the molar conductivity of a solution is proportional to the fraction of the gram mole

which is present as ions or the degree of ionization or dissociation as it is called and to the speed with which the ions move. Assuming that the latter is constant as the solution is diluted, it follows that the degree of ionization of the electrolyte increases with the dilution, and that when the conductivity has reached its maximum, the salt is entirely ionized or completely dissociated. On the basis of this, it follows that the degree of dissociation, at any given dilution, can be found by dividing the molar conductivity at that dilution by the maximum molar conductivity at very great dilution. The results given in the following table have been obtained in this way. Dilution as used here means the number of liters of the solution which con-

Dilution	HCl	HBr	HI	HF	H <sub>2</sub> SO <sub>4</sub> <sup>1</sup>	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
1	.784	.....	.....	.07	.51	.004
10	.95	.95	.95	.10	.57	.013
100	.98	.98	.98	.26	.79	.050
1000	.99	.99	.99	.95	.93	.125

tains one gram mole of the acid. It will be seen from this table that even at moderate dilutions, the first three acids are almost completely dissociated and are as strong as possible. The sulfuric acid is distinctly weaker, but quickly gains in strength. The hydrofluoric and acetic acids are much weaker, but grow rapidly stronger. So the more dilute the acids the stronger they become in the sense that they are more largely dissociated. That acid is the strongest which is most easily broken up into its ions.

Bases, like acids, differ widely in the degree of their dissociation at moderate dilutions. Sodium and potassium hydroxides being highly dissociated. Calcium and barium hydroxides have about the same degree of dissociation as sulfuric acid at any given dilution, while ammonium hydroxide is weak like acetic acid.

Salts, in the common sense of the term, are with few exceptions highly dissociated, and that too whether they are salts of weak or of strong acids. Sodium acetate, for example, at any given dilution is only a little less dissociated than sodium chloride.

<sup>1</sup> The sulfuric acid solutions are equivalent and not molar solutions.

## CHAPTER X

### OXYGEN COMPOUNDS OF CHLORINE

**General.**—Neither oxygen and chlorine nor oxygen, hydrogen and chlorine combine directly, but by more or less roundabout methods three oxides and four acids containing oxygen, oxyacids as they are called, can be prepared. The following table gives the names and formulas of the acids, the sodium salts of these acids, and the oxides.

Acids	Salts
HCl.....Hydrochloric acid	NaCl.....Sodium chloride
HClO.....Hypochlorous acid	NaClO.....Sodium hypochlorite
HClO <sub>2</sub> .....Chlorous acid	NaClO <sub>2</sub> .....Sodium chlorite
HClO <sub>3</sub> .....Chloric acid	NaClO <sub>3</sub> .....Sodium chlorate
HClO <sub>4</sub> .....Perchloric acid	NaClO <sub>4</sub> .....Sodium perchlorate

### OXIDES

Cl<sub>2</sub>O, Chlorine monoxide or hypochlorous anhydride.

ClO<sub>2</sub>, Chlorine dioxide or chlorine peroxide.

Cl<sub>2</sub>O<sub>7</sub>, Chlorine heptoxide or perchloric anhydride.

These oxyacids and their salts furnish excellent illustrations of the law of multiple proportions.

**Nomenclature of Acids and Salts.**—The names of acids formed by the union of hydrogen with one other element and which consequently do not contain oxygen are formed by taking the characteristic part of the name of the element other than hydrogen and adding the prefix hydro- and the suffix -ic. For example hydro-chlor-ic acid. Salts of such acids are named by combining the name of the metal which replaces the hydrogen of the acid with another word formed by dropping the prefix hydro- from the name of the acid and replacing the -ic by -ide. For example, sodium chloride.

In naming the oxyacids the best known is usually designated by adding to the characteristic part of the name of the element other than hydrogen and oxygen the suffix -ic. For example,

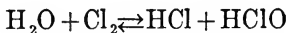
$\text{HClO}_3$  is called chloric acid. The names of the salts of such acids end in *-ate*, as sodium chlorate,  $\text{NaClO}_3$ .

If there is an acid containing more oxygen than the *-ic* acid, it is distinguished by adding to the name of the *-ic* acid the prefix *per-* and similarly for the salt as *per-chloric* acid,  $\text{HClO}_4$ , and sodium perchlorate. That acid containing the next smaller amount of oxygen than the *-ic* acid is distinguished by the suffix *-ous* and its salts are called the *-ites*. For example, chlorous acid,  $\text{HClO}_2$ , and sodium chlorite.

If there is an acid containing a still smaller amount of oxygen than the *-ous* acid, it is distinguished by adding to the name of the *-ous* acid the prefix *hypo-* and its salts are called *hypo- . . . -ites*; for example, hypochlorous acid and sodium hypochlorite.

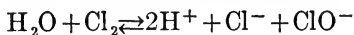
**Energy Relationships.**—The oxides of chlorine all possess more energy than the elements in the free state, while the oxyacids possess more energy than the hydrochloric acid and oxygen, or chlorine, oxygen and water into which they may pass. In this respect they resemble hydrogen peroxide and like it they will spontaneously decompose; several of them with explosion. Like hydrogen peroxide they do not form spontaneously, but require the addition of energy. This energy may be obtained in several ways, but perhaps the most important is by absorption from that liberated during the formation of another substance which is simultaneously produced as part of the same reaction with a greater decrease in energy.

As an example of such a reaction, we may take that between chlorine and water whereby hydrochloric and hypochlorous acids are formed,



The formation of the hydrochloric acid furnishes the energy necessary for the formation of the hypochlorous acid,  $\text{HClO}$ .

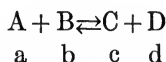
The above reaction is reversible and is very incomplete under ordinary conditions. The equation written in the ionic form is



Equilibrium will result in this reaction when the conditions described by the following law are fulfilled.



**The Law of Mass Action.**—The law of mass action in the form in which it is to be developed here applies to reversible reactions in equilibrium at constant temperature. Let us take a general case and say that we have a reversible reaction between A and B for the formation of C and D. Let a, b, c, and d represent the concentrations of A, B, C, and D respectively, and let R stand for the rate at which A and B combine for the formation of C and D and R' for that at which C and D react for the re-formation of A and B



Then from what we have already learned, page 50, the rate at which A and B react, everything else being constant, is proportional to a, and likewise to b, and therefore is proportional to their product or

$$R = Ka$$

$$R = K'b$$

$$R = K''ab$$

Correspondingly R' the rate at which C and D react is proportional to the concentration of C and to that of D and hence to the product of these concentrations

$$R' = K'''c$$

$$R' = K''''d$$

$$R' = K'''''cd$$

Equilibrium will result in this reaction when the two rates are equal, or

$$R = R'$$

and therefore at equilibrium

$$K''ab = K'''''cd$$

or

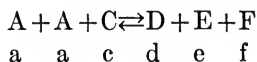
$$\frac{ab}{cd} = \frac{K'''''}{K''} = k$$

Expressed in words this would be: The product of the concentrations of the reacting substances divided by the product of the concentrations of the resulting substances is a constant for a

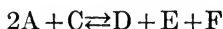
reversible reaction in equilibrium at constant temperature. From this it follows that if the three substances A, B, and C react to form D, E, and F, equilibrium will result when  $abc/def$  reaches a certain definite constant value whose magnitude depends upon the nature of the substances and the temperature, but not upon the absolute values of the concentrations. What is called the mass law equation for this reaction is:

$$\frac{abc}{def} = K$$

Suppose now that A is identical with B, then "a" will be identical with "b." The chemical equation then becomes



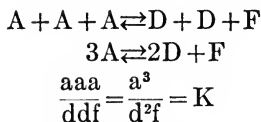
or



and the mass law equation,

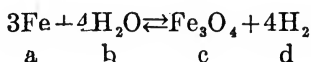
$$\frac{aac}{def} = \frac{a^2c}{def} = K$$

If A is identical with B and C and if D and E are identical, these equations become,



This may be expressed in words as follows: *When equilibrium results in a reversible reaction at constant temperature, the product of the concentrations of the reacting substances divided by the product of the concentrations of the resulting substances—each concentration raised to that power whose exponent is the coefficient of the substance in the chemical equation—is a constant.* The content of this statement is the *Law of Mass Action*.

For an example of its application we may take the equilibrium between water vapor, iron, iron oxide, and hydrogen. The equation is



The mass law equation is

$$\frac{a^3b^4}{cd^4} = K$$

In our former discussion of equilibria it was pointed out that the concentration of a solid substance or of a homogeneous liquid was constant and that only gases and dissolved substances have variable concentrations, see page 51.

The iron and the iron oxide are solids so their concentrations are constant and may be combined with the equilibrium constant  $K$ . The conditions of equilibrium are therefore dependent upon the concentrations of the hydrogen and of the water vapor. The mass law equation then becomes

$$\frac{b^4}{d^4} = \frac{Kc}{a^3} = k$$

or

$$\frac{b}{d} = \sqrt[4]{k}$$

This then tells us that these substances will be in equilibrium when there is a certain definite ratio between the concentrations of the water vapor and of the hydrogen.

It is very easy to see from this that if the concentration of the hydrogen be decreased, the water must react with the iron for the formation of more hydrogen and iron oxide. In a current of steam which sweeps away the hydrogen, equilibrium will never be reached and the reaction will continue until all the iron is used up.

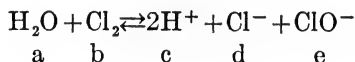
The law of mass action is exceedingly useful in that it enables one to tell just what to do to make a reversible reaction run in either direction as desired, and further, if we know the magnitude of  $k$ , the value of the concentration of one set of substances can be calculated—given that of the others.

In accordance with the law of mobile equilibrium (page 71), chemical equilibrium is shifted in such a way that more and more of the substances, which are formed with the absorption of heat, will be present as the temperature rises.

From this it may be seen that  $K$ , the equilibrium constant, varies with the temperature. At any one temperature it is,

however, independent of the absolute value of the concentrations.

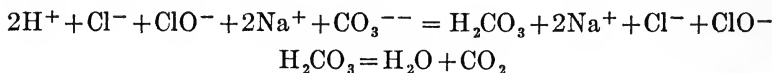
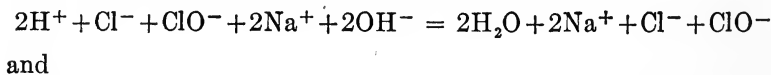
Apply this mass law to the reaction between water and chlorine,



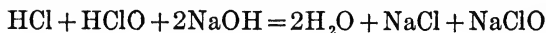
and let a, b, etc., represent the concentrations of the substances just above them. Equilibrium will result when  $ab/c^2de$  has reached a certain definite ratio or

$$\frac{ab}{c^2de} = K$$

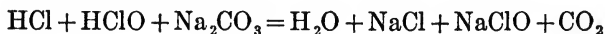
From this it may be easily seen that a decrease in the concentration of one of the substances on the right hand of the equation will decrease the denominator of the constant value fraction, and this will result in the formation of more of the substance on the right hand in order that the numerator of the fraction may decrease to keep the value of the fraction constant. By the addition of any hydroxide, say sodium hydroxide, the concentration of the hydrogen as ion, "c," may be decreased through the formation of water, and practically all the free chlorine may be consumed. Carbonates, say sodium carbonate  $\text{Na}_2\text{CO}_3$ , or anything else which will use up the hydrogen ion will act in the same way. The carbonates use up the hydrogen ion through the formation of carbonic acid,  $\text{H}_2\text{CO}_3$ , which is not much more broken up into its ions than water. The  $\text{H}_2\text{CO}_3$  is unstable and breaks down into water and gaseous carbon dioxide which escapes from the liquid in bubbles. The equations are



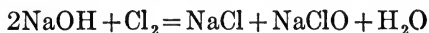
The equations written in the ordinary way become



and

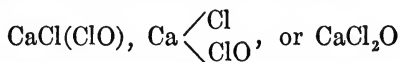


In either case we say that sodium chloride and sodium hypochlorite are formed. The reaction is not usually carried out by saturating water with chlorine and then adding sodium hydroxide, NaOH, but by running chlorine into sodium hydroxide solution and the equation is often written,

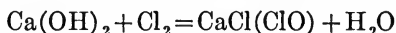


but the action doubtless takes place in the stages indicated above. Other hypochlorites can be made from the hydroxides of the corresponding metals in much the same way by the direct action of chlorine upon the hydroxide, either in solution or in the solid state.

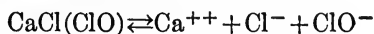
Without question the most important hypochlorite is that of calcium, which in the form of **bleaching powder**, or "chloride of lime," as it is often called, is manufactured by the thousands of tons from chlorine and calcium hydroxide. This bleaching powder is not a pure hypochlorite, but is a mixed salt, half chloride and half hypochlorite, formed by the union of one combining weight of calcium with a combining weight of chlorine ion and one of hypochlorite ion. The formula of the salt is given in various ways. Perhaps the most common of these are



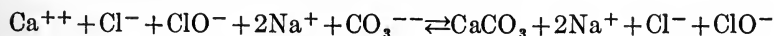
The equation for its formation is as follows,



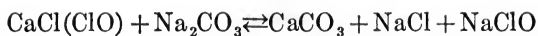
This bleaching powder is a solid and may be conveniently shipped. It is easily converted into chlorine, into sodium hypochlorite and chloride solution, or into hypochlorous acid. Upon passing into solution in water it acts as though it breaks up into calcium as ion and chlorine and hypochlorite ions.



Upon the addition of sodium carbonate the very slightly soluble calcium carbonate,  $\text{CaCO}_3$ , is precipitated, and sodium, chlorine, and hypochlorite ions are left in solution.



or



The solution, containing sodium hypochlorite, obtained in this way is very largely used for bleaching cotton and linen goods in the laundries.

Solutions containing hypochlorite are often formed by electrolysis of solutions of chlorides. Chlorine is liberated at the anode and hydrogen with the simultaneous formation of hydroxide at the cathode. The apparatus is so designed that the chlorine and hydroxide mix almost as soon as formed and hence hypochlorite is produced.

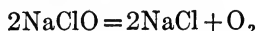
The hypochlorites either alone or when mixed with chlorides are good oxidizing and bleaching agents and also are excellent disinfectants. One very important use for bleaching powder is in the purification of water. This depends upon the fact that very small quantities of the substance will kill typhoid and other pathogenic bacteria without injuring the water for domestic purposes.

It is a rather difficult matter to separate sodium hypochlorite from the chloride, but when this is done the compound is found to be an electrolyte and hence in accordance with the theory of electrolytic dissociation is broken up into ions. The lowering of the freezing-point is about twice the normal amount so two ions are formed per mole of salt. Since the solution has one set of properties identical with those of other sodium salts, one of these ions must be sodium. The other then must be the rest of the salt and has the formula  $\text{ClO}^-$ .



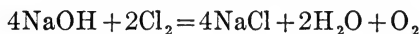
This ion  $\text{ClO}^-$  differs markedly in properties from the  $\text{Cl}^-$ . It is for example, a strong oxidizing agent and does not give a precipitate of silver chloride upon the addition of silver nitrate.

**Decomposition of Hypochlorites.**—As has been mentioned, hypochlorous acid and its salts are unstable and readily undergo change. Sodium hypochlorite, for example, slowly decomposes into the chloride and oxygen:



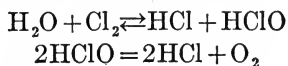
The addition of a small quantity of a cobalt salt results in the formation of a black precipitate of cobaltic hydroxide which acts

as a vigorous catalyzer for the decomposition of the hypochlorites. In this way oxygen may be easily obtained from bleaching powder. By adding some cobalt salt to sodium hydroxide solution and then passing in chlorine, a steady stream of oxygen may be obtained. This reaction may be represented as follows:

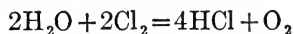


Mixtures of iron and copper sulfates work in practically the same way as cobalt salts and are used in the technical preparation of oxygen from bleaching powder.

This same decomposition of hypochlorites may be accelerated by light and takes place fairly rapidly in sunlight. The action of light on chlorine water finds an explanation from this fact. The chlorine acts on water for the formation of hypochlorous acid and hydrochloric acid, and the hypochlorous acid then decomposes into oxygen and hydrochloric acid:

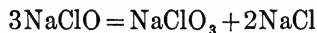


or combining,



This ability of hypochlorous acid and its salts to yield oxygen is closely connected with the oxidizing power of these compounds.

In addition to decomposing into oxygen and chlorides, hypochlorites change slowly into chlorates and chlorides. For example, sodium hypochlorite passes into sodium chlorate and chloride, as shown in the following equation:

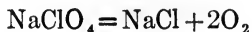


This change takes place more rapidly when the solution is heated and especially if the solution is acid or contains an excess of chlorine. An alkaline solution of a hypochlorite is fairly stable.

The chlorate formed as described above slowly changes into chloride and perchlorate and the latter in turn decomposes into chloride and oxygen. In order that the reactions shall take place at a reasonable rate the temperature must be far above the boiling-point of water, so to obtain them the dry salts are heated. The equations are



and



The final results are that after going through these stages the hypochlorite ultimately is changed completely into chloride and oxygen as is the case with the cold solution in the presence of a cobalt salt. The hypochlorite, chlorate, and perchlorate are unstable substances, while the chloride and oxygen are stable. Except in the presence of cobalt oxide, etc., the system sodium hydroxide and chlorine does not pass directly to its most stable state, sodium chloride, oxygen and water, but goes through a series of stages each more stable than its predecessor until the final stable condition is reached. In this respect, this system seems to be typical of many others which behave similarly. So generally is this the case that it is described in what is called Ostwald's *Law of Successive Reactions*, which states that *a system does not pass directly from the least stable to the most stable state, but does so through a series of steps or stages of gradually increasing stability.*

**Free Energy.**—We may well ask what determines whether a system shall be stable or not. If we turn to mechanical systems we find that these are stable when work must be done upon them in order to produce a change and unstable when they will change of themselves. Every such spontaneous change is able to do work upon other systems. *Energy which may be transferred from one system to another in the form of work is called Free Energy.* Systems other than mechanical systems possess free energy whenever they are unstable and undergo spontaneous change. In fact, we can make the general statement that every spontaneous change is accompanied by a decrease in free energy and hence may be made to do work. The factor then which determines whether a system shall be stable or not is the free energy. The unstable systems have free energy, and the more, the greater the instability. In a stable system the free energy has reached a minimum. All energy is not free energy. For example, there is a great store of heat in the ocean, but this cannot be used to drive the sea-going vessels. A gas at ordinary atmospheric pressure possesses the energy to do considerable work, but can do



nothing so long as it is at the pressure of its surroundings. If introduced into a space in which there is a much lower pressure it can do work. In the first case it had no free energy, while in the second it possessed a certain amount. Unless the pressure of the surrounding space be made and kept absolutely at zero, only a part of the energy due to the pressure of the gas can be transferred to other systems in the form of work and hence is free energy. From this we may see that whether a system possesses free energy or not depends largely upon the conditions under which it exists, and also that the total energy of a system is rarely all free energy. That part of the energy of a given system which is not transferable in the form of work to other systems is called latent or bound energy of the system; the total energy is the sum of the free and the bound energies of the system.

The change in the total energy accompanying a chemical reaction is measured by the heat of reaction. This represents the sum of the changes in the free and in the bound energies. If the reaction takes place of itself, the free energy decreases. The total energy, on the other hand, may or may not decrease because the bound energy is so far independent of the free that it may increase, decrease, or remain unchanged while the free is decreasing. If the bound energy increases more rapidly than the free energy decreases, the total energy of the system will increase during the spontaneous change and heat will be absorbed during the reaction.

That system then is not the most unstable which possesses the most energy, but is that which has the largest amount of free energy. It follows, too, from what has been said above, that the reaction which develops the most heat will not necessarily take place. As a rule, though, a decrease in the free energy is accompanied by a decrease in the total energy, so that most of the reactions occurring under ordinary conditions evolve heat.

Applying what we have just learned to the system  $\text{NaOH} + \text{Cl}_2$ , in the various stages, we learn that the initial substances have the most free energy, and with each step, hypochlorite, chlorate, perchlorate, this energy decreases until the system containing only  $\text{NaCl} + \text{O}_2$  is reached, when the free energy is at a minimum. This may be shown in the following diagram in which distances

plotted downward are made to represent decrease in free energy and the conditions which favor the changes are indicated (Fig. 21).

**Hypochlorous Acid.**—Hypochlorous acid is very volatile and will stand distillation, consequently it is easily prepared from its salts by the first general method, by adding to a hypochlorite a less volatile acid and distilling. The reaction must be carried out in rather dilute solution since the concentrated acid readily decomposes into water and chlorine monoxide,  $\text{Cl}_2\text{O}$ . Since hypochlorites are difficult to prepare pure, a mixture of hypochlorite and chloride is generally used. Hypochlorous acid,  $\text{HClO}$ , is a very much weaker acid than hydrochloric,  $\text{HCl}$ ,

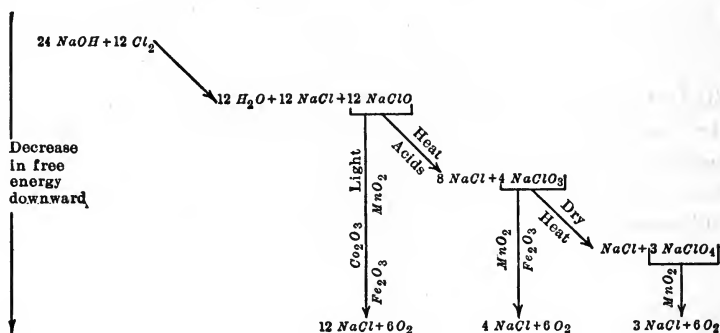
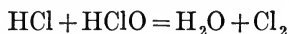


FIG. 21.

and is almost exclusively formed if a little less acid is added than the amount required to act upon the hypochlorite which is present. It is very important that an excess of acid be avoided since  $\text{HCl} + \text{HClO}$  react very rapidly to form  $\text{Cl}_2 + \text{H}_2\text{O}$ .



Bleaching powder is usually used to furnish the hypochlorite and nitric acid is the added acid, care being taken to add it a little at a time and to stir vigorously to avoid any local excess. The equation is



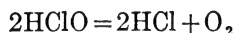
Instead of nitric acid one may use hydrochloric or still better, the very weak boric acid.

The hypochlorous acid formed is volatile and passes over with

the first part of the water. It may be still further concentrated by fractional distillation.

**Properties of Hypochlorous Acid.**—The pure acid cannot be prepared, so it is known only in solution. Its concentrated solutions have a yellow color and smell something like bleaching powder. In dilute solutions it is almost colorless. It neutralizes strong bases and forms hypochlorites.

It is unstable and decomposes in several ways. When warmed or exposed to sunlight, it may decompose into hydrochloric acid and oxygen.

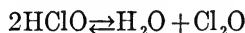


or it may change into hydrochloric and chloric acids.



This latter change takes place even in the dark.

In the two cases given above, hypochlorous acid acts like other hypochlorites, but hypochlorous acid differs in one respect from other hypochlorites, and that is, in very concentrated solution it will decompose into water and chlorine monoxide.



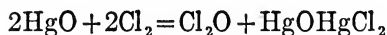
This reaction is reversible and hypochlorous acid is formed by the union of water and chlorine monoxide; consequently the latter is often called hypochlorous anhydride. An **anhydride** is an oxide which will combine with water to form an acid.

As has been mentioned, hypochlorous acid is a powerful oxidizing and bleaching agent, being more active in this respect than other hypochlorites. In fact, there is some little evidence that solutions of hypochlorites owe a part of their bleaching power to the presence in them of hypochlorous acid. Hypochlorous acid bleaches because it oxidizes and destroys the coloring matters which are usually very complex carbon compounds. Each of these compounds owes its color to a certain definite combination of its constituents, and when this combination is broken up by oxidation or otherwise the color is destroyed. Usually the reaction is too complex to be represented by an equation.

It will be recalled that chlorine was not active as a bleaching agent until the article to be acted upon was moistened. It is

probable that it is really the hypochlorous acid formed by the action of the chlorine on the water which does the bleaching. Cotton or linen goods are prepared for bleaching by boiling them in a soap solution for a time to remove grease and oils and then passing them through a dilute solution of bleaching powder and into very dilute sulfuric acid. The last two processes are repeated until the desired results are reached. The goods are then carefully washed to remove the excess of chemicals. The solutions must be very dilute and the operation carried out with care or a large part of the strength of the fabric will be destroyed. Even under the best conditions the cloth is considerably weakened. Wool, silk, and feathers are so greatly altered by chlorine, hypochlorous acid and hypochlorites, that they cannot be bleached by these substances.

**Chlorine Monoxide.**—Chlorine monoxide or hypochlorous anhydride is usually prepared not by the decomposition of hypochlorous acid which was mentioned above, but by the action of chlorine on mercuric oxide whereby mercury oxychloride and the chlorine monoxide are formed according to the following equation:



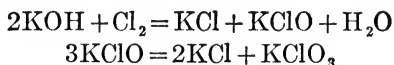
The mercuric oxide must be of a certain degree of fineness which may be obtained by precipitating a solution of mercuric chloride by sodium hydroxide, and heating the precipitate for a few hours to 300°–400° C. During the reaction the tube containing the mercuric oxide must be kept cool by ice or cold water.

The chlorine monoxide is a yellowish-brown gaseous substance which may be condensed to a liquid boiling at +5° C. Its odor is strong but distinctly different from that of chlorine. Both the gas and the liquid are explosive. The gas explodes upon being heated. The liquid explodes if an attempt is made to seal the tube in which it is liquefied, or if it be poured from one vessel into another, or even if the tube in which it is contained be scratched with a file. When brought in contact with an easily oxidizable substance like paper, explosion takes place. The gaseous substance is easily soluble in water. The solution contains hypochlorous acid and therefore this monoxide is also called hypochlorous anhydride.

**Chlorates.**—Chlorates are easily formed by heating solutions of hypochlorites as has been described above. The reactions take place most readily when the solutions are concentrated and slightly acid or contain an excess of chlorine.

Potassium chlorate is the most widely used and important of these salts, although sodium chlorate is taking its place for many purposes because the latter is more soluble.

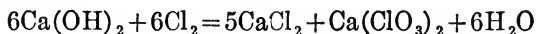
Potassium chlorate may be prepared by passing an excess of chlorine into a warm concentrated solution of potassium hydroxide. The reaction takes place in stages as in the formation of sodium chlorate, the hypochlorite being first formed. The equations are



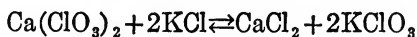
or combining into one and omitting the intermediate stage,



The chlorate is much less soluble than the chloride, so by concentrating the solution and allowing it to cool, the chlorate separates out mixed with only a little of the chloride, which may be removed by a second crystallization. As will be seen from the equation just given, only one-sixth of the somewhat expensive potassium hydroxide is converted into chlorate. The chloride formed at the same time occurs in nature in large quantities and has a comparatively small value. On a manufacturing scale, this waste is avoided by first preparing calcium chlorate,  $\text{Ca}(\text{ClO}_3)_2$ , by the action of an excess of chlorine upon hot calcium hydroxide.



Potassium chloride is then added to the solution in a little more than the required quantity to react with the  $\text{Ca}(\text{ClO}_3)_2$  according to the following equation.



This reaction is reversible and far from complete, but the potassium chlorate is only moderately soluble in cold water, while the potassium chloride is easily and the calcium chloride and chlorate

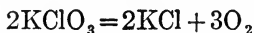
exceedingly soluble; so when the solution is concentrated and cooled,  $\text{KClO}_3$  passes out of solution in the form of crystals. As the potassium chlorate separates from the solution more is formed until finally the greater part of the chlorate has been obtained in the form of the potassium salt.

Chlorates are also very largely made by electrolysis, the process being very much like that for the preparation of hypochlorites, the main difference being that the solution is kept hot and very slightly acid, conditions which it will be recalled are favorable to the change of hypochlorites into chlorates.

**Properties of Chlorates.**—All chlorates are at least moderately soluble in water, and many are so very soluble that they are deliquescent. Potassium chlorate is one of the least soluble of these salts, 100 parts of water at  $0^\circ \text{C}$ . dissolve 3.14 parts of this salt. The solubility increases rapidly with rising temperature so that at  $100^\circ \text{C}$ . it is approximately eighteen times that at zero.

The chlorates all give off oxygen upon being heated and are strong oxidizing agents. Because of this property they are much used in making fireworks, explosives, matches, and in the manufacture of dyes. An intimate mixture of sugar,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , and potassium chlorate is sometimes used as a blasting powder, but like practically all other explosives containing chlorates, it is treacherous and dangerous to handle.

Potassium chlorate, it will be recalled, was used in the laboratory preparation of oxygen. The equation is,



The oxygen so prepared almost always contains a trace of chlorine.

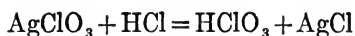
Like sodium chlorate, potassium chlorate if slowly and carefully heated will pass into potassium perchlorate,  $\text{KClO}_4$ :



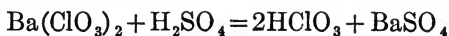
Although chlorates are good oxidizing agents, they are less powerful than the hypochlorites as would be expected from their smaller content of free energy.

**Preparation of Chloric Acid.**—Chloric acid cannot be distilled without decomposition and therefore cannot be prepared from its salts by the first general method for the preparation of acids. It is made by what is known as the second general method for the

preparation of acids from their salts which is briefly as follows: *Add to a solution of a salt of the desired acid another acid which is so chosen that the anion of the added acid shall form a very difficultly soluble compound with the cation of the salt.* This compound is at once formed and passes out of solution, leaving the hydrogen ion of the added acid and the anion of the salt in solution, that is, forming a solution of the desired acid. By careful evaporation, this acid may be then obtained in a pure or at least a more or less concentrated form. Of course the salt to be used, and the acid to be added must be very carefully chosen, and just the correct amount of each used. Even under these conditions, a perfectly pure solution of the acid is never obtained because there is no salt which is absolutely insoluble; but some are so nearly so that practically pure acids may be prepared in this way. Silver chloride and barium sulfate are among the least soluble of the salts, so silver chlorate,  $\text{AgClO}_3$ , with hydrochloric acid, or barium chlorate,  $\text{Ba}(\text{ClO}_3)_2$ , with sulfuric acid are well adapted for the formation of chloric acid according to the following equations:



and

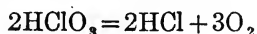


Barium chlorate is much cheaper than silver chlorate, so the latter reaction is the one usually used. The acid solution is filtered from the white precipitate of barium sulfate,  $\text{BaSO}_4$ , and concentrated by evaporation at a temperature below  $40^\circ \text{C}$ . until it has reached a density of 1.282 at  $14.2^\circ$  and contains 40 per cent. of the acid. The dilute solution is colorless while the concentrated has a yellowish tint. It is a strong acid.

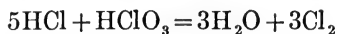
The solution slowly decomposes in a number of ways. It may form perchloric acid,  $\text{HClO}_4$ ,



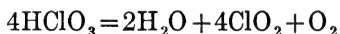
or break down into hydrochloric acid and oxygen,



The  $\text{HCl}$  so formed then reacts with more  $\text{HClO}_3$  to form chlorine and water,



In addition it may go over into water, chlorine dioxide,  $\text{ClO}_2$ , and oxygen.



Chloric acid has found no important application, but its salts are largely used.

**Separation of Salts.**—A solid salt generally separates from its solutions in the form of crystals, and the process of obtaining these is called crystallization. It is very evident from what has been learned, p. 75, that crystals cannot form in an unsaturated solution. In fact the solution must be more than saturated, supersaturated, before they can separate. But in the absence of the solid phase a solution may be considerably supersaturated without crystallization taking place.

Since most substances are more soluble at high temperature than at low, it is usually very easy to prepare supersaturated solutions by making a saturated solution at a somewhat elevated temperature and then cooling the solution after the removal of any excess of the undissolved solid. The cooled solution becomes supersaturated and may often be preserved for a long time in this condition by carefully excluding dust which usually contains enough small particles of the solute to bring about crystallization. Generally, however, it will spontaneously deposit crystals as soon as it reaches a certain degree of supersaturation. After the separation has once started it will continue until only so much of the solute remains dissolved as corresponds to its solubility at that temperature. If the supersaturated solution was prepared from crystals of the substance, the process of reobtaining the crystals is known as recrystallization, and is very commonly used in the purification of substances. The process of recrystallization which has just been outlined is especially adapted to the purification of such substances as change their solubility very rapidly with the temperature. Potassium chlorate is a good example. The process is not so well adapted to potassium chloride, and is of practically no value for things like sodium chloride which are almost as soluble in cold water as in hot (see Fig. 22). In such cases the only way to recrystallize the substances is to evaporate a part of the solvent which will of course cause a corresponding



amount of the solute to crystallize. Obviously all of the solvent should not be evaporated since this would leave the salt as impure as before.

When a mixture of salts is dissolved in water, the numerical value of the solubility of each salt is more or less altered but the general relationships are left unchanged. Before any given salt can crystallize, the solution must become supersaturated with that particular salt. As a general rule each salt tends to crystallize by itself, and if two or more separate at the same time, a mixture of crystals of the salts will be obtained rather than crystals, each of which contains every salt.

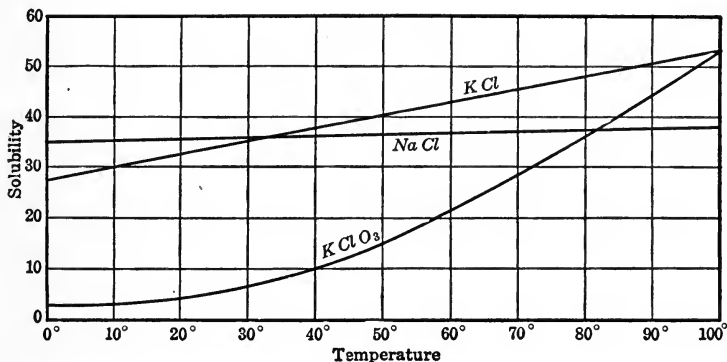


FIG. 22.

As a general rule, however, the solubility of the various salts in a mixture differs sufficiently so that a solution which is supersaturated for one will be unsaturated for the others, and in this case the one salt will separate in an approximately pure condition. The crystals usually enclose small portions of the solution from which they were formed, and this together with the fact that it is very difficult to free them from the adhering liquid is the chief source of their impurities. By recrystallization these may be reduced to any desired degree.

Upon the evaporation of a solution of a mixture of two salts, say for example KCl and KClO<sub>3</sub>, that salt will separate first whose point of saturation is first exceeded; in this case it is the KClO<sub>3</sub>, at ordinary temperatures if the salts are present in anything like equal quantities. By removing the crystals as

they are formed, they may be obtained in an approximately pure state. Ultimately as the concentration proceeds, the solution will become saturated with the other salt, KCl, and a mixture of crystals will then be formed. To secure a further separation, advantage is taken of the fact that the solubility of one salt changes faster with the temperature than that of the other, and the solution is concentrated at a higher temperature. Under these conditions the solution first becomes saturated with KCl and this substance crystallizes and is removed. When the point of crystallization of the  $\text{KClO}_3$  at this temperature is reached, the evaporation is stopped, all the solid KCl is removed and enough water added so that on cooling the solution shall not become supersaturated with KCl. The solution is then cooled, and at the lower temperature a crop of  $\text{KClO}_3$  crystals is obtained. The whole process is repeated as often as is necessary.

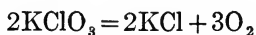
This general scheme is applicable to almost any pair of salts, but the details differ, and must be worked out for each case.

It is not necessarily the least soluble salt which separates first, but that one whose point of saturation is first exceeded. This may easily be the case with the more soluble salt if it is present in relatively large quantities.

**Perchlorates.**—Potassium perchlorate is easily prepared by heating potassium chlorate until it melts and then keeping it at this temperature for some time. A little oxygen is given off and solids begin to form in the molten salt. After a time the whole thing goes solid, although the temperature has not been lowered. The solid so formed is a mixture of potassium chloride, KCl, and potassium perchlorate,  $\text{KClO}_4$ . It is formed according to the following equation,



The evolution of the oxygen had nothing essentially to do with this reaction, and hence is not shown in the equation. It is formed by the side reaction,



The potassium perchlorate,  $\text{KClO}_4$ , is only slightly soluble, so it is easily separated from the potassium chloride, KCl, by finely powdering the mixture and dissolving out the potassium chloride

with cold water. A recrystallization of the residue from hot water yields pure potassium perchlorate,  $\text{KClO}_4$ .

The perchlorates are much more stable than the hypochlorites or chlorates, as corresponds with their smaller content of free energy. Upon being heated they yield oxygen and chlorides, and may also act as oxidizing agents. They are all more or less soluble in water, the potassium salt being one of the least soluble. Some of them are used in matches and fireworks because they are safer than the chlorates.

**Perchloric Acid.**—Perchloric acid is easily formed from the potassium salt by the first general method, using sulfuric acid and distilling under diminished pressure. Dense white fumes are evolved and a colorless or slightly yellow liquid distills consisting of pure perchloric acid,  $\text{HClO}_4$ , which condenses in the receiver. If the distillation be continued, aqueous acid comes over, and the liquid in the receiver changes into a white crystalline mass of perchloric acid monohydrate,  $\text{HClO}_4 + \text{H}_2\text{O}$ , which contains nearly 85 per cent. of the acid.

Mixtures of perchloric acid and water act like mixtures of hydrochloric acid and water in that there is a constant boiling mixture of minimum vapor pressure and maximum boiling-point. This is in accord with the fuming of the strong acid in contact with moist air. This mixture contains 72 per cent. of acid and boils at  $203^\circ \text{C}$ . It follows then that if the crystals of the monohydrate be redistilled, nearly pure perchloric acid will come over leaving the 72 per cent. residue boiling at  $203^\circ \text{C}$ . in the retort. By adding to this constant boiling mixture twice its volume of concentrated sulfuric acid, and distilling, pure perchloric acid may be obtained.

The pure acid is volatile, boiling at  $19^\circ \text{C}$ . under a pressure of 1.1 cm. of mercury; and has a density of 1.78. It is a good oxidizing agent and decomposes with great readiness so that when brought in contact with oxidizable substances it generally explodes with violence. When heated under atmospheric pressure it decomposes at  $92^\circ \text{C}$ . It dissolves in water with a hissing noise and the evolution of much heat. The aqueous acid of all strengths up to the constant boiling mixture is entirely stable. Unlike hypochlorous and chloric acids, it does not liberate chlorine from hydrochloric acid.

**Perchloric Anhydride.**—Perchloric anhydride,  $\text{Cl}_2\text{O}_7$ , may be prepared by adding to perchloric acid phosphorus pentoxide,  $\text{P}_2\text{O}_5$ , keeping the whole cool by a freezing mixture of ice and salt. After standing for a day the mixture is distilled. The anhydride is colorless and boils at  $82^\circ\text{C}$ . It may be distilled under ordinary pressure without danger, but explodes when struck or brought in contact with a flame.

**Chlorine Dioxide and Chlorites.**—As has already been mentioned chloric acid will decompose, for one way, into water, chlorine dioxide,  $\text{ClO}_2$ , and oxygen:

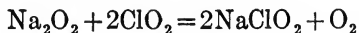


The most convenient way to prepare chlorine dioxide is to treat fine powdered potassium chlorate,  $\text{KClO}_3$ , with concentrated sulfuric acid which has been cooled with ice and salt. The mixture is then cautiously warmed to  $+20^\circ\text{C}$ . when the chlorinedioxide is evolved as a yellow-brown gaseous substance which may be condensed in a tube cooled with ice and salt, to a somewhat more intensely colored liquid. The boiling-point of the liquid is about  $10^\circ\text{C}$ . Both the liquid and its vapor are extremely explosive. The vapor explodes when brought in contact with a metal rod heated to a temperature far below redness. The products of the explosion are chlorine and oxygen.

When passed into sodium hydroxide solution, it yields a mixture of sodium chlorate and chlorite,  $\text{NaClO}_2$ .



If sodium peroxide is used instead of the hydroxide, chlorite and oxygen are formed.



The chlorites are all unstable substances for which no applications have been found. The acid is known only in dilute solutions.

The chlorites appear to stand between the hypochlorites and the chlorates in the order of stability, but the evidence is not entirely conclusive.

**Thermochemistry.**—It might very reasonably be thought that perchloric and chloric acids would be stronger oxidizing agents

than hypochlorous acid, because the former contain more oxygen per mole; but this is not the case. Hypochlorous acid is the strongest, and perchloric the weakest. This is due to the fact that hypochlorous contains the most free energy. The exact value of the change in the free energy, when each acid is decomposed into hydrochloric acid and oxygen, has not been determined, so the change in the total energy, the heat of decomposition, is given in the following table since this probably runs parallel to the change in the free energy.

Equation	Heat per combining wt. of O	
$2\text{HClO} = 2\text{HCl} + \text{O}_2 + 2 \times 39 \text{ Kj.}$	+ 39 Kj.	9300 cal.
$2\text{HClO}_3 = 2\text{HCl} + 3\text{O}_2 + 2 \times 64 \text{ Kj.}$	+ 21 Kj.	5000 cal.
$\text{HClO}_4 = \text{HCl} + 2\text{O}_2 + 0 \text{ Kj.}$	+ 0 Kj.	0 cal.

## CHAPTER XI

### BROMINE, IODINE AND FLUORINE

**General.**—Fluorine, chlorine, bromine and iodine form a group or family of elements which closely resemble one another in their chemical properties and those of the compounds which they form. This group is called the halogen family. From what is to follow, it will be seen that there is a regular change in properties of the halogens and their compounds as the combining weight of the element increases. It will also be very evident that chlorine, bromine and iodine resemble each other much more closely than they do fluorine. For this reason the discussion of chlorine will be followed immediately by that of bromine and iodine and fluorine will be taken up last.

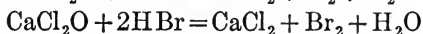
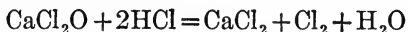
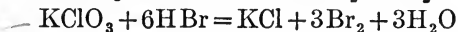
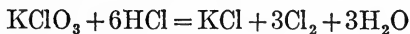
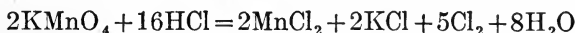
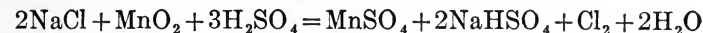
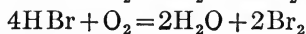
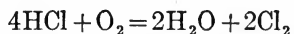
Bromine and iodine are so much like chlorine that a very fair knowledge of their chemistry may be easily obtained by comparison with that of chlorine, noting the many points of resemblance and the few differences. The root of most of these differences lies in the fact that bromine is liberated from its compounds by even weaker oxidizing agents than chlorine, and that iodine is still more readily set free than bromine.

#### BROMINE

**Occurrence.**—Like chlorine, bromine is never found free, but only in combination, chiefly as bromides of sodium, potassium, and magnesium. It is not nearly as abundant as chlorine, and its compounds are never found in anything like a pure state, but are always mixed with very much larger quantities of chlorides. It is found in sea water, many mineral springs, salt wells, and beds of rock salt. These beds of rock salt have doubtless been formed by the evaporation of sea water, so the presence of bromides in them is not surprising. The bromine content of salt beds differs rather widely, and naturally only the richer deposits are utilized as sources of bromine. The chief bromine-producing localities are Stassfurt, in Germany, and Michigan, Pennsylvania, and West Virginia, in the United States.

Bromine was discovered in 1826 by Balard in the residues left in the evaporation of water, from the Mediterranean Sea, for the preparation of common salt.

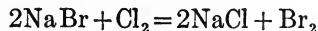
**Preparation of the Element.**—From the fact that bromine is more easily liberated than chlorine, it follows that any of the oxidizing agents used in the preparation of chlorine may be employed for bromine, so we may match each of the methods given in the preceding chapter for the preparation of chlorine by a similar one for bromine, as shown by the following equations:



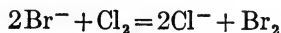
Electrolysis of chlorides and bromides yields respectively chlorine and bromine at the anodes.

Of these reactions, that between the bromides, manganese dioxide and sulfuric acid is the most important because the bromides are much cheaper and more easily obtained than hydrobromic acid.

In addition to the above, bromine is liberated by a number of oxidizing agents which cannot act on chlorides. The element chlorine is an oxidizing agent, not as powerful of course as the ones used to set it free, but still powerful enough to liberate bromine as shown in the following equation:

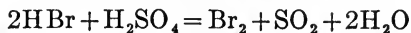


The reaction is really between the free chlorine and bromine as ion:



and consequently is an exchange of charges, and yet the liberation of bromine from a bromide is considered oxidation; so this kind of exchange of charges must be counted oxidation.

Concentrated sulfuric acid is a fairly strong oxidizing agent, strong enough to act on HBr, but not on HCl.



This last action must be kept in mind in the preparation of hydrobromic acid.

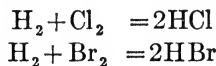
**Physical Properties of Bromine.**—Bromine is a dark, brownish-red liquid, which is almost opaque in thick layers, and has a density of 3.19. It boils at 59° C. and freezes at -7.3° C. The liquid produces very severe "burns" if it comes in contact with the skin. Bromine is an easily volatile liquid since its vapor pressure at ordinary temperature is about 20 cm. The vapor has a deep red color, an exceedingly stifling odor, and is very irritating to the mucous membrane. The name bromine is derived from the Greek word, *βρῶμος*, meaning a stench. The density of the bromine vapors is five times that of oxygen and indicates a molar weight of 160. Since the combining weight of bromine (79.92) is half the molar weight, its formula is Br<sub>2</sub>. At higher temperatures the molar weight becomes somewhat less, indicating a partial dissociation of the Br<sub>2</sub> into Br. Iodine shows this tendency still more strongly.

Bromine dissolves in water to the extent of about 3 parts by weight of bromine to 100 parts of water at ordinary temperature. The solution has a yellowish-red color, smells of bromine, and may often be used in the place of the latter when water does not interfere with the reactions. The solubility of bromine is markedly increased if the water also contains some soluble bromides. It is more soluble in carbon disulfide, alcohol, and many organic solvents than it is in water.

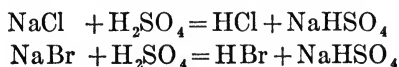
**Chemical Properties.**—The chemical properties of bromine are very much like those of chlorine, modified by the fact that it is slower and less intense in its action than the latter. It is a powerful oxidizing agent, though less so than chlorine. It combines directly with hydrogen and most of the other elements forming bromides. With water it forms a hydrate, Br<sub>2</sub>·10H<sub>2</sub>O, which, in general, is similar to chlorine hydrate.



**Hydrogen Bromide.**—With slight modifications due to the facts mentioned above, that bromine does not combine as vigorously with hydrogen as chlorine does, and that hydrogen bromide is more easily oxidized than hydrogen chloride, practically every method given in the preceding chapter for the preparation of hydrogen chloride may be matched by a corresponding one for hydrogen bromide. This is shown by the following equations,

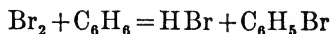


The mixture of hydrogen and bromine does not explode when exposed to sunlight or an electric spark, as that of hydrogen and chlorine does, but combines fairly rapidly at high temperatures under the influence of platinum as a catalyzer.

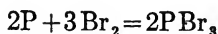


In this case dilute sulfuric acid must be used in the preparation of hydrogen bromide because the concentrated acid is a strong enough oxidizing agent to liberate the bromine.

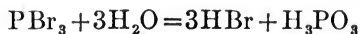
The indirect preparation of hydrogen bromide by the action of bromine upon compounds of hydrogen and carbon corresponds closely to that of hydrogen chloride by the action of chlorine upon these same compounds. For example, bromine and benzene,  $\text{C}_6\text{H}_6$ , react for the formation of hydrogen bromide and monobrombenzene,  $\text{C}_6\text{H}_5\text{Br}$ .



The method which is generally the most convenient for the preparation of hydrogen bromide is by the interaction at ordinary temperatures, of bromine, red phosphorus and water. The action takes place in steps. First the bromine and the phosphorus combine for the formation of phosphorus tribromide,  $\text{PBr}_3$ .



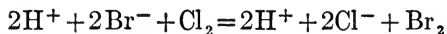
This then reacts with water to form phosphorous acid,  $\text{H}_3\text{PO}_3$ , and hydrogen bromide,  $\text{HBr}$ .



Hydrogen chloride might be prepared in an analogous way but the action is very violent and the method is not so cheap and convenient as that from salt and sulfuric acid.

**Properties of Hydrogen Bromide.**—Like hydrogen chloride, hydrogen bromide is a colorless gaseous substance at ordinary temperatures. Its critical temperature is  $91^\circ\text{C}$ . At low temperatures it condenses to a colorless liquid, boiling at  $-68.5^\circ\text{C}$ . and freezing at  $-86^\circ\text{C}$ . The gaseous density of hydrogen bromide shows that it has a molar weight of 81, and the formula HBr. It is very soluble in water, 600 volumes of HBr to one volume of water, and fumes when brought in contact with moist air, indicating that, like hydrogen chloride it forms a maximum boiling solution with water. The composition of this is 48 per cent. HBr, and it boils at  $126^\circ\text{C}$ .

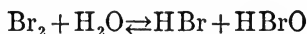
Like hydrogen chloride, dry hydrogen bromide is a rather indifferent substance, but when in solution in water it is as highly acid as hydrochloric acid and its solution is known as hydrobromic acid. It acts upon metals much as other acids do, forming hydrogen gas and solutions of the bromides of the metals. Speaking in terms of the ionic theory, solutions of hydrobromic acid and bromides contain the bromine ion,  $\text{Br}^-$ . The properties of this ion are very much like those of the chlorine ion. It is colorless, forms a very difficultly soluble compound with silver, silver bromide,  $\text{AgBr}$ , which is less soluble than silver chloride and has a slight yellow color. The liberation of bromine from the bromine ion by chlorine is the easiest way to distinguish the bromine ion from the chlorine ion. The equation for the reaction is



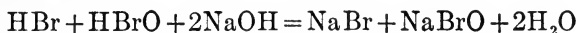
The free bromine colors the solution yellowish-red. If the solution be shaken with a little carbon bisulfide, the latter takes up most of the bromine from the water and becomes highly colored. This makes a very delicate test for bromine.

**Oxygen Compounds of Bromine.**—No one has, so far, succeeded in preparing oxides of bromine, perbromic acid, or perbromates, but hypobromous acid,  $\text{HBrO}$ , and bromic acid,  $\text{HBrO}_3$ , and

their salts are well known. The reactions for their preparation are exactly analogous to those for the corresponding chlorine compounds. The first step is the reversible reaction between bromine and water for the formation of hydrobromic and hypobromous acids,



When equilibrium results, the concentrations of the acids are even less than in the corresponding reaction for chlorine. The addition of sodium or potassium hydroxides will destroy the equilibrium by neutralizing the acids and cause the reaction to run toward the right until nearly all the bromine has been used up, and there results a solution of a mixture of the bromide and hypobromite salts.



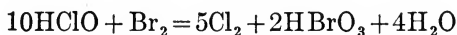
or, combining the two equations



The change of the hypobromites into bromates takes place even more rapidly upon heating, than the corresponding change of the hypochlorites. The equation is



Hypobromous acid is so unstable that even a dilute solution of it is hard to make and soon decomposes. Bromic acid may be made from its salts by the second general method for the preparation of acids, or by the action of hypochlorous acid upon bromine water:

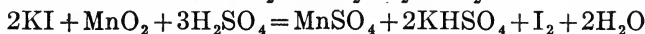
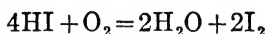


## IODINE

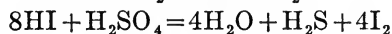
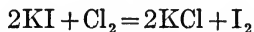
Iodine occurs in nature almost exclusively in combination, chiefly as iodides and iodates. It has, however, been found free in waters of certain mineral springs, having been liberated from hydriodic acid by the action of dissolved oxygen. This is in line with the fact that iodine is more easily liberated by oxidizing agents than either chlorine or bromine.

Iodides are found in sea water, but in much smaller quantities than bromides. Fairly large quantities of iodates, chiefly that of sodium, are found in the Chile saltpeter beds, and the greater part of the iodine of commerce is obtained from the mother liquor left in the purification of this crude sodium nitrate. The other source of iodine is from ashes of certain seaweeds gathered off the coast of Scotland and Ireland. These seaweeds have the notable property of taking up iodine from the water in which they grow and concentrating it in the form of complex compounds which yield sodium iodide when the plants are burned. They were formerly the main source of iodine, and it was in their ashes that the element was discovered by Courtois in 1812.

**Preparation of the Element.**—Iodine may be liberated from iodides by any of the oxidizing agents used for chlorine or bromine, and by some others in addition which are too feeble to serve in the other cases. A few of the equations are given below; others may be easily written by simply substituting the symbol "I" for "Cl" or "Br" in the corresponding equations for these elements:

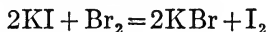


Like bromine, iodine may be liberated by the action of chlorine or strong sulfuric acid upon hydriodic acid or iodides:



Hydriodic acid is oxidized even more readily by sulfuric acid than hydrobromic is, and hence it is not possible to prepare hydriodic acid by the distillation of an iodide with sulfuric acid.

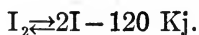
Just as free chlorine will liberate free bromine from hydrobromic acid or bromides, so bromine will set iodine free from the corresponding iodine compounds:



**Physical Properties of Iodine.**—At ordinary temperatures chlorine is gaseous, bromine liquid, and iodine solid; this shows a regular change in the physical state as the combining weight

increases. Iodine crystallizes in large rhombic plates, having a steel gray color and an almost metallic luster. It melts at  $114^{\circ}$  C., and boils at  $184^{\circ}$  C. The vapor has a beautiful violet color which is so strong that it can be seen in a bottle containing iodine at ordinary temperatures.

The vapor density of iodine at ordinary pressures and temperatures below  $700^{\circ}$  C. indicates a molar weight of 254. The combining weight of iodine is 126.92, hence the formula for iodine under these conditions is  $I_2$ . If the temperature be raised above  $700^{\circ}$  C. the molar weight gradually decreases until at about  $1700^{\circ}$  C. it becomes constant again at 127 corresponding to the formula I. Rise in temperature then above  $700^{\circ}$  C. has caused a reversible dissociation of  $I_2$  into I.



Below  $700^{\circ}$  C. iodine exists almost exclusively as  $I_2$ , above  $1700^{\circ}$  C., as I. At temperatures between these the equilibrium mixture contains notable quantities of both forms. As indicated above the transformation of  $I_2$  into  $2I$  is accompanied by the absorption of heat, 120 Kj. Knowing this fact it would follow from the law of mobile equilibrium that the dissociation would increase with increasing temperature. From this same law, since  $2I$  occupies a larger volume than  $I_2$ , other things being equal, it follows that the dissociation will increase with decreasing pressure. This has been confirmed by experiment. The color and absorption spectrum of I is different from that of  $I_2$ , and doubtless if the high temperature did not interfere with its study I would be found to be a strikingly different substance from  $I_2$ .

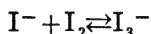
Iodine is but very slightly soluble in pure water, imparting to it a brownish color. It is much more soluble in alcohol, chloroform, and carbon bisulfide than in water. The alcoholic solution is brown, while that in chloroform or carbon bisulfide has the violet color of the vapor. Free iodine will dissolve in solid starch forming a solid solution having a strong blue color. This may be used as a very delicate test either for starch or iodine. In the latter case, it is carried out as follows: a suspension of finely divided starch in water is prepared by pouring boiling water over starch rubbed to a cream with a little water. Some of this is added to the solution suspected to contain iodine. If the latter

is free, the strong blue color of the starch iodide solution at once appears. If the iodine is not free, it is liberated by the cautious addition of a little chlorine water.

**Law of Distribution.**—As mentioned above, iodine is much more soluble in carbon disulfide (bisulfide) than in water. Carbon disulfide and water are not appreciably soluble in each other, and when brought together form two liquid layers, the carbon disulfide at the bottom. If now, some iodine be introduced, it will dissolve both in the water and the carbon disulfide, but to a far larger concentration in the latter. In fact, when equilibrium results it will be found that the weight of iodine per cubic centimeter in the carbon disulfide is 600 times that per cubic centimeter in the water.

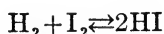
This is an example of the phenomenon described by the law of distribution which states that: *When two immiscible liquids are brought in contact with a third substance, soluble in each, this third substance distributes itself between the two solvents until its concentration in the one solvent bears a perfectly definite ratio to its concentration in the other.* In this case, the ratio of the concentration in the carbon disulfide to that in water is 600:1. This law holds only when the molar weight of the third substance is the same in each of the solvents.

**Chemical Properties of Iodine.**—The chemical properties of iodine are very much like those of chlorine and bromine except that it is much less active and is not so strong an oxidizing agent. It combines directly with hydrogen and many other elements for the formation of iodides. It does not form a hydrate with water. Iodine is much more soluble in solutions of iodides than in pure water. In many ways the solution acts as though the iodine were free, in others, it acts as though it were in combination. This is explained by assuming the existence in the solution of a complex ion,  $I_3^-$  formed by the reversible reaction shown below:



**Hydrogen Iodide.**—The slight difference in the methods for the preparation of hydrogen iodide from those for hydrogen chloride and bromide are due mainly to the fact that it is still less stable and more easily oxidized than the latter. It may be made by the direct combination of the elements. The action is, however,

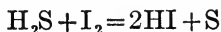
slow, reversible, and far from complete. It is catalyzed by platinum, but this simply brings about the equilibrium quicker without changing the composition of the equilibrium mixture. At 400° C., 80 per cent. of a mixture of equal volumes of hydrogen and iodine gases will be converted into hydrogen iodide, or 20 per cent. of pure hydrogen iodide will be decomposed; and this gaseous mixture will remain unchanged in composition so long as it is kept at this temperature. If increasing pressure is put upon this system, no change will follow because as shown in the equation



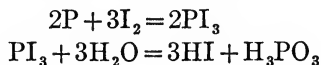
there is no change in volume as the reaction proceeds.

As mentioned above, the preparation of hydrogen iodide by the action of sulfuric acid upon sodium iodide is excluded because of the oxidizing action of the sulfuric acid. By using phosphoric acid instead of sulfuric, HI may be prepared by this method.

It may be made by the action of iodine upon hydrogen compounds. An aqueous solution of hydrogen iodide may be easily obtained by passing hydrogen sulfide into a suspension of iodine in water:



The most common method for the preparation of hydrogen iodide is by the interaction of iodine, phosphorus and water. Phosphorus tri-iodide is first formed and then decomposed by water giving hydrogen iodide and phosphorous acid:

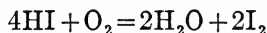


This is analogous to the best method for the preparation of hydrogen bromide.

**Physical Properties.**—Hydrogen iodide is a colorless gaseous substance much heavier than air since its molar weight is 128. It may be condensed to a slightly yellowish liquid, boiling at  $-36^\circ\text{C}$ . and freezing at  $-51^\circ\text{C}$ . Hydrogen iodide is very soluble in water; the solution saturated at  $0^\circ\text{C}$ . contains 90 parts by weight of hydrogen iodide to 10 parts of water. Like hydrogen

chloride and bromide, it forms a maximum boiling mixture with water which boils at 128° C. and contains 57 per cent. hydriodic acid.

**Chemical Properties.**—Hydrogen iodide is the least stable of the hydro-halides and is so easily oxidized that it is an excellent reducing agent. It burns in oxygen, reacts with chlorine with a flash of light and the formation of hydrogen chloride and free iodine. The liquid is a non-conductor of electricity and is inactive chemically. But the solution in water, hydriodic acid, is an excellent conductor of electricity and is a strong acid, being as active as a hydrochloric acid solution containing an equal number of gram moles per liter. When a colorless solution of hydriodic acid is exposed to the air, it takes up oxygen, quickly turns brown, and finally deposits crystalline iodine. The equation is as follows:



It is this reaction which gives the iodine in the rare cases mentioned above in which it occurs free in nature.

**Oxygen Compounds of Iodine.**—The oxygen compounds of iodine are, in general, much more stable than those of bromine. They are formed in analogous ways to the corresponding compounds of chlorine. The interaction of the halogen with water and a base gives an iodide and hypoiodite. The hypoiodites are even more unstable than the hypobromites, and very quickly pass over into the iodides and iodates.

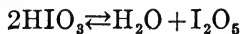
It will be recalled that iodine occurs in nature largely as sodium iodate in the Chile saltpeter beds.

Iodic acid may be prepared from iodates by the second general method, but is more readily obtained by the action of nitric acid upon iodine, as shown in the following equation:



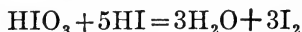
$\text{NO}_2$  is called nitrogen peroxide.

Iodic acid is a stable substance which crystallizes from its very concentrated solutions in lustrous crystals which are extremely soluble in water. The solution is a strong acid. By carefully heating the crystals, they decompose into water and iodine pentoxide,  $\text{I}_2\text{O}_5$ ,

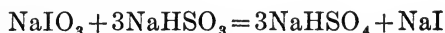




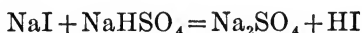
The action is reversible so that the pentoxide is also called iodic anhydride. Iodic acid is a fairly strong oxidizing agent and rapidly reacts with hydriodic acid to form iodine.



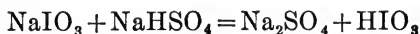
This action is made use of in the commercial extraction of iodine from the mother liquor of the Chile saltpeter. For this purpose sodium acid sulfite,  $\text{NaHSO}_3$ , is added to the solution when the following reaction takes place:



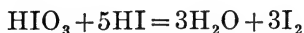
then



and

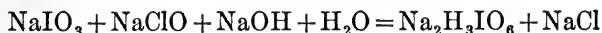


and finally



The iodine crystallizes out, is filtered off, dried and purified by sublimation.

**Periodates and Periodic Acid.**—When sodium hypochlorite in alkaline solution acts upon sodium iodate, rather difficultly soluble sodium periodate,  $\text{Na}_2\text{H}_3\text{IO}_6$ , separates out:



This is the disodium salt of orthoperiodic acid,  $\text{H}_5\text{IO}_6$ , which may be easily prepared by the second general method for the preparation of acids. As will be seen, this does not correspond very closely with perchloric acid,  $\text{HClO}_4$ . By long and careful heating to  $100^\circ\text{C}$ . in a vacuum the ortho acid,  $\text{H}_5\text{IO}_6$ , loses water and passes over into the meta acid,  $\text{HIO}_4$ . Further heating causes it to decompose into water, oxygen and the pentoxide. Orthoperiodic acid belongs to a class of substances known as the polybasic acids, because it contains per mole more than one combining weight of hydrogen replaceable by metals; and one mole of the acid will neutralize more than one mole of sodium hydroxide.

**Oxides of Iodine.**—Iodine forms two oxides, the tetraoxide,  $\text{I}_2\text{O}_4$ , and the pentoxide; the latter is the anhydride of iodic acid.

**Iodine Chlorides.**—Iodine and chlorine will combine directly for the formation of iodine monochloride,  $\text{ICl}$ , and the latter can then take up more chlorine forming the trichloride,  $\text{ICl}_3$ . Iodine monochloride exists in two modifications, one melting at  $14^\circ \text{C}$ . and the other at  $25^\circ \text{C}$ . Of these, the higher melting is the stable one under all conditions; and the lower melting one can be obtained and kept only in the absolute absence of the higher melting compound. After the latter has been formed, the only way to convert it back into the other form is to melt it and rapidly cool the liquid to below  $14^\circ \text{C}$ . when, in accordance with the law of successive reactions, the low melting and less stable form generally appears. Just below  $14^\circ$  either form may be obtained at will from the liquid by sowing it with crystals of the desired kind. When a substance can exist in more than one crystalline form it is said to be polymorphic, and the phenomenon is polymorphism.

The trichloride forms reddish-yellow crystals which decompose into chlorine and the monochloride before they melt when heated at ordinary pressures. Under a pressure of 16 atmospheres they melt at  $101^\circ \text{C}$ .

## FLUORINE

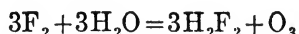
The combining weight of fluorine is 19, which is smaller than that of chlorine, and hence, logically, it should have been considered first; but as said before its properties are not as typical of the halogens as those of chlorine, and consequently it was left until this point.

**Occurrence.**—Fluorine never occurs free in nature, in fact it is one of the most difficult of the elements to liberate. It is generally found as calcium fluoride (fluor spar),  $\text{CaF}_2$ . Two other fairly common compounds are cryolite,  $\text{Na}_3\text{AlF}_6$ , and apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . These are all difficultly soluble, while the most abundant of the naturally occurring compounds of the other halogens have been easily soluble.

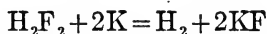
**History.**—The existence of fluorine as an element was established by Scheele in 1771, but the element itself was first isolated by Moissan in 1886.

**Preparation.**—As we passed from chlorine through bromine to iodine, it was noted that it became easier and easier to oxidize

the compounds, and so to liberate the elements, as the combining weight increased. This would lead us to expect that fluorine, the halogen with the smallest combining weight, would be the hardest to oxidize, and this is found to be true; in fact there is no oxidizing agent powerful enough to set the fluorine free. There remains then only one method for its preparation, electrolysis of a compound. Water must be absent because fluorine and water immediately react for the formation of hydrogen fluoride and ozone,



Anhydrous liquid hydrogen fluoride is almost a non-conductor of electricity, but it dissolves potassium acid fluoride readily; this salt dissociates into ions and the solution becomes a conductor. Fluorine is given off at the anode and hydrogen at the cathode. Possibly potassium is first liberated, and then reacts with the hydrogen fluoride,

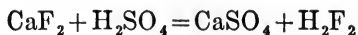


The electrolysis is carried out in a copper U-tube cooled to  $-23^\circ$  using platinum iridium electrodes.

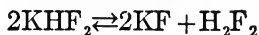
**Physical Properties.**—Fluorine is a gas having a greenish-yellow color much like that of chlorine only less intense. It liquefies at low temperatures, boils at  $-186^\circ$  and freezes at  $-223^\circ$ . Because of the very great activity of fluorine, it is difficult to determine its density; but the molar weight evidently is not far from 38, and since the combining weight is 19 the formula is  $F_2$ .

**Chemical Properties.**—Fluorine combines with all the elements except oxygen and the members of the argon group. Hydrogen fluoride is an especially stable compound and is instantly formed when fluorine is brought in contact with hydrogen even at a temperature of  $-252^\circ$  or with almost any hydrogen compound at ordinary temperatures. The reaction with water has been noted above. Fluorine and hydrogen chloride react for the liberation of chlorine; of course, it will react even more readily on hydrogen bromide and hydrogen iodide.

**Hydrogen Fluoride.**—Hydrogen fluoride may be easily prepared by distilling a fluoride, usually that of calcium, with sulfuric acid;



Here, of course, there is no difficulty caused by the oxidation of the hydrogen fluoride. But there is a complication due to the fact that hydrogen fluoride will readily attack glass, and hence the operation must be carried out in platinum or lead retorts. The anhydrous acid may be easily prepared by heating acid potassium fluoride in a platinum retort.



**Physical Properties.**—Hydrogen fluoride is a clear colorless liquid boiling at 19°. This is exceptionally high when compared with hydrogen chloride, etc. It dissolves readily in water, and like the other hydrogen halides forms a constant boiling mixture with water. This contains 35 per cent. hydrogen fluoride and boils at 120° C. The density of hydrogen fluoride vapors, at temperatures but little above its boiling-point, indicate a molar weight of 40, corresponding to  $\text{H}_2\text{F}_2$ ; at higher temperatures the density decreases, and from the boiling-point of water upward the molar weight is 20 and the formula HF. The existence of the compound  $\text{H}_2\text{F}_2$  is an important point of difference from the other hydrogen halides.

The formula  $\text{H}_2\text{F}_2$  indicates a dibasic acid. This is confirmed by the existence of potassium acid fluoride,  $\text{KHF}_2$ , and others of the same type. The neutral salt,  $\text{K}_2\text{F}_2$  or  $\text{KF}$ , is also well known.

The most remarkable property of hydrogen fluoride is its action on glass and other silicon compounds. When it acts on glass,  $\text{Na}_2\text{CaSi}_6\text{O}_{14}$ , gaseous silicon fluoride,  $\text{SiF}_4$ , and fluorides of sodium and calcium together with water are formed:



Use is made of this for etching designs on glass. The glass is first coated with wax, the design is scratched through, and then the whole exposed to the vapor or a solution of hydrogen fluoride. Because of this action, it is of course impossible to keep hydrofluoric acid in glass, but it may be kept in wax or gutta-percha bottles. The commercial acid is stored and shipped in lead containers.

The action of hydrofluoric acid on glass is not due to its being an especially strong acid, because when we come to examine its

action upon metals we find that a solution containing 20 grm. of hydrofluoric acid in 1000 grm. of water will act much more slowly on a given piece of zinc than will a solution containing 36.47 grm. of hydrochloric acid in the same amount of water; and yet each solution contains the same amount of hydrogen which is capable of being replaced by a metal.

The following table gives in a condensed form a summary of the more important of the properties of the halogens.

Formula of element	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub> , I
Combining weight.....	19	35.47	79.92	126.92
Physical state at ordinary temperature.	gas	gaseous	liquid	solid
Boiling-point.....	-186°	-33.6°	+59°	+184°
Freezing-point.....	-223°	-102.0°	- 7.3°	114°
Color.....	light yellow green	yellowish green	Brown red	Gray (vapor violet)
Oxidizing agent.....	strongest	very strong	strong	weak
Hydrogen compounds.....	H <sub>2</sub> F <sub>2</sub> - HF	HCl	HBr	HI
Physical state.....	gaseous	gaseous	gaseous	gaseous
Boiling-point.....	+19°	-83°	-68.5°	-36°
Freezing-point.....	-92.3°	-112°	-86°	-51°
Color.....	colorless	colorless	colorless	colorless
Solution in water.....	weak acid	strong acid	strong acid	strong acid
Action toward oxidizing agents..	unchanged	oxidized by strong	rather easily oxidized	very easily oxidized
Heat of formation Gaseous.....	161Kj.	92Kj.	35Kj.	-26Kj.
Heat of formation dissolved.....	205Kj.	165Kj.	118Kj.	+55Kj.
Heat of Neutralization NaOH....	68Kj.	57Kj.	57Kj.	57Kj.
Oxyacids.....	none	HClO HClO <sub>2</sub> HClO <sub>3</sub> HClO <sub>4</sub>	HBrO ..... HBrO <sub>3</sub> .....	HIO ..... HIO <sub>3</sub> H <sub>5</sub> IO <sub>6</sub>

This table shows that there are regular changes in a number of the properties of these elements as the combining weight increases. For example the boiling- and melting-points of the elements rise as the combining weight increases. The student will gain considerable information if he follows the other properties of these elements through in the same way.

Hydrogen fluoride has an abnormally high boiling-point. In this connection, it is significant that it alone of the hydrohalides ionizes solutes and that other ionizing solvents boil higher than their inactive analogues.

**Hydrolysis.**—Salts of weak acids or of weak bases when in solution in water act in a very peculiar manner. Their solutions are not neutral as are the salts of strong acids and bases, but the salts of weak acids are alkaline, while those of weak bases are acid in their reactions toward litmus. Since the salts themselves do not contain either the hydroxyl or the hydrogen ions, which give the solutions their reactions, the question of the source of these ions is one which calls for some little explanation. Evidently they must have come from the water. But why should the hydroxyl ion appear in a solution of a salt of a weak acid, and the hydrogen ion in the salt of a weak base when neither is prominent in a solution of a salt of a strong acid and base? The theory of electrolytic dissociation furnishes a satisfactory explanation.

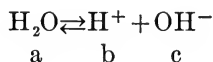
Pure water is a very poor conductor of electricity but it is not an absolute non-conductor. Its conductivity has been measured and indicates that water itself is dissociated to a slight extent so that 1 gm. of hydrogen and 17 gm. of hydroxyl as ion are present in eleven million liters of water. Expressing the concentration in terms of the number of gram ions per liter, the concentration of each of these substances is the same and they balance each other in their action on litmus.

Reactions between substances in the ionic condition tend to take place in such ways that the concentrations of the ions are reduced, either through the formation of substances which pass out of solution or those which are but slightly dissociated.

When a salt of a weak acid and a strong base, say sodium hypochlorite, is dissolved in water, there are present side by side sodium, hypochlorite, hydrogen, and hydroxyl ions. Hypochlorous acid is a very weak acid, and hence, but slightly dissociated, while sodium hypochlorite is highly dissociated. There is then a chance for a decrease in the ions by the union of the hydrogen and the hypochlorite ions, and this they are assumed to do to a certain extent. The solution would then contain sodium as ion, some hypochlorite, enough hydroxyl to make up for the hypochlorite ion which combined with hydrogen as ion, and undissociated hypochlorous acid. The undissociated hypochlorous acid of course does not redden litmus, while the hydroxyl ion turns litmus blue. So the solution reacts alkaline and it is

evident that a salt of any other weak acid should act in the same way.

When the hydrogen ion combines with the anion of the weak acid, not only is the hydroxyl left unbalanced in its action upon litmus, but the concentration of the hydroxyl increases. This comes from more of the water breaking up in an effort to keep up the concentration of the hydrogen. The equation for the ionization of water is



Letting a, b and c represent the concentrations of the water, hydrogen and hydroxyl ions respectively, the Mass law equation becomes

$$\frac{bc}{a} = \text{constant}$$

Now a is constant because it stands for the concentration of a homogeneous liquid, and hence the product bc is constant and as b decreases c must increase.

Salts of weak bases and strong acids react acid because of the combination of the cation of the salt with the hydroxyl of the water for the formation of the undissociated base, thus leaving the hydrogen as ion in excess.

The phenomena which we have just been discussing are included under the name of hydrolysis. Speaking in terms of the ionic theory we may say that hydrolysis consists in the formation of an undissociated acid or base by the action of water upon a salt of a weak acid or base.

Solutions of salts of strong acids and bases are neutral, because under these conditions there is no tendency for either hydrogen or hydroxyl to combine with an ion of the salt; so these salts do not hydrolyze.

#### VALENCE

The formulæ of some of the principal hydrogen compounds of the non-metallic elements are given in the following table:

HF	H <sub>2</sub> O	H <sub>3</sub> N	H <sub>4</sub> C
HCl	H <sub>2</sub> S	H <sub>3</sub> P	H <sub>4</sub> Si
HBr	H <sub>2</sub> Se	.....	.....
HI	H <sub>2</sub> Te	.....	.....

Several of these compounds have not been studied as yet, but they are introduced here simply to show the different types of combination.  $H_2S$  is hydrogen sulfide,  $H_2Se$  hydrogen selenide,  $H_2Te$  hydrogen telluride,  $H_3N$  or  $NH_3$  ammonia, and  $H_3P$  phosphine,  $H_4C$  or  $CH_4$  marsh gas,  $H_4Si$  silicon hydride.

From this table it may be seen that these compounds fall naturally into four groups according to the number of combining weights of hydrogen which unite with one combining weight of the other element. Each element is considered to have a certain combining power or valence which is measured by the *number* of combining weights of hydrogen or of an equivalent substance with which *one* combining weight of that element can unite to form a compound. This number is called the valence of the element. From the definition of valence, it follows that in the compounds given in the above table, fluorine, chlorine, bromine, and iodine are monovalent; oxygen, sulfur, selenium and tellurium divalent; nitrogen and phosphorus trivalent; while carbon and silicon are tetravalent. Hydrogen is our standard substance for measuring valence and is taken to have a valence of one or to be monovalent. Sometimes an element does not combine with hydrogen, and then of course it is not possible to work out the valence from the hydrogen compound, and in this case we must resort to some other method. One of these is to take a compound with some equivalent substance. *An equivalent substance is a substance one combining weight of which can unite with, replace, or be replaced by, one combining weight of hydrogen.*

A combining weight of sodium replaces one combining weight of hydrogen in the compound hydrogen chloride forming sodium chloride,  $NaCl$ , and is therefore monovalent; also one combining weight of silver is replaced from silver chloride,  $AgCl$ , by one combining weight of hydrogen, re-forming hydrogen chloride, therefore, silver is monovalent. Chlorine then in chlorides is determined to be monovalent: directly because it was originally combined with one combining weight of hydrogen in hydrogen chloride; indirectly because it is combined with one combining weight of the monovalent substances silver and sodium. Because chlorine in chlorides is monovalent, phosphorus in phosphorus trichloride,  $PCl_3$ , is trivalent, while in the pentachloride,  $PCl_5$ , it must be pentavalent. It is not necessary, however, that



we take a compound with a substance exactly equivalent to one combining weight of hydrogen; for once we have established the valence of any given element, it may in turn be used to measure that of others. One combining weight of oxygen is united with two combining weights of hydrogen in the compound water, hence oxygen is divalent and is commonly used as a standard for determining valence. Take for example, phosphorous trioxide,  $P_2O_3$ ; the six combining weights of oxygen have together a valence of twelve, which is divided between the four combining weights of phosphorus, showing that each combining weight of the latter has a valence of three. In the pentoxide,  $P_2O_5$ , the valence of the five oxygens is ten, which is divided between the two of phosphorus; and therefore in this compound the phosphorus has a valence of five, as in the pentachloride.

The examples just given show that the valence of an element is not a fixed constant. However, the number of valences belonging to any one element is generally small. Nitrogen has an unusually large number of valences, as may be seen from the following list of its oxides,  $N_2O$ ,  $NO$ ,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_5$ . In these it varies from monovalent to pentavalent. Comparatively few elements have more than two valences so that these magnitudes are not difficult to learn, and they are of great assistance in the formulation of compounds.

**Equivalent Weights.**—The conception of valence enables us to get easily another useful conception, that of equivalent weight. This is the number of parts by weight of an element which will combine with, replace or be replaced by 1.008 parts by weight of hydrogen, or 8 parts of oxygen. Or it may be defined as the combining weight of the element divided by its valence. For example, the equivalent weight of sulfur in hydrogen sulfide is  $32.07/2$ ; of nitrogen in ammonia is  $14.01/3$ ; of carbon in marsh gas is  $12/4$ . From the second form of the definition of equivalent weight, it is evident that an element has as many equivalent weights as it has valences.

These equivalent weights are like the combining weights in many respects, except that they represent directly without any multiple the proportions by weight in which the elements combine.

## CHAPTER XII

### SULFUR

**General.**—Sulfur is an element which has been known since prehistoric times. It occurs fairly abundantly in nature, both free and in compounds. The free sulfur is generally found in volcanic regions, but several deposits of non-volcanic sulfur are known, notably those of Louisiana which now furnish most of the sulfur used in the United States together with large quantities for export. In combination, sulfur occurs chiefly in the form of sulfates, such as gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Glauber salts,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and Epsom salts,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and as sulfides, pyrite,  $\text{FeS}_2$ , zinc blende,  $\text{ZnS}$ , and galena,  $\text{PbS}$ . It is present in combination in many portions of the animal and plant organisms.

In many of its chemical properties, sulfur shows rather close relationship to oxygen. Like oxygen it is able to assume allotropic forms, and is somewhat remarkable for the large number of such modifications which are known to exist, two and probably more crystalline modifications, two liquid, and at least two gaseous forms.

**Extraction of Sulfur.**—Most of the sulfur from volcanic sources comes from Sicily where it is found in large quantities mixed with limestone, gypsum, celestite and other minerals. The sulfur is extracted from the ore by heating in oven-like kilns or cells made of masonry. The greater part of the heat is furnished by burning coke which is mixed with the ore and charged into the cells. Of course, part of the sulfur burns. Economy of fuel is secured by arranging the cells in batteries of two or more and passing the gases from the one in action into a freshly charged cell in order that the waste heat from the first may warm the charge in the second. The sulfur melts and runs down to the floor of the cell from which it is drawn off and cast into conical wooden moulds forming the roll sulfur or brimstone of commerce. In some more recent installations the sulfur is extracted by melting it out with high-pressure steam. This method is being used with success in some rather recently developed mines in Mexico.

In Louisiana, the sulfur is obtained by drilling down about 500 ft. to the sulfur-bearing deposits and forcing down into the holes water heated to a temperature of  $168^{\circ}$  which is far above the melting-point of sulfur ( $120^{\circ}$ ). The water must, of course, be under pressure of about seven atmospheres to reach this temperature. The sulfur melts and collects at the bottom of the hole; from there it is pumped out by compressed air. The sulfur can be obtained in this way very cheaply, and is more than 99.5 per cent. pure. A single well often yields 500 tons of sulfur per day and the entire mine has produced 122,000 tons in two months which is more than the world's consumption for that period. The production of sulfur in the United States in 1910 was 255,534 long tons.

**Purification of Sulfur.**—When it is necessary to purify roll sulfur, the process of distillation is employed. The sulfur is boiled in iron retorts and the vapor is condensed in large brick chambers. At first when the walls of the chamber are cool, the sulfur condenses in the form of a rather fine powder, and is put on the market under the name of flowers of sulfur. When the chamber becomes heated from the heat of condensation of the sulfur, the latter collects in the form of a liquid and is drawn off into moulds as before.

**Crystalline Forms of Sulfur.**—Crystals of rhombic or  $\alpha$  sulfur are found in nature and may be easily prepared by dissolving sulfur in carbon disulfide, in which it is readily soluble, and allowing the solution to evaporate slowly. The sulfur is deposited in octahedral-like crystals which have a density of 2.07, and melt to a clear yellow liquid at  $114.5^{\circ}$ . If the clear crystals are kept for some time at temperatures between  $100^{\circ}$  and the melting-point they gradually become opaque and brittle, and when this change is complete, will melt at  $120^{\circ}$  instead of  $114.5^{\circ}$ , and have a density of 1.96 instead of 2.07. They then have undergone a transformation into  $\beta$  or monoclinic sulfur. This change is hastened by scratching the rhombic crystals with some hard point or by simply touching them with a monoclinic crystal.

Well defined crystals of monoclinic sulfur are easily obtained by melting some sulfur and allowing it to cool until a crust has formed on top. A hole is then made through this, and the still molten sulfur is poured out. The sides and bottom of the vessel

will then be found covered with long needle-shaped monoclinic crystals. When first formed the crystals are amber colored, and may be bent slightly without breaking. They melt at  $120^{\circ}$  and have a density of 1.96. If the crystals are kept at temperatures of  $100^{\circ}$  or above, they retain their properties indefinitely, but if kept at ordinary temperatures for a day or so they change color to the lemon yellow of ordinary sulfur, become opaque, and increase in density to 2.07, in short they change into  $\alpha$  or rhombic sulfur. This transformation is hastened by contact with rhombic crystals. The external form of the crystals is that of the monoclinic, while internally they consist of an aggregation of rhombic crystals. Such crystals as these, which are internally of one form and externally of another, are called pseudomorphs.

**Transition Point.**—The facts given above indicate that the monoclinic form is stable at higher temperatures while the rhombic is at lower. There must be then a temperature at which they are both stable. This temperature is  $96^{\circ}$  and is called the transition point of these modifications of sulfur. From  $96^{\circ}$  to  $120^{\circ}$  the monoclinic modification is stable while the rhombic is stable below  $96^{\circ}$ .

At  $96^{\circ}$  the two modifications are in equilibrium, and hence have the same vapor pressure, solubility, etc. The monoclinic can exist below  $96^{\circ}$ , but in an unstable state and under these conditions it is more soluble than the rhombic and has a higher vapor pressure. Correspondingly, above  $96^{\circ}$  the rhombic is the unstable form and has the greater solubility and vapor pressure. These are simply examples of the general rule that the less stable modification has the higher solubility and vapor pressure.

Although unstable, the monoclinic sulfur can exist for a time below  $96^{\circ}$  and the rhombic above this temperature. This is due to what is called suspended transformation and is much the same phenomenon as the supercooling or superheating of water.

**Influence of Pressure on Transition Point.**—The system monoclinic sulfur, rhombic sulfur, and vapor constitute a one component system with three phases and no degrees of freedom. Its triple point is a very little lower than the transition point,  $96^{\circ}$ . If the vapor be excluded, there will be one degree of freedom; or the solid modifications can be made to exist in equilib-

rium at different temperatures by changing the pressure. The rhombic form has the greater density and the smaller extensivity, and therefore it will tend to form upon increasing the pressure; hence the transition point is raised with the pressure. The rise amounts to  $.05^\circ$  for each additional atmosphere of pressure. The highest transition point is  $151^\circ$  under a pressure of 1288 atm.; above this temperature only rhombic sulfur can exist in the solid state. At  $151^\circ$  and 1288 atm., the three phase monoclinic, rhombic, and liquid sulfur can exist in equilibrium, so this is one of the triple points of sulfur; two others are at the melting-points under the pressure of their vapor of rhombic and monoclinic sulfur respectively.

**Enantiotropic and Monotropic Substances.**—Substances, which like sulfur exist in two modifications, one stable above, and the other below a certain temperature, and which are capable of changing back and forth in either way into one another, are called enantiotropic substances; while such as iodine monochloride which form two modifications, one stable and the other unstable under all conditions, and which can change only in one direction, are called monotropic substances.

**Other Forms of Sulfur.**—Several other crystalline forms of sulfur are known, but they are all of rare occurrence, and unstable with respect to rhombic and monoclinic modifications, and will not be discussed in detail.

Another commercial form of the element is that called milk of sulfur or lac sulfuris. This is a very fine, almost white powder. It is prepared by boiling sulfur with slaked lime. The reddish-brown solution thus obtained is made acid with hydrochloric acid, when the sulfur is precipitated.

**Liquid Sulfur.**—Monoclinic sulfur melts at  $120^\circ$  to a light yellow, mobile liquid, which on cooling passes back into monoclinic crystals. If, however, the temperature be raised to  $160^\circ$  the liquid suddenly becomes dark in color and so viscous that the vessel may be inverted without the contents running out. At  $180^\circ$  the maximum viscosity is reached; at  $260^\circ$  the viscosity begins to decrease noticeably, and at  $448.5^\circ$ , the boiling-point of sulfur, the liquid is mobile once more.

The cause of this remarkable change at  $160^\circ$  is the appearance of a new form of liquid sulfur called  $\gamma$  sulfur. When the dark

colored liquid is slowly cooled the reverse change takes place, and the light yellow form reappears.

**Amorphous Sulfur.**—By heating sulfur which has been exposed to the air and hence contains traces of sulfuric acid and sulfur dioxide, or better still that which contains traces of iodine, to temperatures near its boiling-point and suddenly cooling the mass by pouring it in a thin stream into water, a clear, transparent, plastic, semi-fluid substance is obtained, which is called plastic sulfur. After a few days it becomes hard and opaque and is then found to consist of a mixture of rhombic crystals, soluble in carbon disulfide, and another form of sulfur which is insoluble in carbon disulfide. It is not crystalline and hence is called amorphous sulfur. It is supercooled sulfur, and changes slowly into the crystalline variety. The change takes years for completion at ordinary temperatures, but is finished in an hour at 100°.

There is another amorphous modification, soluble in carbon disulfide, and also soluble in water.

**Molar Weight.**—At 448.5° sulfur boils. The vapor has an orange yellow color when just above its boiling-point. At 500° it is a deep red and then becomes lighter until at 650° it is a light yellow. The molar weight at temperatures near the boiling-point is 230 and gradually falls until at 1000° it reaches 64 and remains constant at this figure as the temperature is raised. Since the combining weight of sulfur is a trifle over 32, the molar weight of 230 would correspond to a formula of something between  $S_7$  and  $S_8$ , while that of 64 indicates a formula of  $S_2$ . The intermediate molar weights may be produced by mixtures of the  $S_8$  and  $S_2$  modifications or there may possibly be such forms as  $S_6$  and  $S_4$ . The molar weight of the element in solution as determined from the lowering of the freezing-point shows that when dissolved it has the formula  $S_8$ .

**Physical Properties of Sulfur.**—Most of the more important physical properties of sulfur have already been given. In addition, it may be said that with the exception of the one amorphous modification noted above, all forms are practically insoluble in water, but most of them are soluble in carbon disulfide, turpentine, and ether.

**Chemical Properties of Sulfur.**—Most all metals when finely

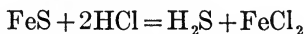
powdered and rubbed in a mortar with sulfur combine directly with the latter to form sulfides. At higher temperatures, the combination takes place so rapidly and with the evolution of so much heat that the general phenomena of combustion, the production of light, etc., are exhibited. The element will also unite with many of the non-metals; the halogens, hydrogen, and oxygen for example.

With oxygen it forms the two very important compounds, sulfur dioxide,  $\text{SO}_2$ , and sulfur trioxide,  $\text{SO}_3$ , and the much less important compounds  $\text{S}_2\text{O}_3$  and  $\text{S}_2\text{O}_7$ .  $\text{SO}_2$  and  $\text{SO}_3$  are the anhydrides of sulfurous and sulfuric acids respectively. With hydrogen it forms the important compound hydrogen sulfide,  $\text{H}_2\text{S}$ .

**Uses of Sulfur.**—Thousands of tons of sulfur are used in the manufacture of sulfur dioxide which in turn is used for making sulfuric acid, in bleaching straw, wool, feathers, etc., and as a germicide. Sulfur is also employed in making carbon disulfide, gunpowder, matches, fireworks, sprays for fruit trees, and vulcanized rubber.

**Hydrogen Sulfide.**—Hydrogen sulfide is a gaseous substance whose molar weight is found to be 34.09 and whose formula is  $\text{H}_2\text{S}$ . It occurs in nature in the gases of some volcanoes, and is found in many mineral waters, which are commonly called sulfur waters. It may be prepared by the direct union of the elements by passing a stream of hydrogen through boiling sulfur. The reaction is not as complete as it is at somewhat lower temperatures, but the action takes place much more rapidly.

Hydrogen sulfide is usually prepared by acting upon a sulfide, generally ferrous sulfide,  $\text{FeS}$ , with either dilute sulfuric or hydrochloric acids. The equation is



The ferrous sulfide is not very soluble in water but what does dissolve is largely broken up into ferrous and sulfur ions. Upon the addition of the acid, the sulfur ion unites with the hydrogen to form the very slightly dissociated compound hydrogen sulfide,  $\text{H}_2\text{S}$ . The water soon becomes saturated with this and then the substance is evolved in the gaseous state. The conditions are

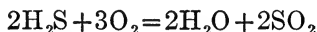
especially favorable for reaction in this case because we have a substance formed which is both slightly dissociated, and only moderately soluble. As fast as the sulfur ions present in solution are used up, more ferrous sulfide dissolves to keep up the supply. So the process continues until either the ferrous sulfide or the acid is used up.

Hydrogen sulfide is also formed during the decay of albuminous substances such as eggs, etc. The odor of such substances under these conditions is partly due to its presence.

**Physical Properties.**—As has been mentioned, hydrogen sulfide is at ordinary temperatures a colorless, gaseous substance whose molar weight is 34.09. Its critical temperature is  $100^{\circ}$ , so it can be liquefied by pressure alone at ordinary temperatures. The critical pressure is 90 atmospheres. It boils at  $-61^{\circ}$  and freezes at  $-83^{\circ}$ . The liquid is chemically inactive. Hydrogen sulfide has a very disagreeable odor much like that of rotten eggs, and acts as a powerful narcotic poison when inhaled. Very dilute chlorine gas is used as an antidote. The inhalation of very moist air or a cloud of so-called "steam" produced by allowing steam to escape into the air in the vicinity of the person overcome by hydrogen sulfide is said to be very effective as a method of treatment for hydrogen sulfide poisoning.

Hydrogen sulfide is somewhat soluble in water. One volume of water dissolves 4.37 volumes at  $0^{\circ}$  and 3.23 at  $15^{\circ}$ . The solubility follows Henry's law *that the volume of a given gas dissolved by a fixed mass of a solvent is independent of the pressure, while the mass of the gas dissolved is directly proportional to the pressure.*

**Chemical Properties.**—Hydrogen sulfide burns in air with a pale blue flame, forming water and sulfur dioxide,  $\text{SO}_2$ ,



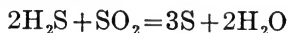
The equation shows that two volumes of  $\text{H}_2\text{S}$  require three volumes of oxygen for complete combustion. When mixed in these proportions the two gases explode violently upon the passage of an electric spark.

When the hydrogen sulfide is burned with an insufficient supply of air, water and free sulfur are the main products. This fact is



taken advantage of for the recovery of sulfur from certain classes of waste products which will easily yield hydrogen sulfide.

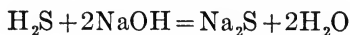
With sulfur dioxide, hydrogen sulfide rapidly reacts for the formation of sulfur and water,



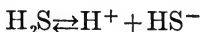
This is probably one of the reactions which gives rise to the volcanic sulfur.

When heated to 300° it is slightly decomposed into hydrogen and sulfur, and at a white heat the decomposition is practically complete. At each temperature, there is a certain mixture of hydrogen, sulfur, and hydrogen sulfide, at which equilibrium results.

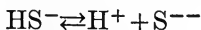
**Solution in Water.**—A solution of hydrogen sulfide in water acts slightly acid toward litmus, and hence is sometimes called hydrosulfuric acid. Hydrogen sulfide is a very weak acid, and is but slightly dissociated. It differs materially from the acids which we have discussed in any detail, in that the two combining weights of hydrogen per mole of hydrogen sulfide are both replaceable by metals and hence are ionizable. This state of affairs is described by the term dibasic, which means that one mole of the acids contains two combining weights of replaceable hydrogen, and will react with two moles of a base like sodium hydroxide,



**Dissociation of Dibasic Acids.**—Hydrogen sulfide like all other dibasic acids, shows a marked tendency to ionize in such a way that only one hydrogen per mole is split off, as shown by the following equation,



This ionization is especially prominent in concentrated solutions. As the solution is diluted or still better as the concentration of the hydrogen ion is reduced by neutralization with a base the hydrosulfide ion,  $\text{HS}^-$ , breaks up into hydrogen and sulfur as ions,

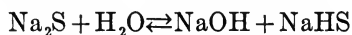


As a result of this tendency of dibasic acids, it is possible to ob-

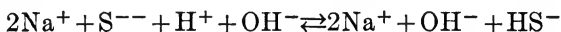
tain two series of salts of these acids according as the one or both hydrogen ions are replaced by metals. For example, we have the compounds NaHS and Na<sub>2</sub>S. The compound NaHS is often called sodium hydrosulfide from its resemblance to sodium hydroxide, NaOH, while Na<sub>2</sub>S is called sodium sulfide. Several other names for the same compounds are in common use as shown by the following table:

NaHS	Na <sub>2</sub> S
Acid sodium sulfide	Neutral sodium sulfide
Primary sodium sulfide	Secondary sodium sulfide
Mono-sodium sulfide	Di-sodium sulfide

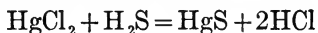
The terms acid and neutral sodium sulfide are rather deceptive, since the so-called acid salt is really just about neutral in its action upon litmus, while the neutral salt is decidedly alkaline. This latter effect is due to hydrolysis which is nearly complete in the case of Na<sub>2</sub>S according to the equation



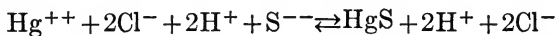
or



**Analytical Reactions of Hydrogen Sulfide.**—The sulfides of many of the metals are very slightly soluble in water and are consequently precipitated when hydrogen sulfide is passed into aqueous solutions of their salts. For example, a solution of mercuric chloride, HgCl<sub>2</sub>, gives a black precipitate of mercuric sulfide, HgS, with hydrogen sulfide,



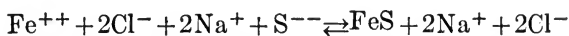
or



Salts of copper, lead, bismuth, antimony, tin, and several other metals act in the same way, and their sulfides are so difficultly soluble that they will be formed even in fairly acid solution.

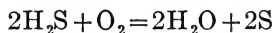
Other sulfides are more soluble, and require a higher concentration of sulfur as ion for their formation. This can be obtained by taking advantage of the fact that salts of weak acids are highly dissociated, and using instead of hydrogen

sulfide, sodium or ammonium sulfide. For example, ferrous sulfide is not precipitated by hydrogen sulfide, but is by sodium sulfide,



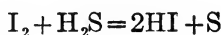
Use is made of these properties of the sulfides to separate the metals into groups according to similarities in their behavior, and this together with the fact that many of the sulfides have distinctive colors, makes hydrogen sulfide an exceedingly important reagent.

**Hydrogen Sulfide as a Reducing Agent.**—An aqueous solution of hydrogen sulfide when exposed to the air loses its odor and becomes milky, finally depositing a white precipitate of milk of sulfur. This is formed by the oxidation of the hydrogen sulfide by the oxygen of the air,

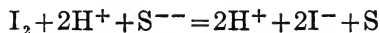


The oxygen oxidizes the hydrogen sulfide, and the latter reduces the oxygen.

When hydrogen sulfide is passed into water in which iodine is present a solution of hydriodic acid is obtained together with free sulfur,



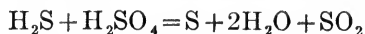
or expressed as ions,



In this case the action is easily seen to be between the sulfur ion and the thing reduced—the iodine. Upon examination of the other cases in which hydrogen sulfide acts as a reducing agent, it will be found that in the majority of cases the action consists in the transformation of the sulfur as ion into free sulfur, and that the hydrogen has nothing to do with it.

Dry hydrogen iodide will react with sulfur for the formation of hydrogen sulfide and iodine, apparently just the reverse of the above reaction. The explanation for the difference in the action may be found in the formation of hydrogen and iodine as ions in the aqueous solution and that these ions are much more stable than the hydrogen iodide.

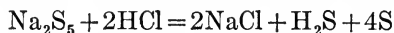
Hydrogen sulfide will reduce concentrated sulfuric acid to water and sulfur dioxide, sulfur being set free,



Because of this action, concentrated sulfuric acid cannot be used to dry hydrogen sulfide.

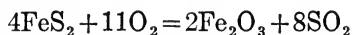
**Polysulfides.**—When a solution of a soluble sulfide or acid sulfide is brought in contact with sulfur, the latter is dissolved and the solution becomes dark yellow in color. If sodium sulfide is used, compounds  $\text{Na}_2\text{S}_2$ ,  $\text{Na}_2\text{S}_3$ ,  $\text{Na}_2\text{S}_4$ , and  $\text{Na}_2\text{S}_5$  may be obtained. Only the compounds  $\text{Na}_2\text{S}_4$  and  $\text{Na}_2\text{S}_5$  are at all well characterized and hence the others may be mixtures of one or both of these with  $\text{Na}_2\text{S}$ . These substances are called polysulfides. They are salts and yield ions which are  $\text{Na}^+$  and anions which vary in composition from  $\text{S}^{--}$  or  $\text{HS}_2^-$  to  $\text{S}_5^{--}$  or  $\text{HS}_5^-$ .

**Hydrogen Persulfide.**—If an acid is added to a polysulfide solution, hydrogen sulfide is evolved and lac sulfur is deposited,



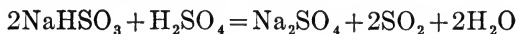
On the other hand if the polysulfide is added to an excess of the acid, neither hydrogen sulfide nor sulfur is formed, but drops of a yellow oil, which is hydrogen pentasulfide or hydrogen persulfide,  $\text{H}_2\text{S}_5$ , fall to the bottom of the vessel. When pure and dry, hydrogen persulfide is nearly colorless, and fairly stable. In the presence of water, it decomposes rather rapidly into hydrogen sulfide and sulfur. It is a good solvent for sulfur.

**Sulfur Dioxide or Sulfurous Anhydride.**—Sulfur dioxide, at ordinary temperatures, is a gaseous substance which is present in the gases given off by many volcanoes. It is formed, as we have seen, by burning sulfur or hydrogen sulfide in the air. It may also be prepared by roasting metallic sulfides, pyrite,  $\text{FeS}_2$ , for example, in the air. When these are raised to the required temperature they burn, forming sulfur dioxide,  $\text{SO}_2$ , and the oxides of the metals,

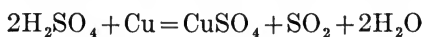


Many of the metals are obtained from their sulfides and such a roasting process is generally a necessary preliminary to the reduction to the metal.

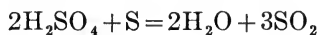
Sulfur dioxide may be very conveniently prepared by the action of acids upon sulfites or acid sulfites. Under these conditions we should expect the formation of sulfurous acid,  $\text{H}_2\text{SO}_3$ , and this is doubtless formed first but breaks down into water and  $\text{SO}_2$ . The most convenient laboratory method for its preparation is based upon this, sodium acid sulfite,  $\text{NaHSO}_3$ , and strong sulfuric acid being used:



It is often prepared by the action of reducing agents upon concentrated sulfuric acid. The most suitable ones are perhaps metallic copper or free sulfur, the equations being:



or



A good deal of sulfur dioxide is prepared for technical purposes by acting upon concentrated sulfuric acid with carbon,



The presence of the carbon dioxide mixed with the sulfur dioxide usually makes this method unsuitable for laboratory purposes. The greater part of the sulfur dioxide which is used in the arts is made by burning sulfur or pyrites.

**Composition.**—When sulfur is burned in oxygen, the volume of the sulfur dioxide formed is practically equal to that of the oxygen consumed. This shows that one mole of sulfur dioxide contains two combining weights of oxygen. Since the molar weight of sulfur dioxide is about 64, and 32 parts of this are oxygen, the other 32 parts are sulfur. As the combining weight of sulfur is 32, this shows that a mole of sulfur dioxide contains one combining weight of sulfur and two combining weights of oxygen, and has the formula  $\text{SO}_2$ .

**Physical Properties.**—Sulfur dioxide is a colorless gaseous substance with a strong odor which is familiar as the odor of burning sulfur. Its critical temperature is  $156^\circ$  and the critical pressure is 79 atmospheres. It may then be liquefied by pressure alone at ordinary temperatures. At  $20^\circ$  a pressure of 3.24 atmospheres is required. Since its boiling-point is  $-10^\circ$ , it may

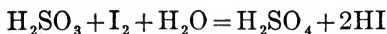
be easily liquefied by a mixture of ice and salt. The liquid is as clear and colorless as water. It is a fairly good solvent and is able to ionize many salts, though to a smaller extent than water. Its freezing-point is  $-73^{\circ}$ . The solid sulfur dioxide is a white, snow-like substance. Liquid sulfur dioxide is now an article of commerce, being sold in metal cylinders from which it may be removed as desired.

At ordinary temperatures sulfur dioxide deviates widely from the gas laws—a fact which is connected with its ease of liquefaction. It is rather soluble in water, one volume of the latter taking up at ordinary temperatures 50 volumes of sulfur dioxide and a smaller quantity at higher temperatures. At higher temperatures the solubility approximately follows Henry's law. The aqueous solution smells strongly of the dioxide which can be completely removed by boiling since it does not form either a maximum or minimum boiling mixture with water.

**Chemical Properties.**—Sulfur dioxide is stable and is decomposed only at very high temperatures. It will unite directly with chlorine for the formation of sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , or with oxygen to form sulfur trioxide,  $\text{SO}_3$ . The solution of sulfur dioxide in water reacts acid and when neutralized with sodium hydroxide and the solution evaporated, it yields the salt,  $\text{Na}_2\text{SO}_3$ , sodium sulfite. We therefore say that the solution contains **sulfurous acid**, and ascribe to this the formula  $\text{H}_2\text{SO}_3$ . A pure acid of this composition cannot be prepared since it breaks down into water and sulfur dioxide as the solution is concentrated. Because of the formation of sulfurous acid, sulfur dioxide is often called sulfurous anhydride.

Like hydrogen sulfide, sulfurous acid is a dibasic acid and yields acid and normal salts. It is a stronger acid than hydrogen sulfide, and the normal salts are not so highly hydrolyzed as the normal sulfides. The hydrolysis, however, is marked.

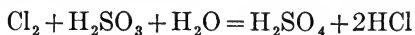
**Reducing Action.**—Sulfurous acid and the sulfites are strong reducing agents, passing into sulfuric acid or sulfates. As an example, we may take the reaction of sulfurous acid upon iodine and water,



Here the oxygen necessary for the formation of sulfuric acid

comes from the water. The sulfurous acid may be replaced by sulfites.

Because of a reaction between chlorine and sulfurous acid which is similar to that given above, sulfurous acid and sulfites are used as "antichlors" in the bleaching industries to remove the last of the chlorine,

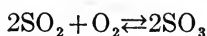


Sulfites are spontaneously oxidized by the oxygen of the air, an action which may be greatly slowed down by the addition of small quantities of sugar, alcohol, or glycerine, which act as negative catalyzers.

**Bleaching Action.**—Sulfurous acid and its salts are rather powerful bleaching agents and are extensively used for bleaching silk, wool, feathers, straw, etc., which would be destroyed by chlorine or hypochlorous acid. The sulfurous acid acts very differently from the chlorine in that it reduces the coloring matter instead of oxidizing it. The coloring matters are not destroyed in this case and after the process is finished the goods must be carefully washed, as otherwise the oxygen of the air would soon restore the color. If sulfur dioxide is used, the goods are first moistened so that sulfurous acid may be formed.

**Action on Organisms.**—Sulfur dioxide, sulfurous acid and sulfites are powerful poisons toward vegetable organisms of all kinds. This is shown by the fact that for long distances around smelters which produce great quantities of sulfur dioxide the vegetation is either completely killed or very much injured. Because of this same property, sulfur dioxide is used as a germicide and fungicide. Sulfurous acid and sulfites have been much used as preservatives in food products, but are now generally forbidden.

**Sulfur Trioxide or Sulfuric Anhydride.**—Sulfur trioxide is formed by the direct union of sulfur dioxide and oxygen,



The action, however, takes place very slowly even at somewhat elevated temperatures. In this case, one cannot resort to raising the temperature to a very high point in order to increase the rate of combination because of the fact that at a high

temperature the action is reversed. However, there are several substances, notably finely divided platinum and ferric oxide,  $\text{Fe}_2\text{O}_3$ , which will actively catalyze the union of the gases. In the case of the finely divided platinum, the process takes place to the best advantage when the temperature is about  $400^\circ$ . The sulfur trioxide so formed may be condensed to a colorless mobile liquid which boils at  $46^\circ$ . When cooled, it forms a transparent glassy solid which melts at  $15^\circ$ . After standing for some time, or more quickly in the presence of a trace of sulfuric acid, it passes over into a more stable form which appears as a white, opaque, glistening mass of needle-shaped crystals. This opaque form does not melt, but at  $50^\circ$  passes directly into the vapor which upon being cooled condenses to the liquid, from which the ice-like solid may first be obtained and then finally the opaque form. There is no transition point between these two solids, so that this substance is monotropic. The white, crystalline solid has a molar weight, as determined from the lowering of the freezing point in different solvents corresponding to the formula  $\text{S}_2\text{O}_6$ , while the other modification has the formula  $\text{SO}_3$ . The  $\text{S}_2\text{O}_6$  is called a polymer of the  $\text{SO}_3$ . The formation of the liquid and glassy solid before the appearance of the stable opaque form is another instance of the phenomena described by the law of successive reactions.

**Action on Water.**—When sulfur trioxide comes in contact with moist air, it forms dense white fumes, consisting of sulfuric acid formed by the union of the sulfur trioxide with water vapor. When the trioxide is brought in contact with water, combination takes place with the production of so much heat that it hisses as though a red hot body were plunged into the water. The result of this action is sulfuric acid, so sulfur trioxide is often called sulfuric anhydride.

**“Contact” Sulfuric Acid Process.**—Sulfuric acid is one of the most important chemical compounds which is manufactured, since its annual production amounts to about 2,000,000 tons, and the process outlined above seems to offer a very simple method for its production. There are, however, a number of practical difficulties in its application. The union of oxygen and sulfur dioxide is a reversible reaction and consequently is never complete. At each temperature there is a certain equilib-



rium mixture containing all three of the substances. At 400° and in the presence of double the required amount of oxygen, about 98 to 99 per cent. of the sulfur dioxide is changed into sulfur trioxide. At 700° only 60 per cent. is transformed, and at 900° practically none. Now any substance which is a catalyzer for one reaction is an equally good catalyzer for the reverse reaction. Consequently catalyzers cannot alter the point of equilibrium in a reversible reaction such as we are considering, but only decreases the time necessary for attainment of equilibrium. For this reason, the most successful catalyzer will be one which will work very rapidly at 400°. Platinum alone meets this requirement. Ferric oxide works rapidly at 625°, but at this temperature can only change 70 per cent. of the sulfur dioxide into sulfur trioxide. By removing the sulfur trioxide

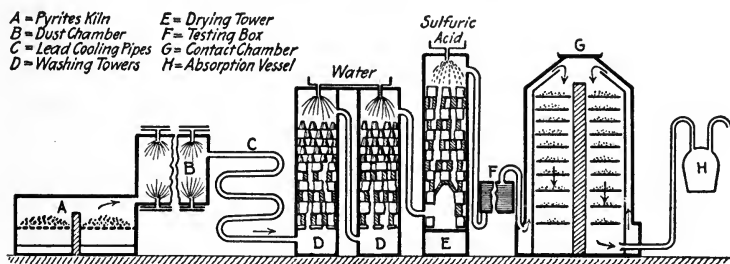


FIG. 23.

and passing the residue over the  $\text{Fe}_2\text{O}_3$  again, a further quantity of sulfur trioxide may be obtained, but this complicates the process.

When attempts were made to use this process on a large scale, it was found that the platinum soon lost its power as a catalyzer. The difficulty was traced to the presence in the sulfur dioxide of dust and particularly of arsenic compounds which poisoned the catalyzer much as they do living organisms. By very carefully purifying the sulfur dioxide, the process is now being successfully carried out on a very large scale. The heat of formation of sulfur trioxide from sulfur dioxide is 86 KJ. and under manufacturing conditions precautions have to be taken to carry off this heat, or otherwise the temperature of the reacting mixture would rise above 400°. The plant is shown diagrammatically in Fig. 23.

Ferric oxide is not poisoned by arsenic, but has the difficulty mentioned above of acting rapidly enough only at so high a temperature that the transformation is necessarily incomplete. At this same high temperature, the platinum would be no more efficient than the ferric oxide.

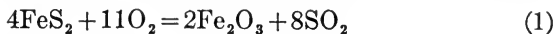
The oxygen necessary for the formation of the sulfur trioxide is obtained from the air. So the sulfur trioxide when it leaves the catalyzer will be mixed with a great quantity of other gases. It is removed from these by absorption in 97 to 98 per cent. sulfuric acid, which very promptly takes up the sulfur trioxide. By running in a stream of water or diluted sulfuric acid at the proper rate, the concentration of the sulfuric acid may be maintained at the desired point. In this way, concentrated sulfuric acid may be cheaply obtained.

By absorbing the sulfur trioxide in concentrated sulfuric acid, fuming or Nordhausen sulfuric acid is produced. When this contains 40 per cent. or more of sulfur trioxide, it is solid at ordinary temperature. The crystals have the composition  $H_2S_2O_7$  and are called pyrosulfuric acid.

The contact process is of especial advantage in the production of sulfur trioxide, fuming sulfuric acid, and very concentrated sulfuric acid. The first two of these are very largely used in the manufacture of dyes. Enormous quantities of somewhat diluted sulfuric acid, containing 60 per cent. to 70 per cent. of acid, are used in the manufacture of fertilizers and for many other purposes. Acid of this strength can be produced more cheaply by the **lead chamber process** which is about to be described, than by the contact process. Sulfur dioxide, water and oxygen combine for the formation of sulfuric acid. The process is spontaneous, being accompanied by a large decrease in free as well as total energy, but takes place so slowly that it cannot be used for manufacturing purposes. Since the process is taking place it is subject to catalysis and in fact may be very effectively catalyzed by the oxides of nitrogen.

**Lead Chamber Process.**—The substances which take part in the principal reactions involved in this very important process are sulfur dioxide, oxygen, nitrogen peroxide,  $NO_2$ , and water. The sulfur dioxide is obtained either by burning sulfur, or by roasting in suitable furnaces some sulfide, generally pyrites,

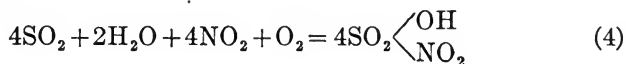
$\text{FeS}_2$ , in contact with air. In the latter case the reaction is



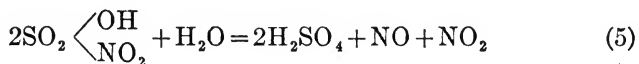
The oxygen comes from the air, the nitrogen peroxide,  $\text{NO}_2$ , from the action of sulfur dioxide and water upon nitric acid, giving sulfuric acid and nitric oxide,  $\text{NO}$ . The latter then reacts with the oxygen of the air to form nitrogen peroxide. The equations are as follows:



The water is introduced either in the form of steam or as a spray of very finely divided water. The reaction which produces the greater part of the sulfuric acid consists in the interaction of the sulfur dioxide, oxygen, nitrogen peroxide and water for the formation of a compound called nitrosylsulfuric acid,  $\text{SO}_2 \begin{smallmatrix} \text{OH} \\ \text{NO}_2 \end{smallmatrix}$  and its subsequent decomposition by water, forming sulfuric acid and a mixture of nitric oxide and nitrogen peroxide. The equations are



and



The nitric oxide then reacts with some more oxygen as shown in equation (3) to reform the peroxide which will at once react with more of the sulfur dioxide, oxygen, and water to form more nitrosylsulfuric acid, which is decomposed by water, forming another lot of sulfuric acid and reproducing the oxides of nitrogen. This cycle of changes goes on until all but one-half a per cent. of the sulfur dioxide is used up. So a very small quantity of the oxides of nitrogen will transform a large amount of sulfur dioxide. These reactions take place in very large lead lined rooms or chambers, Fig. 24, of which there are three or more in each plant. These chambers are often 100 ft. or more in length and hold from 150,000 to 200,000 cu. ft. Lead is used in their

construction because it is but little attacked by dilute sulfuric acid. The temperature in the first chamber is usually about 60° and somewhat lower in each succeeding one. The sulfuric acid formed collects on the bottom of the chambers, while a mixture of the oxides of nitrogen and the nitrogen from the air which

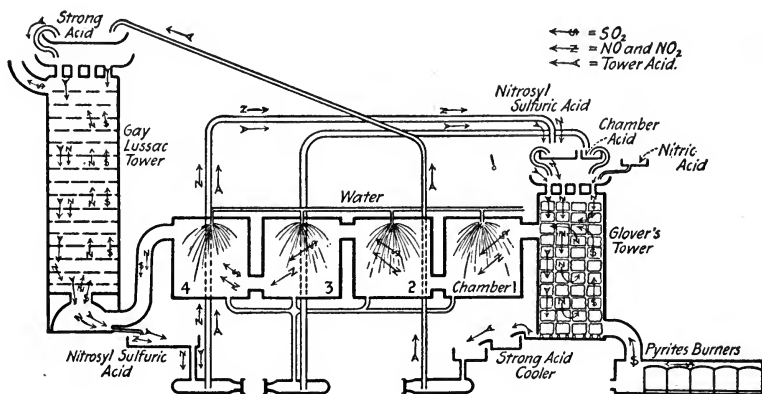
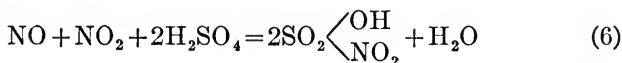


FIG. 24.

furnished the oxygen issue from the last chamber. The oxides of nitrogen are too valuable to be lost so advantage is taken of the fact that they may be absorbed in concentrated sulfuric acid forming nitrosylsulfuric acid,



This, it will be noticed, is equation (5) written reversed. The absorption takes place in what is called the Gay Lussac tower. This is about 50 ft. high and is filled with tiles over which concentrated sulfuric acid runs in a thin stream, while the gases from the last lead chamber enter at the bottom and leave near the top. The acid, which collects at the bottom of the tower, contains the nitrosylsulfuric acid in solution. This may be easily decomposed by water, regenerating the oxides of nitrogen necessary for catalyzing the formation of the sulfuric acid. But to be of service, these oxides of nitrogen must be reintroduced into the first lead chamber. This is done by elevating the acid drawn off from the bottom of the Gay Lussac tower, with com-

pressed air to the top of a similar structure called the Glover's tower which just precedes the first lead chamber. Here the concentrated sulfuric acid is mixed with dilute acid from the chambers. This partly decomposes the nitrosylsulfuric acid. (See equation 5.) The mixture is then allowed to flow slowly down through the tower over the acid resisting stones or tiles. On its way down it meets the hot sulfur dioxide and air from the burners. These gases enter at the bottom of the tower, pass up through and out near the top, going from there into the first lead chamber. The hot gases while flowing through the tower remove the oxides of nitrogen from the diluted sulfuric acid and evaporate a large part of the water. This returns the oxides of nitrogen to the point where they are needed, concentrates the sulfuric acid, and at the same time cools the gases to the temperature favorable for the reactions.

Other reactions than the ones given above take place during the process, whereby a part of the nitrogen compounds is reduced to nitrous oxide,  $N_2O$ , and, as this takes no further part in the reaction, it constitutes a loss of active nitrogen to the system. To make up for this and for mechanical losses, it is necessary to use about 4 parts of sodium nitrate for every 100 parts of sulfur burned, to make nitric acid enough to replace the oxides of nitrogen lost. The nitric acid is usually added at the top of the Glover's tower and here reacts with the sulfur dioxide as shown in equation (2).

The whole process may be briefly summed up as follows: Sulfur dioxide is formed in the pyrite burner, equation (1). The hot gas passes either directly to the Glover's tower or sometimes first through a dust-settling chamber. In the Glover's tower the oxides of nitrogen are removed from the nitrosyl sulfuric acid, equation (5), losses replaced by the addition of nitric acid, equation (2), and part of the chamber acid concentrated. In addition, reactions represented by equations (3), (4), and (5) take place to a certain extent in the tower. From the Glover's tower, the gases pass on through the lead chambers in which the principal reactions are represented by equations (3), (4), and (5). From the last chamber, the residual gases pass through the Gay Lussac tower where the oxides of nitrogen dissolve in the concentrated sulfuric acid, forming nitrosylsulfuric acid

as shown in equation (6). The nitrosylsulfuric acid then goes back to the Glover's tower and the oxides of nitrogen begin the journey once more.

**Concentration of the Acid.**—In the absence of considerable water in the lead chambers the reaction represented by equation (5) does not take place well, and if the chamber acid becomes much stronger than 60–70 per cent. it will dissolve the oxides of nitrogen. Hence the chamber acid from the sulfuric acid plant runs about 65 per cent. acid and 35 per cent. water. Enormous quantities of it are used at this strength, for example, in making fertilizer, but for many purposes the greater part of the water must be removed. This is very commonly done by running the chamber acid together with that from the Gay-Lussac tower through the Glover towers until the acid has reached a concentration of 78 per cent. or higher. It may then be concentrated still further by heating in cast-iron retorts, because sulfuric acid of this strength or stronger does not attack iron, while the weaker acid does. An entirely adequate explanation of this behavior is lacking.

Stills of glass or of platinum lined with gold are sometimes used instead of the cast-iron ones.

Another method of concentration which is sometimes used is to evaporate the chamber acid in lead pans heated from above until the acid has a density of 1.71 corresponding to 78 per cent. acid, when it becomes a strong enough oxidizing agent to attack the lead rapidly. Further concentration must then be done in cast-iron, glass, or platinum. Commercial sulfuric acid or oil of vitriol has a density of 1.83–1.84 and contains 94 per cent. of the acid. The strongest sulfuric acid which can be secured by evaporation has a density of 1.841 and contains 98.2 per cent. of the acid. This is the composition of the maximum boiling mixture. It boils at 330° C. The vapor consists largely of a mixture of sulfur trioxide and water as may be demonstrated by the fact that a flask filled with sulfuric acid vapor will lose water more rapidly by diffusion than it does the more dense sulfur trioxide.

**Hydrates.**—When concentrated sulfuric acid is cooled to a low temperature, crystals of the pure acid,  $\text{H}_2\text{SO}_4$ , separate. These melt at 10.50°. Somewhat diluted acid gives crystals melting at 8°, and having the composition represented by

$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . From still more dilute acid the hydrates  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , separate in the neighborhood of  $-70^\circ$ .

**Aqueous Sulfuric Acid.**—When sulfuric acid is mixed with water a great amount of heat is evolved. The acid should always be poured into the water, as otherwise so much heat is likely to be developed at one point that some of the water will be suddenly converted into steam, causing the sulfuric acid to spatter.

The heat of solution of one mole of sulfuric acid in a great deal of water is 67 KJ., while that of a mole of sulfur trioxide in the same amount of water is 156 KJ. Since in the end there will be two identical solutions of sulfuric acid, the difference between 156 KJ. and 67 KJ. or 89 KJ. must be the heat of formation of sulfuric acid from water and the trioxide.

When concentrated sulfuric acid is mixed with water considerable contraction takes place so that the total volume is less than the sum of the volumes of the water and the acid. The greatest contraction takes place when the diluted acid has a composition of 70 per cent. A total volume of 100 c.c. before the mixing becomes about 97 after the solution of the acid and cooling.

Because of this contraction there is no simple relation between the per cent. of an aqueous solution of sulfuric acid and its density. To determine the per cent. of such an acid from its density one must make use of empirically prepared tables.

The vapor pressure of water from aqueous solutions of the acid varies continuously with the composition, and is very small indeed at ordinary temperatures from the more concentrated acid. Upon this fact depends the usefulness of concentrated sulfuric acid for drying gases. Somewhat diluted acids are used when it is desired to secure definite and small pressure of water vapor.

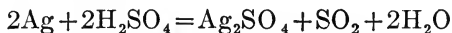
**Dissociation of Sulfuric Acid.**—Pure concentrated sulfuric acid is not a good conductor of electricity, but when the acid is dissolved in water it becomes a very good conductor indeed. It is a dibasic acid, and like all others of its class, dissociates in two ways. In the more concentrated acid, the principal anion is  $\text{HSO}_4^-$ , but as the acid is diluted this breaks down to give  $\text{H}^+$  and  $\text{SO}_4^{--}$ . As has been pointed out it is a strong acid, but not so strong as hydrochloric.

**Applications of Sulfuric Acid.**—Enormous quantities of sulfuric

acid are used in the arts. The largest single use is in the manufacture of fertilizers. A great deal is used in making sodium carbonate. In fact, there is scarcely a manufacturing industry of any importance which does not directly or indirectly make use of sulfuric acid.

Its many applications depend mainly upon the following facts: It is cheap, a fairly strong acid, a moderately strong oxidizing agent, not very volatile and forms slightly soluble salts with several cations. As an acid it is much used, for example, in the preparation of hydrogen, to dissolve the "scale" or coating of oxide from metal plates before further treatment in various manufacturing processes and in the preparation of other acids from their salts.

Advantage is taken of its oxidizing power in the separation of silver from gold in the process of refining of these metals. The silver is oxidized to silver as ion, which then forms silver sulfate, while the sulfuric acid is reduced to water and sulfur dioxide. The gold is not attacked.



The acid must be concentrated and hot to react in this way. Mercury, copper, and several other metals will act in much the same way as silver. Zinc and iron tend to carry the reduction clear down to hydrogen sulphide.

Its extensive use in the manufacture of hydrochloric and other acids by the first general method depends upon its slight volatility, which more than makes up for the fact that sulfuric acid is weaker than many of the acids which it is used to prepare. The slight solubility of the sulfates of barium, lead, and calcium make it very useful in the preparation of acids by the second general method. In fact, its use in preparing fertilizers depends upon the fact that it can convert calcium phosphate into easily soluble phosphoric acid or else calcium acid phosphate and difficultly soluble calcium sulfate.

**Identification.**—Barium sulfate is exceedingly slightly soluble in water, since it requires more than 300,000 times its weight of water for solution. It is promptly formed whenever a solution of a barium salt, barium chloride,  $\text{BaCl}_2$ , for example, is added to a solution of a sulfate or of sulfuric acid. This then is a prop-

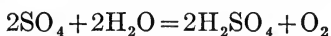


erty of the sulfate ion. The barium sulfate is white, and is not dissolved in dilute hydrochloric acid, and by this is distinguished from all other barium salts, except barium selenate.

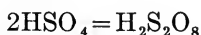
**Sulfates.**—Since sulfuric acid is a dibasic acid, it forms two series of salts, acid and neutral sulfates; for example, sodium acid sulfate  $\text{NaHSO}_4$  and sodium neutral sulfate  $\text{Na}_2\text{SO}_4$ . Sulfuric acid is a strong enough acid so that the names are appropriate because the acid salt actually is acid and the neutral salt neutral. The various sulfates will be discussed in some detail under the different metals.

#### OTHER OXYGEN ACIDS OF SULFUR

**Persulfuric Acid.**—It will be recalled that when dilute sulfuric acid is electrolyzed, hydrogen and oxygen are given off in the proportions for the formation of water. The ions of the acid in dilute solution are  $2\text{H}^+ + \text{SO}_4^{--}$ . So the evolution of the hydrogen at the cathode is easily understood, but not so the appearance of the oxygen at the anode. This latter phenomenon may be most easily explained by assuming that the  $\text{SO}_4^{--}$  is discharged at the anode, but at once reacts with water for the formation of sulfuric acid and oxygen,

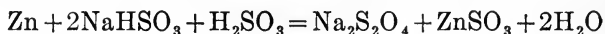


Fairly concentrated sulfuric acid 50 per cent. or more contains principally the ions  $\text{H}^+$  and  $\text{HSO}_4^-$ . When this is electrolyzed, using a very small anode and keeping the solution cold, but little oxygen appears at the anode. At the same time a new substance, persulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , is formed in the solution. The formation of this acid is easily understood. Two combining weights of  $\text{HSO}_4^-$  give up their charges to the anode and at once unite to form  $\text{H}_2\text{S}_2\text{O}_8$ ,



If potassium or ammonium acid sulfate,  $\text{KHSO}_4$  or  $\text{NH}_4\text{HSO}_4$ , is used instead of the sulfuric acid, the rather difficultly soluble potassium or ammonium persulfate soon separates around the anode. These salts are now common commercial articles, and find fairly extensive use because they are good oxidizing agents.

**Hyposulfurous Acid.**—The salts of this acid are formed by the action of zinc upon solutions of acid sulfites containing an excess of sulfur dioxide, or upon sulfur dioxide in solution in absolute alcohol. The sodium salt,  $\text{Na}_2\text{S}_2\text{O}_4$ , sodium hyposulfite is a commercial article which is extensively used in dyeing. It is prepared by acting upon sodium acid sulfite and sulfurous acid with zinc as shown in the following equation,

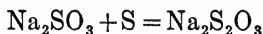


After the action is completed, calcium hydroxide in suspension in water, milk of lime as it is called, is added in the proper quantity to precipitate the zinc as hydroxide and the calcium as sulphite, both of which are only slightly soluble, leaving the  $\text{Na}_2\text{S}_2\text{O}_4$  in solution. This salt forms thin vitreous crystals of the composition  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

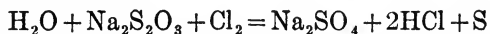
An aqueous solution of the acid may be obtained by adding oxalic acid to a solution of the sodium or better calcium salt. It is very unstable.

The hyposulfites are less powerful reducing agents than zinc, but are much more rapid in their action.

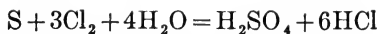
**Thiosulfuric Acid.**—It will be recalled that a sulfite in solution will slowly take up oxygen from the air, passing into a sulfate. In much the same way, but more rapidly a sulfite, say sodium sulfite, will take up sulfur for the formation of a thiosulfate, or a sulfate in which one combining weight of sulfur takes the place of a combining weight of oxygen. This is one of the ways in which sulfur shows its analogy to oxygen,



The salt  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  is known as sodium thiosulfate or incorrectly as sodium hyposulfite or "hypo." It is the most important of the thiosulfates and is much used in photography because it has the power of dissolving silver bromide and chloride as will be explained in discussing silver. It is a good reducing agent and is often used as such in place of sulfites. For example, it may be used as an antichlor for the removal of chlorine from bleached goods,

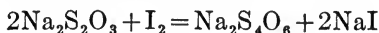


An excess of chlorine will oxidize the sulfur to sulfuric acid,



So a large quantity of chlorine can be transformed into chlorine as ion by a comparatively small quantity of this salt.

Sodium thiosulfate is much used in volumetric analysis for the determination of free iodine and also of the many oxidizing agents which will liberate iodine from iodides. The reaction between iodine and the thiosulfate is different from that of chlorine as shown by the following equation,



The salt  $\text{Na}_2\text{S}_4\text{O}_6$  is called sodium tetrathionate and is a salt of tetrathionic acid, one of the series of acids of which we can do no more than to give the names and formulas.

Dithionic acid,  $\text{H}_2\text{S}_2\text{O}_6$

Trithionic acid,  $\text{H}_2\text{S}_3\text{O}_6$

Tetrathionic acid,  $\text{H}_2\text{S}_4\text{O}_6$

Pentathionic acid,  $\text{H}_2\text{S}_5\text{O}_6$

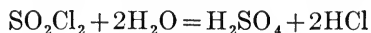
Thiosulfuric acid is so unstable that it decomposes almost as soon as it is liberated, into sulfur and sulfurous acid. So that if a solution of thiosulfate is acidulated it will become milky almost at once. This decomposition is largely prevented by the addition of sulfites.

**Halogen Compounds of Sulfur.**—When dry chlorine gas is passed over heated sulfur, the two elements combine for the formation of sulfur monochloride  $\text{S}_2\text{Cl}_2$ , which is a reddish-yellow liquid boiling at  $138^\circ$ . It is a very good solvent for sulfur and for this reason has been used in vulcanizing rubber. With water, it reacts for the formation of sulfur, hydrochloric acid, sulfurous acid, and thiosulfurous acid. When chlorine is passed into the monochloride cooled to  $-20^\circ$ , sulfur tetrachloride  $\text{SCl}_4$  is formed. This is a mobile yellowish-brown liquid which freezes at  $-31^\circ$ . At ordinary temperatures it gradually decomposes into chlorine and the monochloride.

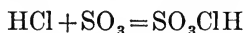
With bromine and iodine, sulfur forms compounds corresponding to the monochloride. They are the monobromide,  $\text{S}_2\text{Br}_2$ , and the moniodide,  $\text{S}_2\text{I}_2$ . Fluorine and sulfur combine so vigorously that they catch fire at ordinary temperatures forming sulfur hexafluoride,  $\text{SF}_6$ . This melts at  $-55^\circ$  and boils at just the same temperature.

**Sulfuryl Chloride.**—Sulfur dioxide and chlorine combine

directly to form sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ . The combination takes place much more rapidly in the sunlight than in diffused daylight and is catalyzed by camphor. It is a colorless mobile liquid, boiling at  $69^\circ$ , and having a density of 1.67. With water it reacts to give sulfuric and hydrochloric acids,



If just the proper amount of water is used, a compound called chlorsulfuric acid,  $\text{SO}_3\text{ClH}$ , which stands half way between sulfuryl chloride and sulfuric acid is formed. It may also be formed by the action of hydrochloric acid on sulfur trioxide,



**Positive and Negative Valence.**—Hydrogen and chlorine in hydrogen chloride as we have learned are both monovalent. When the compound is dissolved in water it dissociates into the monovalent hydrogen ion carrying one positive charge, and the monovalent chlorine ion carrying a negative charge. This at once gives the conception of positive and negative valence, and the explanation of the valence of an ion, which then becomes identical with the number of positive or negative charges which the ion carries. Thus the sulfur ion,  $\text{S}^{--}$ , is negative and is divalent, as is also the sulfate ion,  $\text{SO}_4^{--}$ . We may then say that the sulfate ion unites with two combining weights of hydrogen or sodium as ion; because each of these carries one positive charge or is monovalent, and two are required to neutralize the charge upon the sulfate ion and to form sulfuric acid or sodium sulfate, both of which are electrically neutral. The subject of the valence of ions is simple, and this has led to attempts to ascribe the phenomena connected with valence in general to an electrical origin. In accordance with this view, the elements, even in compounds, which are not salts are supposed to be charged, some positively and some negatively and the valence of each element is supposed to be determined by the number of + or - charges which it carries per combining weight. This view seems to be not entirely free from contradictions and may be incorrect, but it is in agreement with the facts in the great majority of cases and is a very useful conception. According to this hypothesis, the oxygen in water and most other compounds

carries two, the nitrogen in ammonia three, and the carbon in methane,  $\text{CH}_4$ , four negative charges.

While it is very easy to decide that the valence of the sulfate ion is two, it is not so easy to answer the question "What is the valence of the sulfur in this ion?" If we assume that oxygen in compounds always has the valence that it has in water, viz., two negative, we may reach a reasonable conclusion in this and similar cases. Since the sulfate ion as a whole carries two negative charges, it follows that the algebraical sum of the positive and negative charges upon the sulfur and the oxygen must be  $-2$  or  $x + a = -2$ , where  $x$  represents the charges upon the sulfur, and "a" those upon the oxygen. Now from the assumption which we have made about the valence of oxygen, each combining weight of this element carries two negative charges, and the four would then total eight negative charges, and in the equation given above, "a" would have the value  $-8$

$$x + -8 = -2$$

or

$$x = +6$$

From this it follows that the valence of the sulfur in the sulfate ion or in sulfuric acid for that matter, is  $+6$ . This is confirmed by the fact that sulfuric acid is so simply formed from water and sulfur trioxide  $\text{SO}_3$ , in which the sulfur evidently has a valence of  $+6$ . Working in this same way, it is easy to show that the chlorine in chloric acid,  $\text{HClO}_3$ , has a valence of  $+5$ , in chlorites,  $\text{NaClO}_2$ , for example, of  $+3$ , and that the phosphorus in phosphoric acid,  $\text{H}_3\text{PO}_4$ , has a valence of  $+5$ . Nitrogen in ammonia  $\text{NH}_3$ , and in the ammonium ion  $\text{NH}_4^+$ , seems to have a valence of  $-3$ ; while in nitric acid  $\text{HNO}_3$ , it is  $+5$ , so it would appear that the valence of an element can not only change in value but even in sign.

The valence of a free element is considered to be zero.

## CHAPTER XIII

### SELENIUM AND TELLURIUM

Selenium and tellurium are two elements which bear about the same relation to sulfur that bromine and iodine do to chlorine. The resemblance of tellurium to sulphur is perhaps less marked than that of iodine to chlorine, but selenium furnishes fully as close a match for sulfur as bromine does for chlorine. A comparison of the combining weights of the members of these two groups of elements is of some interest.

Chlorine.....	35.46	Bromine.....	79.92	Iodine.....	126.92
Sulfur.....	32.06	Selenium.....	79.20	Tellurium.....	127.50
Difference.....	3.40		.72		-.58

From this it is seen that the combining weights of sulfur, selenium, and tellurium correspond closely to those of chlorine, bromine, and iodine respectively, and that in passing from sulfur to tellurium through selenium the combining weights increase more rapidly than from chlorine to iodine through bromine, so that although the combining weight of sulfur is more than three units smaller than that of chlorine, that of tellurium is actually larger than that of iodine.

Selenium and tellurium correspond to bromine and iodine in that they do not occur abundantly in nature although they are rather widely distributed.

### SELENIUM

The element selenium was discovered by Berzelius in 1817 in the flue dust of a sulfuric acid factory. Just as bromides are often found in chlorides, so compounds of selenium are generally found associated with those of sulfur, and in addition free selenium is sometimes found in the crystals of native sulfur. The principal sources of selenium are the flue dust of certain sulfuric acid factories and the anode mud obtained in the elec-

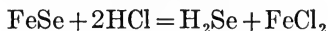
trolytic refining of lead or copper. From this latter source considerable quantities of selenium might be easily prepared if there were sufficient demand, but it has at present only a few technical applications.

**Physical Properties.**—Like sulfur, selenium takes on a number of different forms—amorphous, crystalline and metallic. Amorphous selenium when finely divided has a red color and may sometimes form a colloidal solution with water. It is also obtained in a massive form by rapidly cooling melted selenium. In this condition, it is black and breaks like glass. When finely powdered it takes on a red color. The only differences in these varieties seem to be their state of division. They are both soluble in carbon disulfide. They have no definite melting-point, but gradually soften with rising temperature. There are two kinds of red crystalline selenium, each soluble in carbon disulfide and melting by rapid heating at  $170^{\circ}$ – $180^{\circ}$ . Their density is 4.47. When slowly heated they change at about  $150^{\circ}$  or above, into metallic selenium. This forms steel gray crystals melting at  $217^{\circ}$  having a density of 4.8. It is insoluble in carbon disulfide. This modification is something of a conductor of electricity while the other forms are insulators. The conductivity of the selenium is greatly increased by light. The boiling-point of selenium is  $690^{\circ}$ . At temperatures above  $1400^{\circ}$  the molar weight corresponds to the formula  $\text{Se}_2$ , but at lower temperatures it is higher, indicating something of the phenomenon discussed under sulfur, and the existence of forms containing more than two combining weights per mole.

**Chemical Properties.**—Selenium combines directly with iron and many other metals, and also with hydrogen, oxygen and the halogens. As a rule these compounds are formed less readily than the corresponding sulfur compounds, and from them the element is more easily liberated than is sulfur from its compounds. These relations are about the same as those between bromine and chlorine.

**Hydrogen Selenide.**—The methods for the preparation of hydrogen selenide,  $\text{H}_2\text{Se}$ , are very similar to those for hydrogen sulfide. It may be formed by the direct union of the elements at temperatures above  $250^{\circ}$ . The reaction is reversible and the quantity of hydrogen selenide in the equilibrium mixture

increases up to about 520° and then decreases. This indicates a change in the sign of the heat formation at 520°. At 440° the equilibrium mixture contains 53 per cent. H<sub>2</sub>Se. The most common method for the preparation of hydrogen selenide is to act upon ferrous selenide, FeSe, made by heating together iron and selenium, with hydrochloric acid.

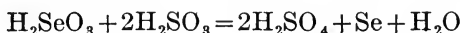


This is very similar to the usual way for preparing hydrogen sulfide.

**Physical and Chemical Properties.**—Like hydrogen sulfide, hydrogen selenide is a colorless gaseous substance at ordinary temperatures. It may be liquefied, and then boils at -41° and freezes at -68°. These temperatures are roughly 20° higher than the corresponding points for hydrogen sulfide. It is easily soluble in water, and the solution reacts somewhat acid toward litmus. Chemically it resembles hydrogen sulfide in that it gives difficultly soluble selenides when passed into solutions of the salts of many of the heavy metals and that free selenium is deposited when hydrogen selenide water is exposed to the air. This change takes place more rapidly than the corresponding reaction of hydrogen sulfide because the hydrogen selenide is so easily oxidized. The gas has a much worse odor than hydrogen sulfide, resembling that of decayed horseradish, and is very poisonous.

**Selenium Dioxide.**—Selenium will burn in oxygen forming the dioxide, SeO<sub>2</sub>, but the latter may be more readily prepared by heating selenious acid H<sub>2</sub>SeO<sub>3</sub> until it decomposes into water and the dioxide. Unlike sulfur dioxide, selenium dioxide is a solid at ordinary temperatures. It forms heavy white needles which do not melt under atmospheric pressure but sublime at 300°; the vapor has the color of chlorine.

**Selenious Acid.**—Selenium dioxide dissolves in water forming selenious acid, H<sub>2</sub>SeO<sub>3</sub>, which is a white crystalline substance easily soluble in water. It is a weak dibasic acid resembling sulfurous acid. Like the latter it acts both as a reducing and an oxidizing agent, but differs in that its oxidizing power is much stronger than its reducing. It oxidizes sulfurous acid to sulfuric,

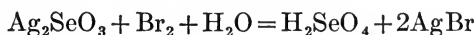




The selenium is deposited in the red amorphous form. This reaction is often used in the preparation of the element from flue dust. The acid acts as a reducing agent toward potassium permanganate, being oxidized to selenic acid,  $\text{H}_2\text{SeO}_4$ ,



**Selenic Acid.**—There is no selenium compound corresponding to sulfur trioxide, but selenic acid which is strictly analogous to sulfuric acid may be easily prepared by acting upon silver selenite,  $\text{Ag}_2\text{SeO}_3$ , with bromine and water,



By carefully concentrating this solution selenic acid may be obtained as a white crystalline solid melting at  $58^\circ$ . It is exceedingly soluble in water with which it combines to form a number of hydrates similar to those of sulfuric acid.

It is in general a more powerful oxidizing agent than sulfuric acid since it liberates chlorine from hydrochloric acid and dissolves gold, but curiously enough, it is without action upon either hydrogen sulfide or sulfur dioxide.

**Chlorides.**—Like sulfur, selenium forms two chlorides, the mono  $\text{Se}_2\text{Cl}_2$  and the tetra  $\text{SeCl}_4$ , but unlike the analogous compounds of sulfur, the tetrachloride is the more stable.

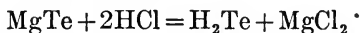
**Isomorphism.**—It often happens that two substances have almost if not quite exactly the same crystalline form, and in such cases these substances are spoken of as being isomorphous (same form). If both are present when crystallization takes place, each crystal which separates will be a homogeneous mixture of the two substances and will therefore be a solid solution. These isomorphous substances are usually, though not always, closely related chemically.

One of the monoclinic modifications of selenium is isomorphous with monoclinic sulfur, and some natural specimens of rhombic sulfur contain selenium in solid solution, from which we may draw the conclusion that selenium is capable of taking on the rhombic form. But this form has never been observed. Not only are selenium and sulfur in the free state isomorphous, but the selenates are often isomorphous with the sulfates of the same metals.

## TELLURIUM

Tellurium has been known for a long time but it was first recognized as a distinct element by Müller v. Reichenstein in 1783. It is decidedly rare. It occurs free but mostly as tellurides of gold, silver, lead and bismuth. Tellurium is more metallic in its characteristics than the other members of the sulfur family. It forms both amorphous and crystalline modifications; the latter has a silvery white metallic luster, a density of 6.3, melts at 450°, and boils at 1390°. At 1750° the molar weight indicates that the formula is  $\text{Te}_2$ . The crystalline modification is a slight conductor of electricity. The element combines directly with oxygen, the halogens and many of the metals.

**Hydrogen Telluride.**—Hydrogen telluride is even less stable than hydrogen selenide, and is very difficult to prepare in a pure state. It is formed in small quantities by heating tellurium in hydrogen, but is generally prepared by the action of hydrochloric acid upon magnesium telluride,  $\text{MgTe}$ ,



It is colorless and gaseous at ordinary temperature, with an odor like that of hydrogen sulfide. It condenses to a liquid boiling at 0° and freezing at  $-48^\circ$ . It rapidly decomposes into the elements in the light, more slowly in the dark, and cannot be kept long even in a sealed tube in a freezing mixture. It is instantly oxidized to water and tellurium upon exposure to moist air. It burns to water and tellurium dioxide. Its solution does not redden litmus, but potassium telluride is formed when it acts upon a solution of potassium hydroxide. This solution will precipitate the tellurides of many of the heavy metals upon the addition of their salts, but the gas as a rule is unable to precipitate the tellurides directly, because of its slight dissociation into the ions.

**Tellurium Dioxide.**—Tellurium burns in oxygen forming the dioxide which is a white, crystalline substance, slightly soluble in water. The solution does not redden litmus.

**Tellurous Acid.**—Tellurous acid,  $\text{H}_2\text{TeO}_3$ , is made by dissolving the element in nitric acid and diluting the solution. It forms a white powder, slightly soluble in water but dissolved by either

potassium hydroxide or strong acids. It then acts both as a base and as an acid, but is neither strongly acid nor basic; nothing which acts in both these ways is ever strong in either.

Strong oxidizing agents convert tellurous acid into telluric acid which has the formula,  $H_6TeO_6$ , although it forms salts of the type  $K_2TeO_4$ . It is not very soluble, and the solution does not redden litmus, so it is a very weak acid; in addition, it shows basic properties. It is a strong oxidizing agent and unlike selenic acid, is reduced by hydrogen sulfide and sulfur dioxide. When the acid is heated, it decomposes forming water and the trioxide,  $TeO_3$ , which is almost totally indifferent to water, and is therefore very different from sulfur trioxide. Tellurium forms two chlorides;  $TeCl_2$ , and  $TeCl_4$ . These are stable toward most changes but are decomposed by water, corresponding to the sulfur compounds.

## THE SULFUR FAMILY

	Sulfur	Selenium	Tellurium
Formula.....	$S_8-S_2$	$Se_8-Se_2$	$Te_2$
Melting-point.....	120°	217°	450°
Boiling-point.....	448.5°	690°	1390°
Hydrogen compounds.....	$H_2S$	$H_2Se$	$H_2Te$
Melting-point.....	-83°	-68°	-48°
Boiling-point.....	-61°	-41°	0°
Oxidized.....	Easily	Very easily	Most easily
Dioxide.....	$SO_2$	$SeO_2$	$TeO_2$
State.....	Gaseous	Solid	Solid
Acid.....	$H_2SO_3$	$H_2SeO_3$	$H_2TeO_3$
State.....	Solution	Solid	Solid
Reducing agent.....	Good	Weak	Weak
Oxidizing agent.....	Weak	Strong	Strong
Trioxide.....	$SO_3$	.....	$TeO_3$
Acid.....	$H_2SO_4$	$H_2SeO_4$	$H_6TeO_6$
Oxidizing agent.....	Fair	Strong	Strong

## CHAPTER XIV

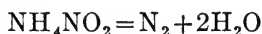
### NITROGEN

**General.**—The element nitrogen occurs in nature both free and in combination. The free element is found in the air of which it constitutes approximately four-fifths by volume. The greater part of the remainder is oxygen. The element is decidedly inactive, but its compounds are among the most reactive of chemical substances. This will be seen at once when it is mentioned that they include gun cotton, nitroglycerine, and almost all of our modern high explosives. The inorganic compounds of nitrogen which occur in nature are principally ammonia, ammonia compounds, and salts of nitric acid. Large quantities of very complex carbon compounds of nitrogen are present in coal. Nitrogen compounds are of great importance to us, since it is with them that the vital phenomena seem to be directly connected. The albuminoids constitute an important class of such compounds, and contain almost 15 per cent. of nitrogen. No animal, and but few plants can utilize the free nitrogen of the air in the formation of these vital substances. Because of this fact they must, in general, be built up by the plants from the nitrogen compounds present in the soil. All fertile soils contain these substances and any deficiency must be made up by the application of natural or artificial manures.

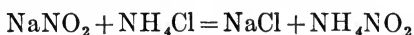
**Preparation of the Element.**—Pure nitrogen cannot be easily obtained directly from the air. The oxygen, water vapor, and most of the other constituents of the air may be removed without difficulty, but the nitrogen which remains is contaminated with a number of gases of the argon group (which see). These seem to be entirely wanting in chemical activity. However, this atmospheric nitrogen has nearly all the essential properties of nitrogen, and may for the great majority of purposes be substituted for it. The main difference between atmospheric nitrogen and the pure gas lies in the fact that the former is a trifle more dense. To obtain atmospheric nitrogen, all that is

necessary is to take out the carbon dioxide with sodium hydroxide, and ammonia and water vapor with sulfuric acid, and then remove the oxygen, either with phosphorus or by passing the air over heated copper. This residue so obtained contains about 99 per cent. nitrogen and 1 per cent. of the members of the argon group.

To prepare pure nitrogen, some of its compounds must be decomposed. This is most conveniently done by heating ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , until it breaks down into nitrogen and water as shown below:

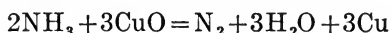


Since the ammonium nitrite is hard to prepare pure, a concentrated solution of sodium nitrite  $\text{NaNO}_2$ , to which either ammonium chloride or sulfate has been added is heated. Ammonium nitrite is first formed and then decomposed,

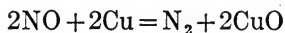


The equation for the decomposition of the ammonium nitrite is given above.

Nitrogen may also be prepared by passing ammonia,  $\text{NH}_3$ , over heated copper oxide,  $\text{CuO}$ , or nitric oxide,  $\text{NO}$ , over heated copper. The equations are as follows:



and



**Physical Properties.**—Nitrogen is a colorless, tasteless, odorless gas, which is very slightly soluble in water; 100 volumes of the latter dissolve 1.6 volumes of nitrogen. The density of nitrogen from chemical sources is .0012508, while that of the atmospheric nitrogen is .00125718. It was this difference in density of the gas from the two sources that led to the discovery of argon and its congeners. The critical temperature of nitrogen is  $-146^\circ$  and the critical pressure is 35 atmospheres. The critical temperature shows that the gas cannot be liquefied at ordinary temperature while it may be liquefied at any temperature below  $-146^\circ$ . Its boiling-point is  $-194^\circ$ . The liquid nitrogen is colorless and has a density, at its boiling-point, of .8103. By lowering the

pressure, the boiling-point is lowered until at  $-203^{\circ}$ , under a pressure of 6 to 7 cm. of mercury, the nitrogen freezes to a white solid.

The molar weight of nitrogen is 28, and therefore, since its combining weight is 14.01, its formula is  $N_2$ .

**Chemical Properties.**—Toward most of the other elements, nitrogen ordinarily shows itself to be inactive. At higher temperatures, or under the influence of the electric glow discharge it becomes fairly active. When the gas is passed over strongly heated lithium, magnesium, calcium, or boron, direct combination takes place with the formation of the nitrides of these metals,  $Li_3N$ ,  $Mg_3N_2$ ,  $Ca_3N_2$ , and  $BN$ . A mixture of powdered lime (calcium oxide,  $CaO$ ) and magnesium react so vigorously when heated in a current of nitrogen that after the action has once started at one point, the heat given out raises the surrounding mixture to incandescence, and the action is propagated throughout the entire mass. A mixture of nitrides and oxides is formed. The phenomena strongly resemble those of combustion of many substances in oxygen.

When nitrogen is mixed with either oxygen or hydrogen and heated, but little action takes place. When an electric spark is passed through either of these mixtures some change occurs, but soon comes to an end since the reactions are reversible. In the case of nitrogen and oxygen, nitric oxide,  $NO$ , is first formed and this then combines with the excess of oxygen present to form  $NO_2$ , nitrogen peroxide. The nitrogen and hydrogen unite to form ammonia,  $NH_3$ . Nitrogen rendered active by the electric glow discharge will continue to glow for some time after the discharge has ceased, and will react with phosphorus, sodium, mercury, and with some compounds of carbon and hydrogen. In many respects it seems to be analogous to ozone, but is less stable than the latter.

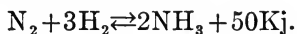
**Hydrogen Compounds of Nitrogen.**—By far the most important of the compounds of hydrogen and nitrogen is ammonia,  $NH_3$ , a substance which was first obtained in the gaseous state by Priestly in 1774. Some idea of its importance may be gained from the fact that the yearly production of the compound and its salts is equal to 260,000 tons of ammonia. In addition to ammonia we have the less important compounds, hydrazine,

$N_2H_4$ , hydronitric acid,  $HN_3$ , and hydroxylamine,  $NH_3O$ . The latter is really a hydrogen-oxygen compound of nitrogen, but has properties so like those of ammonia that it will be discussed in this connection.

**Ammonia Occurrence.**—Ammonia is present in very small quantities in the air and in all river and rain waters, both as uncombined ammonia and as ammonium nitrate,  $NH_4NO_3$ , and ammonium nitrite,  $NH_4NO_2$ .

**Preparation.**—Ammonia may be prepared in a number of ways. As was mentioned above, the elements may be made to combine directly when heated or under the influence of the electric spark. Equilibrium is reached, however, when a very small per cent. of the mixture has been transformed.

The equation for the reaction is:

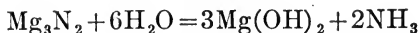


As indicated, the reaction takes place with the evolution of heat, and hence as foretold by the law of mobile equilibrium, the per cent. of ammonia in the equilibrium mixture decreases with rising temperature. If the experiments are made at atmospheric pressure, the change is from 0.22 per cent. by volume of ammonia at  $700^\circ$  to 0.12 per cent. at  $800^\circ$  or to 0.07 per cent. at  $900^\circ$ .

The equation also shows that one volume of nitrogen and three volumes of hydrogen combine to form only two volumes of ammonia. The law of mobile equilibrium predicts that at any given temperature the per cent. of ammonia in the equilibrium mixture will increase with rising pressure. Under a pressure of thirty atmospheres the equilibrium mixture contains 0.654 per cent. ammonia at  $700^\circ$ , 0.344 per cent. at  $801^\circ$ , and 0.207 per cent. at  $901^\circ$ . These results are shown graphically in the accompanying curves (Fig. 25).

This reaction is subject to catalysis with the condition that the catalyzer must work rapidly at temperatures not higher than  $750^\circ$ . Finely divided iron does fairly well and uranium still better. The process is yet in the experimental stage, but it is probable that a method of preparing ammonia by heating highly compressed nitrogen and hydrogen in the presence of a catalyzer will prove commercially successful.

Water acts upon nitrides for the formation of ammonia and the hydroxide of the metal. The equation for the decomposition of magnesium nitride is given below:



A somewhat analogous method consists in the formation of calcium cyanamide,  $\text{CaCN}_2$ , by the action of nitrogen upon calcium carbide,  $\text{CaC}_2$ , at fairly high temperatures:

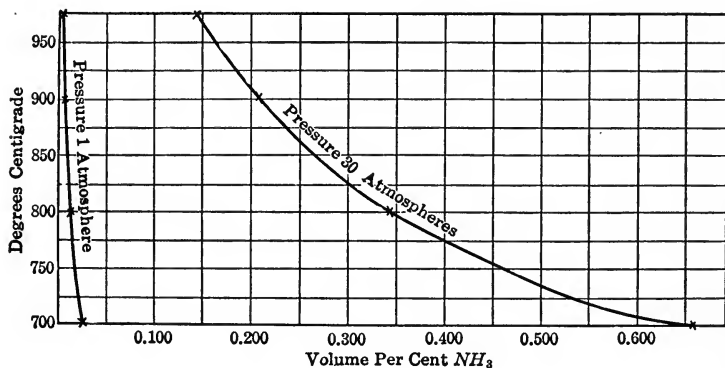
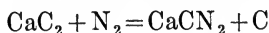
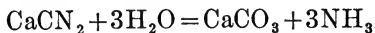


FIG. 25.

Water decomposes this calcium cyanamide and yields calcium carbonate,  $\text{CaCO}_3$ , and ammonia,



Animal refuse including horns, hides, hair, feathers, etc., contain very complex compounds of carbon, hydrogen, nitrogen, and oxygen, and when heated give off a part of the nitrogen in the form of ammonia. A solution of ammonia in water was formerly prepared in this way and was known as spirits of harts-horn; a name that is sometimes used at the present day. Decaying animal and vegetable matter gives off ammonia, and this is doubtless the chief source of atmospheric ammonia. Some ammonia is given off from volcanoes and collects around them in the form of ammonium chloride,  $\text{NH}_4\text{Cl}$ .

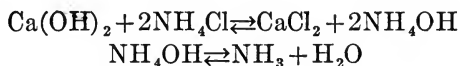
Coal contains upward of 2 per cent. of nitrogen in combi-



nation with carbon, hydrogen, etc.; and when the coal is heated in the absence of air, as in the manufacture of coal gas, and in some of the methods for making coke, a part of this nitrogen is given off in the form of ammonia. Unfortunately the greater part of our coke is made in such a way that this ammonia together with other valuable by-products is wasted. To obtain the ammonia from coal gas, the gases are led through water which dissolves the greater part of the ammonia and also many other substances. This "ammoniacal liquor" is then mixed with sufficient slaked lime to liberate the ammonia from any ammonium salts which may be present, and heated. The ammonia is given off and absorbed in dilute hydrochloric acid or sulfuric acid, forming ammonium chloride,  $\text{NH}_4\text{Cl}$ , or ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ .

Practically all the ammonia of commerce is prepared from coal in this way.

In the laboratory, ammonia is usually obtained by gently heating a mixture of slaked lime,  $\text{Ca}(\text{OH})_2$  and ammonium chloride, in a flask provided with a delivery tube. Ammonium hydroxide is first formed and then decomposed into ammonia and water.



It may also be secured by heating a strong aqueous solution of ammonia.

Ammonia cannot be dried by either sulfuric acid or calcium chloride, since it forms ammonium sulfate with the one and a compound,  $\text{CaCl}_2 \cdot 8\text{NH}_3$ , which strongly resembles a salt with water of crystallization, with the other. Either unslaked lime,  $\text{CaO}$ , or sodium or potassium hydroxide is usually used to dry the ammonia.

**Physical Properties.**—Ammonia is a colorless gaseous substance whose molar weight is 17.034. It has a very strong characteristic odor which is familiar to everyone.

Its solubility in water is exceedingly great, one volume at room temperature takes up 800 times its volume or .6 of its weight of ammonia. At zero degrees, water will dissolve even more of the gas. In spite of the great solubility of ammonia, it still follows Henry's law approximately, especially at higher

temperatures. The solution saturated at room temperature contains about 35 per cent. by weight of ammonia, has a density of .882 and is sold as "concentrated ammonia." The whole of the gas may be removed from its solution in water by boiling which shows that it does not form a maximum or minimum boiling mixture.

The critical pressure of ammonia is 111 atmospheres, and its critical temperature is  $132^{\circ}$ . It may therefore be liquefied by pressure alone at ordinary temperatures. Its vapor pressure  $20^{\circ}$  is 8.4 atmospheres. The boiling-point is  $-33.5^{\circ}$ . It is a colorless, very mobile liquid which freezes to a white, crystalline solid at  $-77^{\circ}$ . The density of the liquid at its boiling-point is .677. The liquid ammonia is a very good solvent indeed for many substances, including a large number of salts. When salts are dissolved in liquid ammonia, they are dissociated very much as they are in water, though to a smaller degree at any given concentration than when dissolved in water. The ions travel faster in ammonia than in water, so that solutions of salts in ammonia are often better conductors of electricity than aqueous solutions of the same salts.

Liquid ammonia is a very common article of commerce, compressed in strong iron cylinders. The greater part of this is used in plants for the **manufacture of ice** and for **cold storage**. Its use for such purposes depends upon the fact that, like all other liquids, it absorbs a great amount of heat when it evaporates—the "heat of vaporization" as it is called. The ammonia does not enter into the ice in any way, but is simply used as a carrier of heat from a lower to a higher temperature. Such a process is not a spontaneous one, and can be brought about only by the expenditure of work. The process may be briefly outlined as follows:

The gaseous ammonia is compressed, generally by a steam driven pump (Fig. 26), until it liquefies in a coil of iron pipes cooled by a stream of water. In liquefying, it gives out to the water the heat of condensation. The liquefied ammonia is then allowed to escape into another coil of pipes, called the expansion coil, in which it evaporates, thereby taking up from its surroundings the heat of evaporation. The gaseous ammonia passes back from the expansion coil to the pump where it is re-compressed

and liquefied, giving up the heat absorbed in evaporating. It then passes once more into the expansion coil and so is kept circulating through the system. The expansion coil is usually immersed in brine which is cooled by the evaporating ammonia to temperatures below the freezing-point of water. Manufactured ice is made by placing cans containing about 200 lb. of distilled water in the brine and letting them stand until the water is all frozen. The ice prepared in this way is very pure, and much superior to most natural ice for domestic purposes.

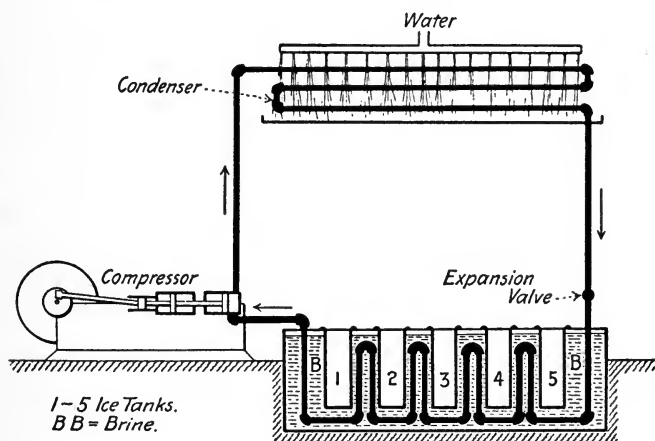
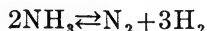


FIG. 26.

As was mentioned above, the ammonia simply serves to carry the heat from a lower to a higher temperature at the expense of the work done by the engine. Any other very easily volatile liquid might be used instead of the ammonia, and several others have been so employed.

**Chemical Properties of Ammonia.**—If a certain volume of ammonia be confined over mercury, in which it is not soluble, and electric sparks passed through the gas, it will be found to increase slowly in volume owing to the fact that it decomposes into nitrogen and hydrogen as shown in the following equation:



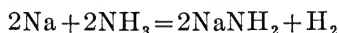
If the reaction were not a reversible one the volume of the result-

ing gases would be just twice that of the ammonia, but the action stops when there is a little ammonia left undecomposed. That is, the composition of the mixture is the same as that of a mixture of hydrogen and nitrogen through which sparks have been passed until equilibrium has been reached. So the volume will be almost, but not quite doubled by the sparks. By introducing a little acid into the tube, this ammonia will be quickly absorbed and changed into the ammonium salt of the acid. The gases will no longer be in equilibrium at the spark, and ammonia will be slowly formed and promptly taken up by the acid; thus the mixture is kept out of equilibrium and the reaction goes on until the whole of the nitrogen and hydrogen have been re-converted into ammonia. The reaction may be thus made to run in either direction, and furnishes an excellent illustration of what may be done with a properly handled reversible reaction.

Ammonia will burn in oxygen but not in air. It burns with a pale yellow flame forming water, nitrogen, ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , and ammonium nitrate,  $\text{NH}_4\text{NO}_3$ .

When ammonia is passed over heated copper oxide or other easily reducible oxide, the metal, water, and nitrogen are usually obtained.

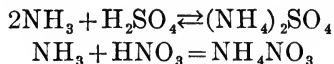
When dry ammonia is passed over heated potassium or sodium, hydrogen and potassium or sodium amide,  $\text{KNH}_2$  or  $\text{NaNH}_2$  are formed:



The most prominent chemical property of ammonia is its ability to combine directly with acids for the formation of ammonium salts. For example, with hydrogen chloride, it forms dense white fumes of ammonium chloride:

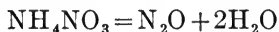


With other acids the action is very similar as shown by the following equations:



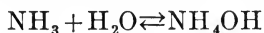
Most of these salts, when heated to a sufficiently high temperature, break down into ammonia and the acid from which they

were formed, just the reverse of the above process. Ammonium nitrate and nitrite are exceptions. The decomposition of ammonium nitrite into nitrogen and water has already been given. The nitrate decomposes into nitrous oxide,  $N_2O$ , and water,



Perfectly dry ammonium chloride may be vaporized without decomposition, or at least the decomposition is very slow. Correspondingly, absolutely dry hydrochloric acid and ammonia combine so very slowly that the action apparently does not take place. The merest trace of water will cause both actions to go very rapidly.

When ammonia dissolves in water, a part of it combines for the formation of ammonium hydroxide,  $NH_4OH$ ,



The reaction is reversible, and only a portion of the substances are present as hydroxide. At a temperature of  $-79^\circ$ , ammonium hydroxide may be prepared as a white crystalline solid. Another crystalline compound of ammonia and water can be obtained at a low temperature. It has the composition  $(NH_4)_2O$ , and may be called ammonium oxide. Its freezing-point is  $-79^\circ$ .

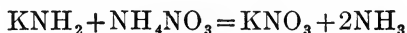
Ammonium hydroxide is a weak base and in normal solution is dissociated to the extent of about .4 per cent. The ions are hydroxyl and ammonium,  $NH_4^+$ . This ammonium ion has many properties which are very similar to those of the potassium ion.

Upon neutralizing ammonium hydroxide with acid and evaporating the solution, salts are obtained which are identical with those formed by direct union of the acids and ammonia. These salts like other salts, are highly dissociated when dissolved in water. With solutions of strong bases, they at once react for the formation of undissociated ammonium hydroxide which then breaks down into ammonia and water as was shown in the discussion of the preparation of ammonia. This reaction is used for the recognition of ammonium compounds. The ammonia is detected by its action on wet litmus, by the white fumes formed with hydrochloric acid, and even by its odor.

Ammonium salts, when dissolved in liquid ammonia, act

in almost every way as acids do in water. Such solutions attack metals with the evolution of hydrogen and the formation of a salt of the metal. They act upon indicators as acids do, turning phenolphthalein colorless, etc.

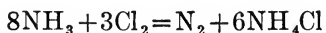
Potassium and sodium amides, on the other hand, when dissolved in ammonia, act as bases do when dissolved in water. Their solutions in ammonia react with ammonium salts for the formation of salts and ammonia as shown below:



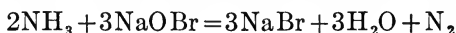
Ammonia, in many ways, shows itself to be very similar to water and the ammonium ion dissolved in ammonia is like the hydrogen ion dissolved in water; while the amid ion,  $\text{NH}_2^-$ , in ammonia is like the hydroxyl ion in water.

Ammonium salts, especially the sulfate and chloride, are much used as fertilizers to supply the necessary nitrogen for the growth of plants. The greater part of the 1,000,000 tons of ammonium salts which are annually produced is used as fertilizer.

An excess of ammonia reacts with chlorine and bromine for the formation of ammonium salts and nitrogen. The equation for the reaction with chlorine is given below; that for bromine is similar:

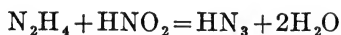


Hypobromites and hypochlorites act upon ammonia in such a way that all the nitrogen is set free in the gaseous state:

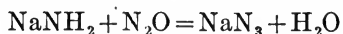


**Hydrazine.**—Hydrazine,  $\text{N}_2\text{H}_4$ , is a colorless liquid which boils at  $114^\circ$  and freezes at  $1^\circ$ . It combines with water for the formation of a hydrate,  $\text{N}_2\text{H}_6\text{O}$ , which is volatile without decomposition. It will react with acids for the formation of salts. Two series of such salts are known,  $\text{N}_2\text{H}_5\text{A}$  and  $\text{N}_2\text{H}_6\text{A}_2$ , in which A stands for any anion carrying one negative charge. Hydrazine is formed by the reduction of nitrogen compounds and is itself a very strong reducing agent.

**Hydronitric Acid or Hydrazoic Acid.**—Hydronitric acid or hydrazoic acid as it is often called may be prepared by the action of nitrous acid on hydrazine:



The sodium salt,  $\text{NaN}_3$ , may be easily obtained by the action of nitrous oxide,  $\text{N}_2\text{O}$ , upon sodium amide,  $\text{NaNH}_2$ :



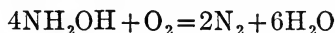
From this salt, the acid is prepared by distillation with dilute sulfuric acid. The acid tends to pass over first, and by the action of dehydrating agents, may be obtained in a pure state. It is a colorless liquid with a strong and very disagreeable odor. It boils at  $37^\circ$  and explodes violently on contact with hot objects. The substance sometimes explodes at ordinary temperatures, thus making it very dangerous to handle.

It is a rather weak acid though somewhat stronger than acetic acid. Its salts resemble the chlorides except that the salts of the heavy metals are explosive and the difficultly soluble silver salt is soluble in the stronger acids, while the chloride is not.

**Hydroxylamine.**—Hydroxylamine,  $\text{NH}_2\text{OH}$ , is formed by the reduction of nitric acid and other nitrogen compounds by fairly strong reducing agents.

It is a white crystalline solid which melts at  $33^\circ$  and boils at  $58^\circ$  under a pressure of 2.2 cm. of mercury. When heated to from  $90$  to  $100^\circ$ , it decomposes and explodes at higher temperatures. It dissolves in water forming a feebly alkaline solution. By neutralizing this solution with acids, salts of the general formula  $\text{NH}_3\text{OHA}$  may be obtained. These yield the cation  $\text{NH}_3\text{OH}^+$  and the base has the formula  $\text{NH}_3\text{OH.OH}$ . It is weaker than ammonium hydroxide.

Hydroxylamine and its salts are strong reducing agents, passing readily into nitrogen and water:



**Air.**—Air is a mixture of a rather large number of gaseous substances and in addition always contains some floating particles of dust. The main gaseous constituents which are present in almost constant proportions are nitrogen, oxygen and members of the argon group; in addition, it contains variable amounts of water vapor, carbon dioxide, and ammonia. In the neighborhood of cities sulfur dioxide, hydrogen sulfide, hydrochloric acid and a few other gases are found. These may be

regarded as accidental impurities and neglected in the discussion of air.

The quantity of carbon dioxide varies from about 3 to 4 parts per 10,000 in the air of the country to 6 to 7 parts in the cities and in badly ventilated rooms may run up to 50 parts. This carbon dioxide is formed during the burning or decay of any carbonaceous materials, and is also given off during the breathing of animals. It is however taken up by green plants, and with the aid of the energy absorbed from the light of the sun, is utilized in building up the various plant tissues, oxygen being set free at the same time. This tends to keep the carbon dioxide content of the air approximately constant.

**Composition of the Air.**—The quantity of water vapor present in the air is so variable that no definite statement concerning it can be made, but the composition of dry air is shown in the following table:

Dry Air contains:

Per cubic meter	Per kilogram
781.3 liters nitrogen.....	755.14 grm.
209.9 liters oxygen.....	231.47 grm.
9.4 liters argon, etc.....	12.92 grm.
0.3 liters carbon dioxide.....	.46 grm.
0.1 liters hydrogen.....	.01 grm.

The term argon, etc., includes argon, helium, neon, krypton and xenon.

In spite of the many factors which tend to change the composition of the air, the winds produce such a thorough mixing that its composition remains practically fixed, although measurable variations do occur.

The density of the air is .001293 under standard conditions. In contact with water, each gas dissolves in proportion corresponding to its solubility and its partial pressure as described by Henry's law. The solubility of oxygen is so much greater than that of nitrogen that in spite of its smaller partial pressure relatively more oxygen than nitrogen dissolves.

**Liquid Air.**—The critical temperature of air is  $-140^{\circ}$  and its critical pressure about 39 atmospheres. Liquid air boils from



—194 to —185° according to its composition, and when first prepared contains from 28 to 50 per cent. of oxygen. As it stands, the nitrogen (boiling-point —194°) tends to pass off first and leaves the oxygen (boiling-point —182.5°) behind. This is made the basis of very practical methods for obtaining both oxygen and nitrogen from the air sufficiently pure for many commercial purposes. Liquid nitrogen has a smaller density than that of water, while the case is the other way with liquid oxygen. Liquid

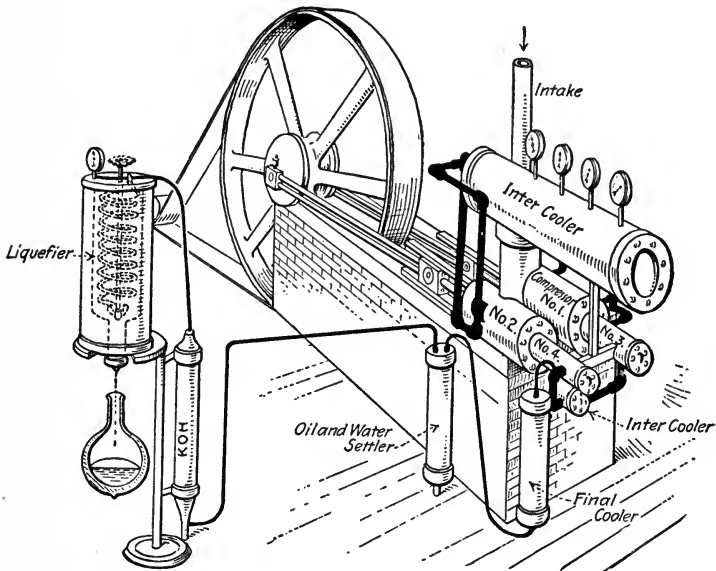


FIG. 27.

air when freshly prepared is specifically lighter than water, but on standing becomes heavier. The color also changes from practically colorless to the blue of liquid oxygen.

To liquefy air it is first partially freed from carbon dioxide by slaked lime, and then compressed to 150 to 200 atmospheres. A great deal of heat is developed in this process so the gas is cooled to ordinary temperatures by water in the jackets around the compressor (Fig. 27), and by passing it through a coil surrounded by water. The greater part of the water vapor in the air condenses at this high pressure and the remainder together

with the rest of the carbon dioxide is removed by potassium hydroxide. The purified highly compressed air then enters the liquefier at the temperature of the room. The liquefier consists of a coil of very small copper tubing carrying at its lower end a valve for controlling the flow of the air. The whole is inclosed in a metal jacket and thoroughly insulated from its surroundings by wool. Through the copper tube, the air flows in a continuous stream and as it escapes from the valve at the lower end of the coil, it becomes somewhat cooler. By the construction of the apparatus, this cooled air is compelled to pass up over the coil thereby cooling it together with the oncoming air which reaches the valve at a lower temperature than the first of the stream, and in expanding becomes still cooler and in turn lowers the temperature of the coil. This process goes on until a few minutes after starting the machine the temperature has been so far lowered that about 5 per cent. of the air issuing from the expansion valve is liquefied. The rest is returned to the machine, recompressed and sent around the cycle once more. In large plants part of the cooling is accomplished with carbon dioxide and ethylene.

The liquid air cannot be corked up and will evaporate as rapidly as it can get the necessary heat, so after it is obtained it is preserved in double walled vacuum jacketed vessels which are usually coated on the inside of the walls with silver. Such vessels are very good heat insulators indeed.

Liquid air on account of its low boiling-point is an exceedingly useful substance for investigations at low temperatures.

**Experiments.**—Many interesting and striking experiments may be performed with liquid air. These depend essentially upon two properties; first that it has a very low boiling-point, and second that it is a source of oxygen. When cooled to the temperature of liquid air, most of the familiar gases such as  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{S}$  become odorless solids. Liquids such as alcohol and kerosene freeze, and rubber becomes as brittle as glass and may be easily pulverized in a mortar. Metals such as copper and steel become a third stronger toward a steady pull, but break readily under a quick blow. Crystalline metals, on the other hand, are distinctly weaker in every way at this low temperature. The heat absorbed during the evaporation of 1 gm. of liquid air plus the heat required to warm the

gaseous air to  $0^{\circ}$  is about 80 cal., so the cooling effect of a pound of liquid air in a refrigerator would be about equal to that of a pound of ice.

When liquid air boils, the nitrogen goes off faster than the oxygen, and after a time almost pure liquid oxygen is left. This furnishes oxygen of such concentration that charcoal or steel will burn with exceeding brilliancy in the liquid. Cotton or charcoal wet with just the proper amount of oxygen to complete the combustion will explode when set off with a mercury fulminate cap with the violence of an equal weight of dynamite. Aluminum powder made into a paste with liquid oxygen will burn with a blinding flash upon contact with a flame, and the temperature of the mass is changed in a small fraction of a second from  $183^{\circ}$  below to something like  $3000^{\circ}$  above zero.

**Air is a Mixture.**—That air is a mixture and not a chemical compound is shown by several arguments.

1. Nitrogen and oxygen may be mixed in the proportion in which they are present in the air, and no heat effect will result, no changes in volume, nor any other evidence of chemical transformation and yet the mixture behaves like air in every respect.

2. The composition of the air varies while that of a compound is perfectly fixed.

3. Relatively more oxygen than nitrogen is dissolved by water, while a compound dissolves as a whole, without any change in the proportions of the components.

4. The properties of the air are a mean of the properties of its components, which would not be true if it were a compound.

5. The separation of the gases by liquefaction and fractional distillation indicates a mixture.

**Air and Life.**—Oxygen is absolutely indispensable for the continuance of all forms of animal life. The purely aquatic forms get their oxygen from air dissolved in the water, while the rest breathe the air directly. We, for example, take in about half a liter of air at each breath, and remove from this about 5 per cent. of the oxygen, giving to it about 3.7 per cent. of carbon dioxide. The nitrogen is unchanged. The oxygen taken up in the lungs largely enters into a loose combination with a substance called hemoglobin in the red corpuscles of the blood and is carried to

all parts of the body, gradually oxidizing the various body substances, chiefly to carbon dioxide, water, and fairly simple compounds of carbon, nitrogen, hydrogen, and oxygen. The carbon dioxide is largely given up by the blood to the air upon its return to the lungs. The oxidation of these substances is the source of the body heat, and of the energy which we spend as work.

**Analysis of Air.**—The percentage of oxygen in the air is easily obtained by exposing a measured volume of air to phosphorus at ordinary temperatures until the oxygen has all been used up, and determining the volume of the residue. Of course, if temperature and pressure have changed between the two measurements, corresponding corrections must be applied.

**Oxides and Oxyacids of Nitrogen.**—There are five oxides of nitrogen. Three of these are anhydrides of acids. The names and formulas of these oxides are given in the following table with the names and formulæ of the acids opposite their anhydrides.

Nitrous oxide or hypo-		
nitrous anhydride....	$N_2O$	Hyponitrous acid..... $H_2N_2O_2$
Nitric oxide.....	$NO$	.....
Nitrogen trioxide or		
nitrous anhydride....	$N_2O_3$	Nitrous acid..... $HNO_2$
Nitrogen peroxide.....	$NO_2$ or $N_2O_4$	.....
Nitrogen pentoxide or		
nitric anhydride.....	$N_2O_5$	Nitric acid..... $HNO_3$

Since nitric acid is the direct or indirect source of all these compounds, it will be discussed first.

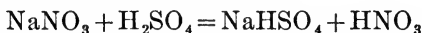
**Nitric Acid.**—Nitric acid does not occur free in nature, but its salts are present in all fertile soils. Potassium nitrate,  $KNO_3$ , has been known for centuries under the name of saltpeter. The sodium salt,  $NaNO_3$ , occurs in great deposits in the desert regions of Chile, and hence is called Chile saltpeter. Enormous quantities of this are extracted and shipped all over the world for use in preparing other nitrogen compounds, and as a fertilizer.

Under the influence of electrical discharges nitrogen, oxygen, and water will combine for the formation of nitric acid, and this, together with the ammonia of the air, is doubtless the source of the ammonium nitrate contained in rain water.

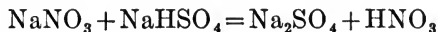
Certain forms of soil bacteria are able to convert ammonia and

nitrogenous organic substances into nitric acid which then reacts with the calcium carbonate of the soil to form calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ .

Nitric acid is prepared by the first general method by distilling sodium nitrate with sulfuric acid. The reaction goes on in two stages, as in the preparation of hydrochloric acid. First nitric acid and sodium acid sulfate are formed:



and then at a higher temperature the sodium acid sulfate reacts with more sodium nitrate to form normal sodium sulfate,  $\text{Na}_2\text{SO}_4$ , and nitric acid



This second reaction takes place at so high a temperature that a good deal of the nitric acid is decomposed into nitrogen peroxide, oxygen and water. This difficulty can be almost entirely removed by carrying out the distillation under diminished pressure, which so far lowers the temperature that the acid comes over undecomposed.

On a manufacturing scale, nitric acid is prepared by heating sodium nitrate and sulfuric acid in cast-iron retorts; and enough of the sulfuric acid is used to make the acid sulfate which is either sold as such or heated with sodium chloride to make hydrochloric acid and the neutral sulfate.

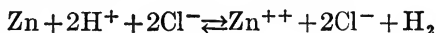
Pure nitric acid is a colorless liquid having a density of 1.53 at 15°. It boils at 86°. It gradually decomposes, especially under the influence of light into oxygen, water, and oxides of nitrogen, which color the acid yellow. The addition of water makes the acid much more stable, perhaps because of the transformation of the acid into ions. As water is added to the acid, the boiling-point gradually rises until when a 68 per cent. acid is formed, the boiling-point reaches a maximum at 120°. The relations here are very similar to those between hydrochloric acid and water.

**Chemical Properties of Nitric Acid.**—The chief chemical properties of nitric acid depend upon the fact that it is both a strong acid and very powerful oxidizing agent.

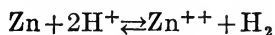
As an acid it is as strong as any, being as highly dissociated

into its ions at any given dilution as hydrochloric acid. Consequently it is able to do anything that depends upon the concentration of the hydrogen ions, which any other acid can do. Dilute nitric acid has a sour taste, reddens litmus, neutralizes bases, and dissolves metals just as hydrochloric does. It is even able to dissolve some metals, silver, mercury and copper, for example, which are not dissolved by hydrochloric acid. This, as will presently be seen, is due to the fact that nitric acid is a strong oxidizing agent.

As will be recalled, the ordinary reaction between an acid and a metal whereby the metal is dissolved and hydrogen is liberated is regarded as taking place between the metal and the hydrogen ion, and as consisting of the oxidation of the metal to its ion and the reduction of the hydrogen ion to the free element. For example, in that between zinc and hydrochloric acid, the chlorine ion is considered to take no part, the entire reaction being between the zinc and the hydrogen ion,



or, leaving out the idle chlorine ion,



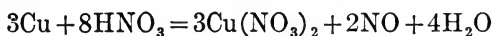
Like most other reactions this is to be looked upon as reversible. It takes place from left to right because the hydrogen ion is a stronger oxidizer than the zinc ion,  $\text{Zn}^{++}$ , and also because the zinc is a stronger reducing agent than the hydrogen,  $\text{H}_2$ . We have already learned that the oxidizing or reducing power of a substance can be increased by raising its concentration. It therefore follows that we should be able to reverse the above reaction and make it run from right to left by treating a very concentrated solution of a zinc salt with hydrogen under great pressure. The pressure of the hydrogen, however, necessary to bring this about, is so great that it is hardly practicable to reverse this reaction. Some of the metals are much weaker reducing agents than zinc and their ions are stronger oxidizing agents than the zinc ion. In such cases the action is easily reversed. In fact the ions of copper, mercury and silver at ordinary concentrations are stronger oxidizing agents than hydrogen as ion, and the reaction is reversed by hydrogen even at atmos-

pheric pressure. That is to say, that hydrogen gas will precipitate metallic copper, silver, and mercury from their salts, leaving the acid in solution. Under ordinary conditions, this action is so slow as to be inappreciable, but in the presence of platinum, which acts as a catalyzer, it takes place fairly rapidly.

Copper, mercury, and silver are not dissolved by dilute hydrochloric acid because the hydrogen ion,  $H^+$ , is not a strong enough oxidizing agent to change them into their ions. These metals are attacked, however, by hot concentrated sulfuric acid. This is due to the fact that sulfuric acid under these conditions is a strong oxidizing agent, stronger than the hydrogen ion,  $H^+$ . A further point to be noticed is that no hydrogen gas is given off; but sulfur dioxide and water, reduction products of sulfuric acid, are formed. As an example of this kind of action the equation for the reaction between sulfuric acid and copper is given:



Nitric acid even at ordinary temperatures is a stronger oxidizing agent than hydrogen ion,  $H^+$ , and hence dissolves these metals easily. In none of these cases is hydrogen given off, but the nitric acid is reduced, generally to water and nitric oxide,  $NO$ . The equation for the reaction with copper is as follows:



When dilute nitric acid acts upon metals like magnesium which dissolve in other acids with the evolution of hydrogen, the action depends largely upon the dilution of the acid. If it is very dilute, hydrogen will be given off, but if more concentrated, the nitric acid will be reduced instead of the hydrogen. With these metals the reduction usually goes farther than with metals like copper, often going clear to ammonia, the lowest reduction product of nitric acid. The action varies with the nature of the metal, the concentration of the acid, and the temperature.

Gold and platinum are not oxidized by nitric acid in the absence of chlorine as ion, and therefore this acid is used in the refining of these metals to dissolve the silver, etc., with which they may be alloyed.

Because of the vigor of its action on metals, nitric acid was formerly called *aqua fortis*.

In addition to its use as indicated above, nitric acid is largely employed in the laboratory and in the manufacture of nitrates, dyestuffs, sulfuric acid, nitroglycerine, guncotton, etc.

**Aqua Regia.**—Aqua regia is a mixture of nitric and hydrochloric acids, and is capable of attacking gold and platinum, metals which do not dissolve in either of these acids alone. The action is not due to aqua regia being a stronger oxidizing agent than the nitric acid but to the fact that under these conditions the chlorides of the metals may be formed. The chlorides of gold and platinum are much more stable than their nitrates and hence are formed with a greater decrease in free energy. It is this which enables the nitric acid to oxidize these metals in the presence of hydrochloric acid when it cannot do it alone.

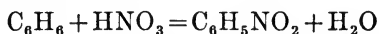
Aqua regia received its name long ago when the alchemists found that it was a solvent for gold which they considered to be the king of metals.

When aqua regia is heated alone, it gives off chlorine and compounds of nitrogen, oxygen, and chlorine; one of these is nitrosyl chloride, NOCl.

**Nitrates.**—Nitric acid, as is indicated by its formula, is a mono-basic acid and yields only one series of salts, the nitrates. These are formed by the action of the acid upon the metals or bases.

These salts are all readily soluble in water and hence there is no cation which precipitates the nitrate ion,  $\text{NO}_3^-$ . They are detected by the dark coloration which they give in acid solutions of ferrous salts. This will be explained in connection with nitric oxide. The nitrates are decomposed rather readily at elevated temperatures, generally giving oxygen, oxide of nitrogen, and the oxide of the metal. Most of the applications of nitrates depend upon their action as oxidizing agents. When heated with charcoal they often detonate. Potassium nitrate, charcoal, and sulfur in the proper proportions constitute gunpowder.

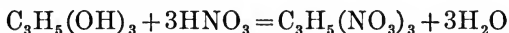
**Nitro Compounds.**—Very concentrated nitric acid acts upon compounds of carbon and hydrogen for the formation of nitro compounds and water. For example, nitric acid and benzene,  $\text{C}_6\text{H}_6$ , react for the formation of nitrobenzene,  $\text{C}_6\text{H}_5\text{NO}_2$ , and water.





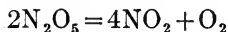
The group  $\text{NO}_2$  is known as the nitro group. These nitro compounds are not salts and the reaction is not ionic. It takes place only in the most concentrated nitric acid and in the absence of appreciable quantities of water. The water formed in the reaction is detrimental, so concentrated sulfuric acid is mixed with the nitric acid to take up this water.

Alcohols (carbon, hydrogen and oxygen compounds containing hydroxyl) react with nitric acid for the formation of compounds which in their formulæ are similar to nitrates, but which are not salts. A mixture of nitric and sulfuric acids is used in case the water formed in the reaction is detrimental. The reaction is not ionic, and is really very different from that for the formation of salts. Glyceryl nitrate or nitroglycerine,  $\text{C}_3\text{H}_5(\text{NO}_3)_3$ , is formed by the action of this mixture of acids upon an alcohol called glycerine,  $\text{C}_3\text{H}_5(\text{OH})_3$ :

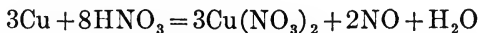


**Nitrogen Pentoxide.**—When pure nitric acid is mixed with phosphorus pentoxide and the mixture distilled after standing for some time, nitrogen pentoxide,  $\text{N}_2\text{O}_5$ , passes over; the water formed at the same time remains behind combined with the phosphorus pentoxide.

Nitrogen pentoxide is a colorless, mobile, very volatile liquid which soon passes over into a white crystalline solid, melting at  $30^\circ$ . It combines with water for the formation of nitric acid and hence is called nitric anhydride. It readily decomposes into nitrogen peroxide and oxygen:

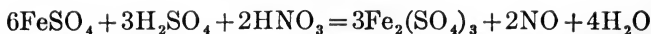


**Nitric Oxide.**—Nitric oxide,  $\text{NO}$ , is formed by the action of somewhat dilute nitric acid, sp. gr. 1.2, upon copper, as shown in the following equation:



The gas so obtained is never pure, since it always contains some nitrous oxide,  $\text{N}_2\text{O}$ , and often nitrogen.

The pure oxide may be obtained by adding nitric acid to a boiling solution of ferrous sulfate,  $\text{FeSO}_4$ , in dilute sulfuric acid. The equation is as follows:



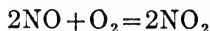
The ferrous sulfate is oxidized to ferric sulfate,  $\text{Fe}_2(\text{SO}_4)_3$ , and the nitric acid reduced to nitric oxide.

**Properties of Nitric Oxide.**—Nitric oxide is a colorless gas whose molar weight is 30 corresponding to its formula NO. It is only slightly soluble in water. The critical temperature of the gas is  $-93^\circ$ , and its boiling-point is  $-150.2^\circ$ . So it is more like the so-called permanent gases, oxygen, hydrogen, etc., than most of the gaseous substances which we have been discussing.

Nitric oxide is the most stable of the oxides of nitrogen. Even when heated to a temperature of  $2000^\circ$  only about 1 per cent. of it is decomposed. In fact it is formed from its elements at very high temperatures, and may be obtained by passing the electric spark through air. This is made the basis of a successful method for the preparation of nitric acid and nitrates on a commercial scale as will be explained later.

Burning phosphorus will continue to burn in NO. The flame is about as bright as when the combustion takes place in oxygen. Most other combustible substances, for example burning candle, charcoal or sulfur, are extinguished. Since the heat of formation of nitric oxide is  $-90$  KJ. considerable heat is evolved in its decomposition, and a given quantity of a substance like phosphorus burning in NO will liberate more heat than if it had burned in oxygen.

Nitric oxide combines directly with oxygen at ordinary temperatures, forming the reddish-brown nitrogen peroxide,  $\text{NO}_2$ :



This nitrogen peroxide is at once formed whenever the nitric oxide comes in contact with the air, consequently it is impossible to say anything about the odor of nitric oxide.

Nitric oxide is soluble in solutions of ferrous salts with the production of a dark brown solution. From this solution the oxide is driven out by heating to the boiling-point. In this way pure NO may easily be obtained from mixture with other gases, since the latter are either not absorbed in the first place or are retained when the solution is boiled.

The formation of this dark colored solution may be utilized as a test for nitric acid, a nitrate, or in general any oxygen compound

higher than nitric oxide. To do this, advantage is taken of the fact that an acid solution of a ferrous salt will reduce such compounds to nitric oxide which will then react with the excess of the salt to form this dark brown compound. The test is performed as follows: The substance to be tested is dissolved in water and mixed with a concentrated solution of ferrous sulfate in a test-tube. Concentrated sulfuric acid is then poured slowly down the side of the test-tube, taking care that the liquids do not mix. If nitrates, etc., are present, a brown ring will gradually form at the junction of the two liquids. The brown coloration is due to the ion,  $\text{FeNO}^{++}$ .

**Nitrogen Peroxide.**—Nitrogen peroxide as has already been mentioned is formed by the direct union of oxygen and nitric oxide. It may also be prepared by heating certain nitrates. Lead nitrate, for example, decomposes to give nitrogen peroxide, oxygen, and lead oxide, as shown by the following equation:



By means of a freezing mixture, the nitrogen peroxide may be condensed to a yellowish-red liquid which has the fainter color the lower the temperature. It boils at  $22^\circ$  and at low temperatures freezes to an almost colorless solid, melting at  $-12^\circ$ .

The molar weight of the gaseous compound varies with the conditions of temperature and pressure under which it is determined. At low temperatures and rather high pressures it is nearly 92, corresponding to a formula for the compound of  $\text{N}_2\text{O}_4$ . As the temperature is raised and the pressure diminished, the molar weight gradually falls until it reaches a lower limit of 46, corresponding to the formula  $\text{NO}_2$ . The intermediate molar weights are evidently due to mixtures of the two forms. At any given temperature, the molar weight becomes smaller the lower the pressure. This shows that as the pressure decreases the compound  $\text{N}_2\text{O}_4$  is changed into  $\text{NO}_2$ . This change from one form to the other is accompanied by a marked change in color. At rather low temperatures the gas has a yellow-brown color, as the temperature is raised it becomes darker and darker until at  $154^\circ$  it has reached such a deep black-red that it is almost opaque, even in thin layers.

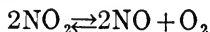
The transformation from one form to the other is reversible,

and for each temperature and pressure, there exists a certain definite mixture of the two substances at which equilibrium will result. The composition of the equilibrium mixture may be readily obtained from its apparent molar weight. At 50° and 18.3 cm. pressure the molar weight,  $M$ , is 55. If  $x$  be the fraction of the total volume formed by the  $\text{NO}_2$ , then  $1-x$  represents that of the  $\text{N}_2\text{O}_4$ , and a mixture of the two has a molar weight of  $M = 46x + (1-x)92$ . From this

$$x = \frac{92 - M}{46}$$

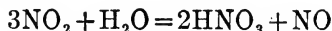
Substituting in this the molar weight 55 for the  $M$ , we get for  $x$  the value .805. This shows that 80.5 per cent. of the total volume is made up of the simple compound, and 19.5 per cent. of the more complex form. The formation of  $\text{NO}_2$  from  $\text{N}_2\text{O}_4$  upon lowering the pressure is in accord with the law of mobile equilibrium, because the production of two moles from one tends to increase the pressure and thereby relieve the constraint. Heat is absorbed when  $\text{N}_2\text{O}_4$  is changed into  $\text{NO}_2$ , and therefore this decomposition with rising temperature is in agreement with this same law.

When  $\text{NO}_2$  is heated to temperatures above 154°, it gradually loses its dark color as the temperature rises, and finally becomes colorless. This color change is due to the transformation of  $\text{NO}_2$  into  $\text{NO}$  and oxygen.

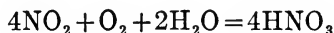


This decomposition becomes practically complete at 620°.

Nitrogen peroxide reacts with water for the formation of nitric acid and  $\text{NO}$ ,



In the presence of air,  $\text{NO}$  will pass into  $\text{NO}_2$ , which in turn will form more nitric acid. So the reaction of  $\text{NO}_2$ , air, and water will ultimately yield the whole of the nitrogen in the form of nitric acid.

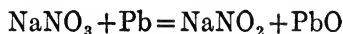


When an electric spark is passed through air, a small quantity of

nitrogen and oxygen is converted into nitric oxide by the high temperature. When the temperature has fallen sufficiently, the NO combines with the oxygen of the air to form NO<sub>2</sub>, and the latter with air and water will form nitric acid. At Notodden, Norway, this process is carried out on a very large scale. The NO<sub>2</sub> formed is taken up by water in towers similar to the Glover or Gay Lussac towers and converted into calcium nitrate by letting the nitric acid formed act upon slacked lime. The calcium nitrate is a good fertilizer and is put on the market at a low enough price to compete with the Chile saltpeter.

The yield corresponds to 500 kgrm. of nitric acid per kilowatt-year or 57 grm. per kilowatt-hour.

**Nitrites.**—When potassium or sodium nitrates are heated, especially in the presence of a reducing agent like lead, they lose one combining weight of oxygen per mole and are changed into nitrites,

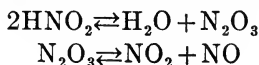


To carry out this reaction the nitrate is melted and stirred up with the lead. After the operation is finished the nitrite is separate from the difficultly soluble litharge, PbO, by solution in water, and purified by recrystallization.

When acids act upon a cold dilute solution of a nitrite, a pale blue solution is obtained which contains nitrous acid. This quickly decomposes, especially upon warming, as shown in the following equation,

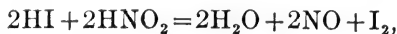


When an acid is added to a strong solution of a nitrite, the nitrous acid formed breaks up immediately into water and nitrous anhydride, N<sub>2</sub>O<sub>3</sub>; but the latter at once almost completely decomposes into nitrogen peroxide and nitric oxide,



In this way a nitrite is easily distinguished from a nitrate, since the nitrogen peroxide is so highly colored.

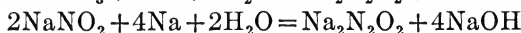
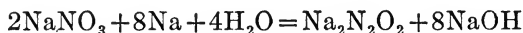
Nitrous acid oxidizes good reducing agents while it is itself oxidized by strong oxidizing agents. For example, it oxidizes HI,



and reduces potassium permanganate,  $\text{KMnO}_4$ ,  
 $2\text{KMnO}_4 + 5\text{HNO}_2 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{HNO}_3 + 3\text{H}_2\text{O}$   
 The nitrites are largely used in the manufacture of organic dyes.

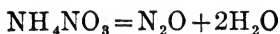
**Nitrous Anhydride.**—In addition to the method mentioned above for the formation of a mixture of  $\text{NO}$  and  $\text{NO}_2$  in the preparation of nitrous anhydride, this same mixture may be obtained by heating arsenic trioxide,  $\text{As}_2\text{O}_3$ , with nitric acid having a density of 1.30 to 1.35. The arsenic trioxide is oxidized to the pentaoxide,  $\text{As}_2\text{O}_5$ , and the nitric acid reduced to nitrous which at once breaks down into water and the mixture of the two oxides. This mixture of the two oxides may be condensed by a freezing mixture to a dark-blue liquid which boils at  $3.5^\circ$ . If the liquid is completely dried, it may then be vaporized without dissociating into  $\text{NO}$  and  $\text{NO}_2$ . So dry  $\text{N}_2\text{O}_3$  can exist while the moist compound cannot.

**Hyponitrous Acid.**—Solutions of sodium nitrate or nitrite may be reduced to sodium hyponitrite,  $\text{Na}_2\text{N}_2\text{O}_2$ , by the action of sodium amalgam. Sodium amalgam is a solution of metallic sodium in mercury. It acts much less vigorously than metallic sodium and hence is more easily controlled than the latter for use as a reducing agent. The equations for the reactions are as follows:



Silver hyponitrite is easily prepared from the sodium salt since the former is but slightly soluble in water. Anhydrous hyponitrous acid may be obtained by passing hydrogen chloride into an ethereal solution of the silver salt. It is a white crystalline substance which is very unstable and readily explodes. A water solution of this acid is unstable and decomposes slowly into water and hyponitrous anhydride,  $\text{N}_2\text{O}$ , or nitrous oxides as it is often called. This decomposition is not reversible, so hyponitrous acid cannot be obtained from water and nitrous oxide.

**Nitrous Oxide.**—Nitrous oxide is readily prepared by heating ammonium nitrate, which decomposes into this substance and water,

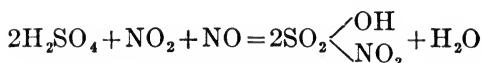
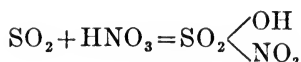


It is a colorless gaseous substance which has a faint odor and is fairly soluble in cold water. At room temperatures, water will dissolve about its own volume of the oxide. Its critical pressure is 75 atmospheres and its critical temperature  $+ 36^{\circ}$ ; so it is easily liquefied by pressure alone at ordinary temperatures. The boiling-point is  $- 90^{\circ}$  and the freezing-point  $- 102^{\circ}$ . The molar weight of the oxide is 44 and its formula  $N_2O$ .

Nitrous oxide parts with its oxygen rather more readily than nitric oxide so that it will not only continue to support combustion of brightly burning wood as nitric oxide does, but will even cause a glowing splinter to burst into flame. It is somewhat difficult to cause phosphorus to kindle in the gas, but after the combustion has once been started, it goes on almost as vigorously as in oxygen. Feebly burning sulfur is extinguished by nitrous oxide, while that which is in a brisk state of combustion continues to burn. In all cases, oxides are formed and nitrogen set free. The heat of combustion of a given substance in nitrous oxide is greater than that of the same substance in oxygen because of the fact that the oxide decomposes with the evolution of heat, 86 KJ. per gram mole.

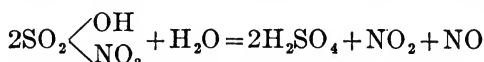
Nitrous oxide when breathed produces insensibility, and hence it is used as an anesthetic. The body does not decompose the nitrous oxide in such a way as to utilize the oxygen, so when it is to be breathed for any length of time, it is mixed with the amount of oxygen required to support life. For use as an anesthetic, very pure nitrous oxide is put on the market in the liquid form in strong iron cylinders.

**Nitrosylsulfuric Acid.**—Nitrosylsulfuric acid is an important substance because of the part which it plays in the manufacture of sulfuric acid. Its composition and many of its properties may be represented by the formula  $SO_2 \begin{matrix} \text{OH} \\ \text{NO}_2 \end{matrix}$ . As indicated by this formula, it behaves as a nitro and as a hydroxyl compound. This acid may be prepared in a number of ways: for example, by passing sulfur dioxide into strong nitric acid or by acting upon concentrated sulfuric acid with a mixture of nitrogen peroxide and nitric oxide in the proportion for the formation of nitrous anhydride. The equations are given below:



This last equation is especially important since it represents the reaction which takes place in the Gay Lussac tower when the oxides of nitrogen are dissolved in the concentrated sulfuric acid at the end of the lead chamber process for the manufacture of this acid.

Nitrosylsulfuric acid is a white crystalline substance which melts with decomposition at 73°. It rapidly reacts with water for the formation of sulfuric acid and nitrous acid. The latter at once decomposes into water, nitrogen peroxide and nitric oxide. The equation for the completed reaction is as follows:



The nitrosylsulfuric acid is soluble in concentrated sulfuric acid forming a stable solution which will stand being diluted somewhat with water. Some decomposition takes place, however, when the water is added, and if the oxides are removed the reaction will continue until the whole of the nitrosylsulfuric acid has been transformed. This takes place in the Glover's tower of a sulfuric acid plant. Here the concentrated sulfuric acid containing nitrosylsulfuric acid in solution from the Gay Lussac's tower is mixed with dilute acid from the chambers. The water so added brings about the above reaction to a certain extent, and as the acids trickle down over the stones of the Glover's tower the oxides of nitrogen are removed from solution by the oncoming stream of hot sulfur dioxide, thus causing the reaction to go on to completion. So the valuable oxides of nitrogen are taken up at the end of the process for the manufacture of sulfuric acid, and reintroduced at its beginning by the successive formation and decomposition of nitrosylsulfuric acid.

Nitrosylsulfuric acid is also of considerable theoretical importance since it is generally supposed that the accelerating influence of the oxides of nitrogen upon the reaction between sulfur dioxide, oxygen and water for the formation of sulfuric acid in the lead chambers is due to its successive formation and decomposition,



as has been explained under the lead chamber process for the manufacture of sulfuric acid, page 206.

There is this to be said in favor of the theory that nitrosyl-sulfuric acid is formed as an intermediate step in the preparation of sulfuric acid, that when the supply of water in the chambers is inadequate, large crystals of the nitrosylsulfuric acid collect upon the walls of the chambers. Because of this fact, the substance is often called "lead chamber crystals." As against the theory, we may say that in a properly working chamber no signs whatever of the formation of these lead chamber crystals can be detected. If the theory is correct, the nitrosylsulfuric acid is decomposed as rapidly as it is formed.

**Transfer Catalysis.**—The acceleration of a reaction through the formation of an intermediate compound which decomposes with the formation of the end-products and the reproduction of the catalyzer is called transfer catalysis. In order that the reaction shall be hastened, it is of course necessary that the formation and decomposition of the intermediate substance takes place more rapidly than the direct transformation. The oxides of nitrogen are considered to be transfer catalyzers in the manufacture of sulfuric acid.

**Nitrogen and Life.**—Compounds of nitrogen are always present in all living organisms. They are especially abundant in the brain, nerves, and muscles, or in short in the tissues which seem to be most closely connected with the vital functions. Most organisms are entirely unable to make any use of the great store of free nitrogen in the air, but must get it from ready formed compounds. The plants as a rule get theirs from the nitrates, etc., which are present in the soil, while the animals obtain the compounds directly or indirectly from the plants.

Upon the decay of these organisms a portion of the nitrogen is liberated in the free state. From this it would seem that the supply of available nitrogen compounds must be continually decreasing. However, there are two important natural processes going on which tend to keep up the supply of nitrogen compounds available for plants. The first of these is the formation of nitric oxide during the passage of lightning through the air. The oxide is then transformed into nitric acid by the action of oxygen and water. This combines with the ammonia of the air to form

ammonium nitrate which is carried by the rain into the soil. The second process takes place with the aid of certain forms of bacteria. Some forms are free in the soil, but the most efficient live in tubercles on the roots of leguminous plants such as clover, peas, alfalfa, etc. These bacteria have the power to transform the free nitrogen of the air into compounds which are closely related to the albumins, and which may be easily assimilated by the plant. Such plants will grow and produce abundant crops, and yet leave in the soil an increased amount of nitrogen compounds. This, then, is the explanation for the well-known fact that the fertility of certain soils may be restored by growing upon them these leguminous plants. In the older parts of the country, it is the custom of farmers to raise a crop of such plants on each portion of cultivated land about once in 3 years. The farmers of the West will doubtless have to adopt this same custom in the course of time, if they continue to remove everything from the land and return nothing to it, and to burn the stalks and straw as so many do at present.

In addition, as has been mentioned, the compounds of ammonia which are obtained in the manufacture of coal gas and coke as well as the calcium cyanamide and calcium nitrate which are being made from the nitrogen of the air are available as fertilizers. So there seems to be no danger that the earth will lose its fertility because of lack of combined nitrogen.

**Oxidation and Reduction.**—Oxidation and reduction processes have been frequently mentioned in what has gone before, but have not been discussed in detail. While oxygen is the typical oxidizing agent, attention has been called a number of times to the fact that we have well marked cases of oxidation into which oxygen does not enter in any way. Similarly hydrogen is the typical reducing agent, but a great many reduction processes are known which do not involve this element.

A study of these processes soon shows that they always produce changes in the valence of the elements oxidized or reduced. That this is so may be easily seen from the table given below.

An inspection of the last three columns in the first table will show that oxidation is always accompanied by an increase in the number of positive charges upon the element oxidized, a decrease in negative being of course equivalent to an increase in the

## TYPES OF CHANGES WHICH ARE CONSIDERED OXIDATION

Substance oxidized	Oxidizing agent	Substance formed	Valence of the oxidized substances		Change in valence
			Before	After	
Mg	O <sub>2</sub>	MgO	0	+2	+2
Zn	H <sup>+</sup>	Zn <sup>++</sup>	0	+2	+2
I <sub>2</sub>	KClO <sub>3</sub>	IO <sub>3</sub> <sup>-</sup>	0	+5	+5
Fe <sup>++</sup>	Cl <sub>2</sub>	Fe <sup>+++</sup>	+2	+3	+1
Cl <sup>-</sup>	MnO <sub>2</sub>	Cl <sub>2</sub>	-1	0	+1
S <sup>--</sup>	I <sub>2</sub>	S	-2	0	+2
S <sup>--</sup>	Br <sub>2</sub> (H <sub>2</sub> O)	SO <sub>4</sub> <sup>--</sup>	-2	+6	+8
SO <sub>3</sub> <sup>--</sup>	O <sub>2</sub>	SO <sub>4</sub> <sup>--</sup>	+4(of S)	+6(of S)	+2

## TYPES OF CHANGES WHICH ARE CONSIDERED REDUCTION

Substance reduced	Reducing agent	Substance formed	Valence of the reduced substance		Change in valence
			Before	After	
Cu <sup>++</sup>	Zn	Cu (metal)	+2	0	-2
Ag <sup>+</sup>	H <sub>2</sub>	Ag (metal)	+1	0	-1
I <sub>2</sub>	S <sup>--</sup>	I <sup>-</sup>	0	-1	-1
NO <sub>3</sub> <sup>-</sup>	Cu	NO	+5 (N)	+2(N)	-3
NO <sub>3</sub> <sup>-</sup>	Al (in KOH)	NH <sub>3</sub>	+5	-3	-8
ClO <sub>3</sub> <sup>-</sup>	SO <sub>3</sub> <sup>--</sup>	Cl <sup>-</sup>	+5	-1	-6
O <sub>2</sub>	Mg	O <sup>--</sup>	0	-2	-2

positive charges. The corresponding columns of the second table indicate that reduction involves a decrease in the number of positive or an increase in the number of negative charges upon the element reduced. The most general conception of oxidation and reduction then is that *oxidation consists in an increase in the number of positive charges upon the element oxidized or what amounts to the same thing, a decrease in the number of negative charges. Reduction consists in a decrease in the number of positive charges upon the element reduced, or what amounts to the same thing, an increase in the number of negative charges.* Oxidation and reduction are opposed processes, and one of them

cannot take place without the other occurring simultaneously and to the same extent. This will be seen by examining the above table more closely. In each of these reactions, there is an oxidizing agent and a reducing agent, and in every case the one loses exactly as many charges as the other gains.

## CHAPTER XV

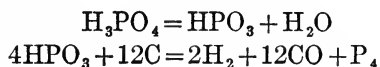
### PHOSPHORUS

**General.**—Phosphorus belongs to a group of elements of which nitrogen is the member with the smallest combining weight. Just as fluorine, the first member of the halogens, has some points of resemblance to chlorine but many of difference, so the nitrogen compounds have at least a formal similarity to those of phosphorus, but show many marked differences. It might be said that the root of the differences lies in the fact that the more highly oxidized compounds of nitrogen are unstable and tend to go to the lower, while just the reverse is the case with phosphorus. Phosphorus, however, differs radically from nitrogen in that the element itself is extremely active chemically. When exposed to the air even at ordinary temperatures it is slowly oxidized, at the same time emitting light. It was on account of this property that phosphorus received its name, which means light bearer.

**Occurrence.**—Phosphorus does not occur free in nature, but is found widely distributed chiefly in the form of phosphates. The most important naturally occurring phosphate is that of calcium,  $\text{Ca}_3(\text{PO}_4)_2$ , which is found in most soils. It constitutes a large part of the bones and teeth of animals. Great beds of calcium phosphate which have been formed in part at least from the fossil bones of animals are found in Florida and Tunis. These are at present the chief producing regions of the world, furnishing as they do 39 per cent. and 28 per cent. respectively of the world's annual production of approximately 5,000,000 long tons. Explorations by the United States Geological Survey have shown that enormous beds, probably the largest in the world, of phosphate rock exist in Utah, Montana, Wyoming, and Idaho. A single township has been found to contain 293,000,000 long tons of this mineral and a very partial survey of the field has located 2,500,000,000 tons of rock averaging 70 per cent. calcium phos-

phate. The Florida deposits will probably be exhausted within a generation, but there is evidently enough in sight to supply the needs of the country for a long time to come, particularly as there are extensive fields in Tennessee and other states which have not been mentioned. Another mineral which is closely related to calcium phosphate is apatite,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ . This is a component of many rocks and is found in large quantities in Canada. The importance of these compounds of phosphorus may be realized when it is known that phosphorus like nitrogen is an absolutely essential component of all living organisms, and that soluble compounds of this element must be present in a soil in order that it may be fertile. In nearly all of the older agricultural countries, artificial manures containing phosphoric acid must be applied to the land.

**Preparation.**—The element phosphorus was first prepared by the German alchemist Brandt in 1669 by distilling in an earthenware retort the residue from the evaporation of urine. This continued to be the method employed for its preparation until 1771 when Scheele published a description of a process for preparing it from bone ash. At the present day, it is largely obtained from the fossil calcium phosphate. Two different methods are in use. In the first one, the calcium phosphate is converted into phosphoric acid,  $\text{H}_3\text{PO}_4$ , by the second general method for the preparation of acids, sulfuric acid being used and calcium sulfate precipitated. The solution of phosphoric acid so obtained is then evaporated to a syrupy consistency, mixed with carbon in some form and distilled in an earthenware retort. The phosphoric acid first loses water, and is thereby changed into metaphosphoric acid,  $\text{HPO}_3$ , which is then reduced by the carbon, forming carbon monoxide,  $\text{CO}$ , hydrogen, and phosphorus which passes over in the form of vapor and is condensed under water. The equations are as follows:



The second method involves the heating of a mixture of calcium phosphate, sand (silicon dioxide),  $\text{SiO}_2$ , and carbon to a very high temperature in an electric furnace. Calcium silicate,  $\text{CaSiO}_3$ , carbon monoxide,  $\text{CO}$ , and phosphorus are formed.

The carbon monoxide and phosphorus pass out of the furnace in the gaseous state, the phosphorus being condensed as before. The calcium silicate is liquid at the temperature of the reaction and is drawn off from the furnace from time to time. The whole process may be made continuous by feeding in the reaction mixture as rapidly as it is used up. The equation is:



**The Allotropic Modifications of Phosphorus.**—The element phosphorus exists in two different modifications which are so very unlike that it is hard to believe that they are composed of the same element. One of these is called ordinary, yellow, or sometimes white phosphorus; the other is known as red phosphorus.

**Ordinary phosphorus** is prepared by the methods described above and is a slightly yellowish almost colorless wax-like solid. It melts at  $+44^\circ$  and boils at  $270^\circ$ . By slow sublimation in a vacuum, it may be obtained in the form of crystals. It is readily soluble in carbon disulfide and some other organic solvents, but is nearly insoluble in water, under which it is always preserved. From its solution in carbon disulfide, crystals of phosphorus may be easily obtained.

When exposed to the air, this form of phosphorus is slowly oxidized with the formation of phosphorus oxide,  $\text{P}_4\text{O}_6$ , and at the same time shines so that it may easily be seen in the dark. The temperature of the phosphorus is but little higher than its surroundings, so a part of the chemical energy of the change must be converted directly into light. The fumes given off have a strong garlic-like smell and their continual inhalation produces a very serious disease in which the bones of the jaw decay. Matchmakers are particularly liable to this trouble. The element itself is very poisonous, a tenth of a gram being a fatal dose. During the slow oxidation of the phosphorus, a part of the oxygen of the air is changed into ozone. If an excess of phosphorus be placed in a limited amount of air, the luminosity will continue until the last detectable trace of oxygen has been used up. If the temperature of phosphorus exposed to air is gradually raised, the oxidation goes on more and more rapidly until at about  $45^\circ$  it passes into rapid combustion.

Since the luminosity of phosphorus is due to its reaction with oxygen, it might be expected that the phenomenon would be especially vigorous in pure oxygen. This is not the case, however, for phosphorus does not become luminous in pure moist oxygen at ordinary temperatures under atmospheric pressure. Upon diminishing the pressure, the luminosity appears at a pressure which is the greater the higher the temperature. At a pressure of one-fifth of an atmosphere, the phosphorus begins to shine at a temperature of  $-7^{\circ}$ . This is also the lowest temperature at which phosphorus will glow in the air, in which, of course, the partial pressure of the oxygen is about one-fifth of an atmosphere. From this, it may be seen that the nitrogen does not in any way interfere with the oxidation of the phosphorus and that the reason the latter is luminous in the air is that the partial pressure of the oxygen is below the "luminescence pressure" for ordinary temperatures. While the nitrogen of the air has no especial influence on the oxidation, many other substances have, especially turpentine and alcohol vapors, very small quantities of which will entirely prevent the luminosity.

When the oxygen is dried by means of sulfuric acid, it reacts much more rapidly with the phosphorus and slow oxidation takes place at ordinary temperatures, even when the pressure of the oxygen is 2.5 atmospheres. But if the oxygen be made absolutely dry, the phosphorus will not combine with it and may be distilled in the pure gas without undergoing change.

The molar weight of phosphorus, both as vapor and in solution is 124 and since its combining weight is 31, the formula is  $P_4$ .

**Red phosphorus** is very different from the ordinary form. It is a dull red powder consisting of small tabular crystals, and may be obtained by heating the yellow variety to  $250^{\circ}$  with the exclusion of the air. The red phosphorus so obtained is then ground under water and boiled with sodium hydroxide to free it from the last traces of the ordinary kind. The velocity of the transformation into the red modification depends very largely upon the temperature: at  $300^{\circ}$  it is moderate, and at  $350^{\circ}$  so rapid as to be almost explosive in its violence. Heat is evolved in the change. The transformation is catalyzed by iodine so that in the presence of a trace of this substance the transition



takes place very rapidly indeed at 200°. Light also hastens the change, and sticks of phosphorus which have been exposed at ordinary temperatures to the action of light are covered with a thin layer of red phosphorus.

Red phosphorus does not melt but passes directly into the vapor which is identical with that of yellow phosphorus, and yields the latter modification when it is rapidly cooled. In fact, it is only by converting the red phosphorus into the vapor and condensing the latter that the change from the red into the other modification can be made.

Red phosphorus is not poisonous, is not soluble in carbon disulfide, does not oxidize in the air at ordinary temperatures, nor take fire until heated to about 260°. It is then very different

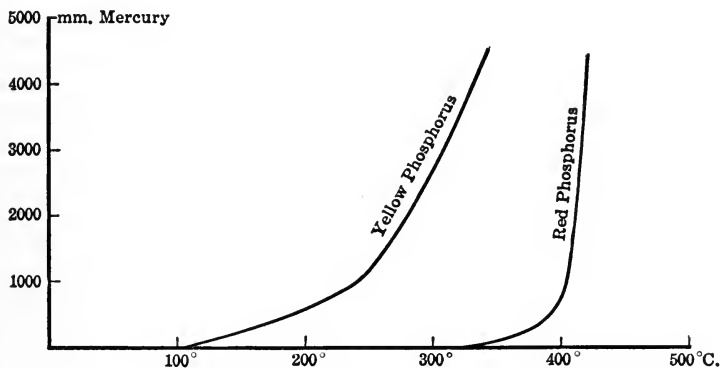


FIG. 28.

from the ordinary phosphorus, and yet the two modifications can be converted, the one into the other without any change in weight.

Although it is possible to transform yellow phosphorus in so many ways into the red, the reverse transformation can only be brought about through the vapor, as indicated above. The yellow modification is at all temperatures unstable with respect to the red, and we are dealing with a monotropic substance. In accord with this, is the fact that yellow phosphorus is more soluble than red and has the greater vapor pressure as shown in the curves given in Fig. 28. The vapor pressure curves of

monotropic substances do not cut, while those of enantiotropic intersect at the transition point.

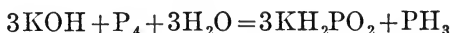
**Applications of Phosphorus.**—By far the greater part of the phosphorus made is used in the manufacture of matches. These may be divided into two classes, those which will strike anywhere, and those which will ignite only when rubbed on a specially prepared surface. The first kind are made by dipping the sticks into melted paraffine, and then into a paste containing glue, powdered glass, iron oxide, lead oxide, and either yellow phosphorus or the sesquisulfide,  $P_4S_3$ . The phosphorus is enclosed within the mass and so protected from the air. Upon striking the match the friction raises the temperature, at the point of contact, above the kindling point of the phosphorus. The whole very combustible mixture in the head then burns and sets fire to the wood. The chief objection to matches containing free phosphorus is that the latter is very poisonous and dangerous to the workmen engaged in their manufacture as well as to those who use them. Children sometimes eat these matches of which one is enough to produce serious symptoms of poisoning, while three have been known to prove fatal. The matches are also so easily ignited that they are liable to produce accidental fires. On these accounts the use and manufacture of this form of match is prohibited in most countries. Matches containing phosphorus sulfide are comparatively non-poisonous. It is said that 3.5 grm. of phosphorus sulfide, which is enough to make 6000 matches, is without harmful action. The sole objection to its use is that it is slightly more expensive than free phosphorus.

The second type of match is the safety match which lights on the box. The head of this match contains potassium chlorate and dichromate, sulfur, manganese dioxide, iron oxide, powdered glass, glue, and gum arabic, but no phosphorus. The striking surface on the box is composed of a mixture of red phosphorus, antimony trisulfide, dextrine, and lampblack. These safety matches may sometimes be ignited by friction on a non-conducting surface such as that of glass. Since these matches contain no ordinary phosphorus they are relatively non-poisonous and can be manufactured without injury to the workmen. For the same reason, and also because it is practically impossible that they should be ignited accidentally, this form of match is much

superior to the other for domestic purposes. In the laboratory red phosphorus is used wherever possible, because it is more moderate in its action and less dangerous than the yellow.

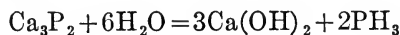
**Hydrogen Compounds of Phosphorus.**—Hydrogen and phosphorus form three compounds, phosphine,  $\text{PH}_3$ , liquid hydrogen phosphides,  $\text{P}_2\text{H}_4$ , and solid hydrogen phosphide,  $\text{P}_4\text{H}_2$ . Phosphine is similar to ammonia in its formula and is slightly like it in its properties.

Phosphine may be prepared by the action of a hot solution of potassium hydroxide upon phosphorus. The two substances are boiled together in a flask, the phosphine is given off as a spontaneously inflammable gas, and a solution of potassium hypophosphite,  $\text{KH}_2\text{PO}_2$ , is left behind. Since the phosphine is spontaneously inflammable, to avoid an explosion, the air in the flask must be displaced by hydrogen or some other indifferent gas before the mixture is heated.



As each bubble of phosphine rises to the surface of the water into which the delivery tube dips, it catches fire with a little explosion and burns to phosphoric acid which forms a beautiful smoke ring. Pure phosphine is not spontaneously inflammable. The compound prepared as described above contains small quantities of the vapor of the liquid hydrogen phosphide, and it is to this that it owes the property of catching fire on contact with the air.

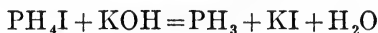
Phosphine may be prepared by the action of water upon calcium phosphide,  $\text{Ca}_3\text{P}_2$ ,



The action is very like that between magnesium nitride and water for the formation of ammonia. The phosphine prepared in this way is also spontaneously inflammable and on this account, calcium phosphide has found application in connection with life buoys to indicate their position at night when they are thrown into the water.

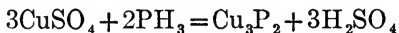
The phosphine prepared by either of these methods may be so far purified from the liquid compound by passing it through a tube surrounded by a freezing mixture that it will not take fire

upon contact with air, but even after this treatment it still contains impurities, chiefly hydrogen. The pure gas is prepared by allowing a strong solution of potassium hydroxide to run slowly into a flask containing pieces of phosphonium iodide,  $\text{PH}_4\text{I}$ , the size of a pea. The reaction is very similar to that between potassium hydroxide and an ammonium salt,



Phosphine is a colorless gaseous substance which smells like decayed fish and is very poisonous. It boils at  $-86^\circ$  and freezes at  $-133^\circ$ ; the critical temperature is  $53^\circ$  and the critical pressure 64 atmospheres. At high temperatures it is decomposed into its elements. It resembles ammonia in its formula and because it will combine directly with the hydrohalogen acids such as HI for the formation of phosphonium compounds. It differs from ammonia in that it is scarcely at all soluble in water and does not form a basic compound with this substance nor does it combine with the oxyacids for the formation of phosphonium salts.

Phosphine reacts with solutions of certain metals for the formation of phosphides of the metals,



**Phosphonium Compounds.**—Phosphonium iodide is the most stable of these compounds and is easily formed by bringing together at ordinary temperatures and pressures phosphine and hydrogen iodide,



It forms beautiful large transparent quadratic crystals which sublime at  $62^\circ$ . In the vapor state, it is very largely decomposed into phosphine and HI, just as ammonium salts are decomposed into ammonia and the acid. It is a powerful reducing agent and finds use as such in the laboratory.

Phosphonium bromide is very similar to the iodide, and is prepared from hydrogen bromide and phosphine at ordinary temperatures and pressures. It decomposes into its components much more readily than the iodide, so that the sum of the partial pressures of the phosphine and hydrogen bromide is one atmos-

phere at  $38^{\circ}$ , and this temperature is then called its subliming point.

Phosphonium chloride cannot be prepared by bringing hydrochloric acid and phosphine together at ordinary temperatures and pressures. At  $-35^{\circ}$  it can be obtained at ordinary pressures, but requires a total pressure of at least 20 atmospheres at  $14^{\circ}$  to produce it or to keep it from decomposing into its components. Phosphonium compounds are decomposed by water into phosphine and the acid. From this we gather that the phosphonium ion,  $\text{PH}_4^+$ , is not stable.

**Liquid Hydrogen Phosphide.**—Liquid hydrogen phosphide boils at  $57^{\circ}$ . The vapor is spontaneously inflammable. Its analysis and molar weight indicate that the formula is  $\text{P}_2\text{H}_4$ , and in this respect it is analogous to hydrazine, but unlike this substance it will form no salts with acids. When exposed to the light, it decomposes into phosphine and the solid hydride,  $\text{P}_4\text{H}_2$ .

**Halogen Compounds of Phosphorus.**—Each of the halogens will combine directly with phosphorus for the formation of fairly stable compounds. The formulæ of these substances together with their physical state at ordinary temperatures are given in the following table:

.....	.....	.....	$\text{P}_2\text{I}_4$ (solid)
.....	$\text{PCl}_3$ (liquid)	$\text{PBr}_3$ (liquid)	$\text{PI}_3$ (solid)
$\text{PF}_5$ (gaseous)	$\text{PCl}_5$ (solid)	$\text{PBr}_5$ (solid)	.....

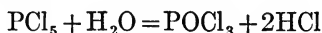
Each of these compounds is decomposed by water with the formation of an oxyacid of phosphorus and the hydroacid of the halogen. It will be recalled that this property was made use of in the preparation of hydriodic and hydrobromic acids. The chlorine compounds are rather more important than the others and will be described in some detail.

**Phosphorus trichloride**,  $\text{PCl}_3$ , is formed by passing chlorine over phosphorus contained in a retort to which is connected a receiver. Before beginning the operation, the air should be replaced by carbon dioxide to keep the phosphorus from catching fire. The phosphorus and chlorine combine directly with the evolution of so much heat that the greater part of the trichloride formed distills over and condenses to a colorless liquid in the receiver. An excess of chlorine is to be avoided since in its

presence the pentachloride will be formed. The product so obtained is purified by distillation. It boils at  $78^{\circ}$  and has a density of 1.6. Its molar weight is 138. From this and its analysis we get the formula  $\text{PCl}_5$ . It reacts with water and other compounds containing oxygen and hydrogen for the formation of phosphorous acid and hydrogen chloride. Because of this reaction, phosphorus trichloride fumes when in contact with moist air.

**Phosphorus pentachloride**,  $\text{PCl}_5$ , is prepared by the action of an excess of chlorine upon the trichloride. It is a pale yellowish-green solid which when heated under atmospheric pressure does not melt, but passes directly into the vapor without going through the liquid state. This is due to the fact that the temperature at which the vapor pressure of the solid is equal to the pressure of the air is lower than its melting-point. We might say that its boiling-point is lower than its freezing-point. When the vapors are cooled they pass directly back to the solid state. That kind of distillation in which the solid passes directly into the vapor and reappears in the solid state upon cooling without the liquid modification coming in as an intermediate step is called sublimation. By heating the pentachloride under a pressure of several atmospheres, the boiling-point may be so raised that it lies above the melting-point which is  $148^{\circ}$ . In the vapor state, phosphorus pentachloride,  $\text{PCl}_5$ , is partially decomposed into chlorine and the trichloride.

Phosphorus pentachloride fumes strongly in contact with air and has a very irritating action on the mucous membranes. It rapidly reacts with water, forming phosphoric acid,  $\text{H}_3\text{PO}_4$ , and hydrogen chloride, or if the supply of water is limited, hydrogen chloride and phosphorus oxychloride,  $\text{POCl}_3$ , are produced;



Very much this same reaction takes place with most substances which contain hydroxyl, phosphorus oxychloride, hydrogen chloride, and a compound formed from the hydroxyl compound by the replacement of the hydroxyl group with chlorine being produced. For example, alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , will react with the pentachloride for the formation of ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}$ , etc.;



This property is made use of as a test for the presence of the hydroxyl group in substances which are not bases.

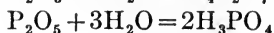
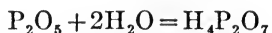
**Oxygen Compounds of Phosphorus.**—The oxides of phosphorus are the tetroxide,  $\text{P}_2\text{O}_4$ , and trioxide,  $\text{P}_2\text{O}_3$  or  $\text{P}_4\text{O}_6$ , and the pentoxide,  $\text{P}_2\text{O}_5$  or  $\text{P}_4\text{O}_{10}$ . The simpler formulæ for the last two oxides are the ones which are the most commonly used for these substances, but the more complicated ones correspond to their molar weights.

Phosphorus pentoxide is a white powder which is formed when phosphorus burns in dry air. It is exceedingly hygroscopic, and combines with water with great violence to form metaphosphoric acid,  $\text{HPO}_3$ . It is the most thorough drying agent known, and leaves less than 1 mgrm. of water vapor in 40,000 liters of gas, while sulfuric acid leaves a milligram in every 400 liters. Owing to its great affinity for water, it is much used as a dehydrating agent, and will even withdraw the elements of water from compounds containing hydrogen and oxygen. Its use in the preparation of nitric anhydride depends upon this property.

The trioxide is formed when phosphorus burns in a limited supply of air. It differs from the pentoxide in that it has a low melting-point,  $22.5^\circ$ , and boiling-point,  $173^\circ$ , and hence may be easily separated from the higher oxide by distillation. It is a colorless substance whose molar weight shows that the formula is  $\text{P}_4\text{O}_6$ . With cold water it reacts very slowly forming phosphorous acid, and hence is often called phosphorous anhydride. It acts very vigorously on hot water forming a large number of products among which are phosphine, red phosphorus, hypophosphoric and phosphoric acids. When heated in sealed tubes to  $440^\circ$  it decomposes into red phosphorus and the tetroxide,  $\text{P}_2\text{O}_4$ .

**Acids of Phosphorus.**—Phosphorus pentoxide is the anhydride of three important acids, metaphosphoric acid,  $\text{HPO}_3$ , pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ , and orthophosphoric acid,  $\text{H}_3\text{PO}_4$ . These are formed by the interaction of varying quantities of water and the anhydride:





In addition to these three acids there are the less important ones, phosphorous acid,  $\text{H}_3\text{PO}_3$ , hypophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_6$ , and hypophosphorous acid,  $\text{H}_3\text{PO}_2$ . The pentoxide is not the anhydride of these last three acids and it will be noticed that the valence of the phosphorus is 3, 4 and 1 respectively.

**Orthophosphoric acid** is of greater importance than any other acid of phosphorus and is always in mind when phosphoric acid is mentioned without qualification. It may be prepared as indicated above, or obtained from its salts by the second general method for the preparation of acids. The first general method is not available since the acid cannot be distilled. It is most conveniently made in pure state by oxidizing ordinary phosphorus with dilute nitric acid, nitric oxide being formed at the same time. By concentrating the solution, the excess of nitric acid is driven off. The orthophosphoric acid obtained in this way is a thick viscous liquid which crystallizes slowly and with difficulty. The melting-point of the pure acid is  $41^\circ$ .

The preparation of phosphoric acid by the action of sulfuric acid upon bone ash or upon calcium phosphate has been mentioned in connection with the manufacture of phosphorus.

Orthophosphoric acid is very soluble in water, and even minute quantities of the latter will so lower the freezing-point of the acid that liquid solutions will be formed at room temperatures. Its solution in water reddens litmus and has a pure agreeable acid taste. Measurements of the electrical conductivity of the aqueous solution show that it is not very strongly dissociated. A solution of one gram equivalent of phosphoric acid in a liter of water contains only about one-fourteenth as much hydrogen as ion as a hydrochloric acid solution of the same concentration.

Orthophosphoric acid is a tribasic acid as is indicated by its formula,  $\text{H}_3\text{PO}_4$ . It forms three series of salts according as one, two, or all three of the combining weights of hydrogen per mole are replaced by metals. We have then normal salts and two kinds of acid salts. These latter are distinguished by using Greek numerals to show how many combining weights of metal are present. Thus we have normal sodium phosphate,



$\text{Na}_3\text{PO}_4$ , which is often called trisodium phosphate; disodium phosphate,  $\text{Na}_2\text{HPO}_4$ ; and monosodium phosphate,  $\text{NaH}_2\text{PO}_4$ . The names tertiary, secondary and primary are also used to designate these salts. Solutions of the mono salt are slightly acid in reaction while those of the disodium salt are faintly alkaline, and of the tri- exceedingly so. These phenomena are connected with the fact that phosphoric acid is a weak acid and also polybasic. Like all other polybasic acids,  $\text{H}_3\text{PO}_4$  dissociates one combining weight of hydrogen more strongly than the rest. The dissociation  $\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$  takes place to a fair degree, while that of  $\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{--}$  is slight, and  $\text{HPO}_4^{--}$  scarcely breaks down at all into  $\text{H}^+$  and  $\text{PO}_4^{---}$ . Because of the weakly acid character of the ions  $\text{HPO}_4^{--}$  and  $\text{H}_2\text{PO}_4^-$ , the trisodium salt is almost completely hydrolyzed into the di-salt and sodium hydroxide, and the disodium phosphate is also slightly affected. Because of this hydrolysis, when a solution of phosphoric acid is neutralized with sodium hydroxide, the red color of the litmus slowly changes to blue, and the solution becomes alkaline when a little less than two moles of the hydroxide have been added per mole of acid. The color change of the litmus is not sharp. The trisodium salt is formed by adding the proper amount of sodium hydroxide to the di-salt and evaporating the solution to dryness.

The phosphates which occur in nature are the normal salts and the principal one is that of calcium,  $\text{Ca}_3(\text{PO}_4)_2$ . This salt is almost universally present in the soil. It is, however, very slightly soluble so that it is only slowly available as a source of phosphorus compounds for plants. Monocalcium phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , is easily soluble and makes an excellent fertilizer. It is known in commerce as "superphosphate" and is prepared by treating bone ash or the calcium phosphate minerals with dilute sulfuric acid from the lead chambers. So extensive is the use of phosphate fertilizers that the larger part of the sulfuric acid made is used in their manufacture.

**Pyrophosphoric Acid.**—When orthophosphoric acid is carefully heated to about  $250^\circ$ , it loses water and is changed into pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ ,



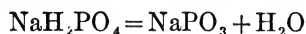
This acid may also be prepared by the second general method, using the lead salt and hydrogen sulfide. When dissolved in water, it gradually reacts with the latter forming the ortho acid. This reaction takes place more rapidly at higher temperatures, and is catalytically accelerated by hydrogen as ion; so the change takes place faster if some stronger acid is added to the solution. The formula indicates that it is tetrabasic, and it forms four series of salts,  $\text{NaH}_3\text{P}_2\text{O}_7$ ,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ,  $\text{Na}_3\text{HP}_2\text{O}_7$ , and  $\text{Na}_4\text{P}_2\text{O}_7$ . Of these the second and fourth are the best known.

**Metaphosphoric Acid.**—Metaphosphoric acid,  $(\text{HPO}_3)_n$ , may be obtained by heating orthophosphoric acid to a higher temperature than that required for the preparation of pyrophosphoric acid, or by adding the proper amount of water to the pentoxide. There are several metaphosphoric acids, each having the general formula given above, but differing in the value of  $n$ . The  $n$  in the formula stands for some whole number which is definite and fixed for any given acid and apparently varies in the different acids from 1 to 14. Because of the number and complexity of these acids, their chemistry has not been cleared up.

Metaphosphoric acid melts at a rather high temperature and solidifies to a wax-like mass on cooling. It is put on the market in the form of transparent sticks and is known in commerce as glacial phosphoric acid. These sticks are hard and glass-like because they contain a little  $\text{NaPO}_3$ . At high temperatures it passes into vapor, and in this state has the formula  $(\text{HPO}_3)_2$ , as is shown by its molar weight.

At room temperatures, a solution of metaphosphoric acid is changed rather rapidly into pyrophosphoric acid and the latter then more slowly into the ortho acid.

The sodium salt of metaphosphoric acid is formed by heating monosodium orthophosphate to a high temperature,



or by heating sodium ammonium phosphate,  $\text{NaNH}_4\text{HPO}_4$ ,



Sodium metaphosphate fuses to a clear glass-like mass and in the fused state is able to dissolve most of the oxides of the metals,

receiving from them in many cases, colors characteristic of the metals. This property is made use of in blowpipe analysis.

**Phosphorous Acid.**—Phosphorous acid,  $H_3PO_3$ , is formed by the action of cold water upon phosphorus trioxide,  $P_4O_6$ , or of water upon the trichloride, bromide, or iodide of phosphorus. Its formula indicates that it is a tribasic acid, but it will form only two series of salts,  $NaH_2PO_3$  and  $Na_2HPO_3$ . This property is often interpreted to mean that one of the hydrogens is related to the rest of the compound in a way which is radically different from the relationship of the others, but it is more likely that it is an extreme case of the difference in the degree of dissociation of the hydrogens of a polybasic acid, to which attention was called under phosphoric acid.

Phosphorous acid is a crystalline solid melting at  $70^\circ$ . When heated strongly, it decomposes into phosphine, metaphosphoric acid, and water. It is a powerful reducing agent, being oxidized to phosphoric acid.

**Hypophosphorous Acid.**—Salts of hypophosphorous acid,  $H_3PO_2$ , are obtained by boiling a soluble base with phosphorus; phosphine is formed at the same time. From barium hypophosphite,  $Ba(H_2PO_2)_2$ , the acid may be prepared by adding sulfuric acid. It is a white crystalline substance melting at  $17^\circ$  and is very soluble in water. In spite of its formula, the acid is monobasic. Hypophosphorous acid and its salts are very powerful reducing agents. They are also used in medicine.

**Sulfur Compounds of Phosphorus.**—Ordinary phosphorus and sulfur form solutions which are liquid at the temperature of the room. When heated together to a fairly high temperature these substances combine with explosive violence. If red phosphorus be substituted for the white, the action is rapid but easily controlled. A mixture of the two substances in the proper proportions is placed in a glass flask and heated at one spot. After the combination is once started the action spreads of itself throughout the entire mixture. In this way the compounds  $P_2S_5$  and  $P_2S_3$  may be easily prepared. The pure substances are yellow crystalline solids a little paler than sulfur. They do not take fire spontaneously in the air, but ignite when gently heated. In addition to these compounds, the sulfides  $P_4S_3$  and  $P_3S_2$  are known. These are formed in much the same way, using the

materials in the proper proportions, and are purified by distillation under diminished pressure.

The patents upon the use of sulfides of phosphorus in matches have recently been surrendered to the public, and by act of Congress, such a high tax has been put upon the manufacture of the ordinary phosphorus match that it will doubtless become obsolete. This change will save the lives of many persons each year.

With water the sulfides react for the formation of hydrogen sulfide and the acids of phosphorus.

## CHAPTER XVI

### CARBON

**General.**—Carbon belongs to a family of elements, which in their highest state of oxidation are tetravalent; the other members of the family are silicon, germanium, tin, and lead. Carbon and silicon are non-metallic elements, while the others are metals and will be discussed later. The compounds of carbon are exceedingly varied, more than a hundred and fifty thousand of them being known. In fact, the chemistry of carbon is so complex that it is considered a separate branch, and is called organic chemistry. It received this name because all living organisms contain carbon compounds, and it was for a long time supposed that most of these substances could be produced only by the life processes of such organisms. At the present day so many of these compounds have been synthesized in the laboratory that we are now of the opinion that it is possible to prepare any carbon compound artificially.

The great importance of the compounds of carbon may be realized when we consider that nearly all of our foods, and most of our medicines, consist essentially of these substances, and that the principal source of the energy which we use in our various industries is the carbon in coal, gas, oil, etc.

**Occurrence.**—Carbon occurs free in nature in two distinct allotropic crystalline modifications, which are known as diamond and graphite. In combination, it is found as an essential constituent of all living organisms; as carbon dioxide in the air and water; as calcium carbonate in the great beds of limestone; as very complex compounds chiefly in combination with hydrogen in coal and oil; and as methane,  $\text{CH}_4$ , in natural gas. A third form of elementary carbon, known as amorphous carbon, or charcoal, may be obtained by heating organic substances, such as wood, sugar, etc., to a high temperature in the absence of air. Many persons consider that amorphous carbon is present in coal

and so would say that this form of carbon occurs in nature. The various allotropic modifications of carbon differ materially in their physical properties and in their energy content, as is shown by the fact that they have quite different heats of combustion, although the same substance, carbon dioxide, is formed in each case.

**Diamond.**—As is well known, diamond is a clear colorless substance which crystallizes in octahedrons and is exceedingly hard. Because of these properties, its rarity and the fact that it has a very brilliant luster, diamond has long been valued highly as a gem. The principal localities in which diamonds are found at the present day are Brazil and South Africa. In Brazil, they are obtained from alluvial deposits, while in South Africa they occur within and in the immediate vicinity of old volcanic chimneys. The diamonds have apparently been formed from carbon under great pressure, at the high temperature of the lava. They are usually small, very rarely weighing more than a few grams; but one, the Cullinan diamond, was found in 1905 at Premier mine in Transvaal which weighed 620 grams, or 3024 carats, or 1.37 pounds, and even then the stone was evidently merely a fragment of a much larger one.

Very small diamonds have been prepared artificially by Moissan. He found that when carbon crystallizes rapidly from its solution in cast-iron under such circumstances that great pressure is produced, a portion of it appears as diamond. His process may be briefly described as follows: About two hundred grams of cast-iron contained in a crucible was heated to a very high temperature in an electric furnace; a small cylinder of wrought iron tightly packed with the purest obtainable sugar charcoal was then plunged into the crucible and the latter at once withdrawn from the furnace and cooled as rapidly as possible. Water did not cool the mass quickly enough because of the formation of a layer of steam, so it was plunged into melted lead. Under these conditions a rigid shell of solid cast-iron was quickly formed around the outside of the mass, while the interior still remained molten. Now cast-iron upon solidification increases in volume, so that, as the interior gradually froze, great pressure was produced. Under these conditions the carbon was simultaneously exposed to very high temperature and pressure, and a

small portion of it crystallized as diamond. By dissolving the iron in acid, minute crystals of diamond were left behind, which were identical in all their properties with those which occur in nature. The largest crystals which have been obtained in this way were about half a millimeter in diameter. As has been mentioned above, the diamond is extremely hard. Because of this it is used for cutting and writing on glass and many other purposes where extreme hardness is required. Diamond drills are often employed to get a "core" which will show the composition of the earth's strata. The diamonds used in such drills are called carbonadoes. They are rough and discolored, but are as hard as the ordinary diamond and somewhat tougher. Because of their color they cannot be used for gems, but their usefulness gives them a high price. The density of diamond, 3.5-3.6, is greater than that of the other forms of carbon. When diamonds are heated in the air, or oxygen, they burn to carbon dioxide. The weight of this carbon dioxide is equal to the weight of the diamond plus that of the oxygen consumed, and therefore the diamond consists of carbon and nothing else. It has often been stated in the past that when diamonds are heated to a very high temperature in the absence of air, graphite is produced. Recent experiments indicate, however, that instead of graphite a coke-like substance is formed. Toward most chemical reagents it is very indifferent.

**Graphite.**—Graphite is the second crystalline modification of carbon. It occurs in many localities, chiefly Austria and Ceylon, in rather poorly formed hexagonal crystals. It is black in color, non-transparent, so soft that it may be readily scratched with the finger nail, and leaves a black streak on paper, has a density of 2.25, and so differs radically in its properties from diamond. It may easily be prepared artificially by heating petroleum coke, anthracite coal, or any other nearly pure form of carbon, to a very high temperature in the electric furnace. The presence of the comparatively small amounts of impurities in the anthracite coal is thought to accelerate its transformation into graphite. At the present day, a large part of the graphite used in commerce is prepared artificially at Niagara Falls by the Acheson process. The yearly production is about 13,000,000 lbs. This is about one-tenth the annual consumption in the United States. Graph-

ite is highly resistant to chemical action, but rather less so than diamond. When heated in the air, or oxygen, it slowly burns to carbon dioxide. When heated alone it undergoes no change until the highest temperature of the electric arc is reached, when it passes slowly into vapor without melting. Because of its infusibility, graphite when mixed with a small portion of clay to act as a binder, is used in making crucibles which have to stand high temperatures. Owing to the slight combustibility of graphite, these crucibles may be heated in the air without any special precautions. Because of these same properties and the further fact that it is a good conductor of electricity, graphite is extensively used at the present for making electrodes for use in electric furnaces and in the electrolytic industries. Crystals of graphite very easily break up into fine scales which slip over one another with but little friction. On this account it is often used as a lubricant. Finely ground graphite mixed with clay and slightly baked, constitutes the "lead" of our lead pencils. The more clay the harder the pencil.

**Amorphous Carbon.**—As has been mentioned above, amorphous carbon is prepared by heating certain carbon compounds to a high temperature in the absence of air. A rather large number of different forms are distinguished according to their state of division and the substances from which they were formed. We have, for example, charcoal of various kinds, soot or lamp black, and coke. The density, hardness and electrical conductivity of all forms of amorphous carbon increase with the temperature to which it is heated. At the highest temperatures of the electrical furnace, the various forms of amorphous carbon are transformed into graphite. Like graphite, amorphous carbon is infusible. It is, however, much more easily combustible than graphite.

**Soot** is a comparatively pure form of carbon and is formed by the combustion of various carbon and hydrogen compounds with an insufficient supply of air. Under these conditions a portion of the carbon is deposited in the form of very fine particles. It usually contains small quantities of hydrogen compounds from which it may be purified by strongly heating in the absence of air. It is very soft, intensely black in color, has a small density, is easily combustible, and is a good non-conductor of heat or



electricity. It finds application as a pigment in printer's ink, paint, etc., under the name of lampblack.

**Charcoal.**—The most common form of charcoal is that prepared by heating wood to fairly high temperatures. This was formerly done by piling wood up in heaps and covering it with earth, leaving small openings at the top and bottom. This was then set on fire and slowly burned. The burning of a small part of the wood charred the remainder. This method is wasteful because, while the wood is being charred, a large number of valuable substances such as methyl or wood alcohol,  $\text{CH}_3\text{OH}$ , acetic acid,  $\text{CH}_3\text{COOH}$ , and creosote are formed, which it is impossible to save with this arrangement. In addition, a considerable part of the wood which might otherwise be converted into charcoal, is burned up. At the present day the greater part of the charcoal is made by heating the wood in cast-iron retorts, and all these valuable by-products saved, in fact the charcoal has become the by-product and the other things the main output. Bone charcoal or bone-black as it is called, is made by carbonizing bones in retorts. At the same time a valuable by-product known as bone oil is produced. The bone-black is largely used in the refining of sugar since it has the property of taking up from solutions the coloring matters which are present in the crude substance. This property is closely connected with that shown by all charcoals of adsorbing gaseous and dissolved substances. All solid substances seem to have a tendency to increase right at their surface the concentration of any gaseous substance with which they may be in contact. This property was mentioned in connection with the discussion of water vapor. Charcoal has this property to an extraordinary degree, and it is rather more pronounced in bone charcoal than in most other forms. This is due to the fact that in charcoal the cellular structure of the wood, or bone, from which it was formed, is preserved, and since the cells of the bones are very small indeed, the surface exposed by a given weight of bone charcoal will be much greater than that presented by ordinary wood charcoal. Very hard woody substances—cocoanut shells, for example, have a very fine cellular structure, and charcoal prepared from them is especially efficient. This property of charcoal of adsorbing gases is more pronounced the lower the

temperature of the charcoal and the higher the molar weight of the gas. Odors are gaseous substances usually of high molar weight, and consequently are easily adsorbed by charcoal. The use of charcoal as a deodorant is dependent upon this property. When cooled to the temperature of liquid air, charcoal made from the shells of coconuts will adsorb very completely all gases except hydrogen, helium, and neon. One of the most convenient ways for producing a high vacuum is to seal a bulb containing coconut charcoal to the vessel to be exhausted, and then cool the bulb with liquid air. In a short time the air in the vessel will be so completely taken up by the charcoal that a very high vacuum will be produced.

When charcoal is added to solutions it always adsorbs upon its surface some of every substance present. This is a surface phenomenon and is more pronounced with bone-black than other charcoal for the reason given above. Here again, the adsorption is the more complete the higher the molar weight of the substance affected, and since coloring matters are usually very complex, they are adsorbed to a greater extent than most other substances. In the refining of sugar, some of the latter is taken up together with the coloring matter. The quantity so lost is comparatively small. The bone charcoal is much more efficient for this purpose if it is freed from the calcium phosphate which it contains by treatment with hydrochloric acid. Charcoal is a catalyzer for many reactions, particularly between gases. Here again we are dealing with a surface phenomenon, and the charcoals prepared from the more finely cellular substances are the more active.

**Coal** may be considered natural charcoal, and has probably been formed by the partial decomposition of vegetable matter under water. Various varieties of coal are distinguished, such as anthracite, semi-anthracite, bituminous, and lignite. These differ rather widely in the relative proportions of carbon, hydrogen, nitrogen, oxygen, sulfur, and mineral matters which they contain, the anthracite being the nearest pure carbon, and the others decreasing in purity in the order named. The supreme importance of coal is indicated by the fact that 1,278,577,812 tons were mined in 1910, of which the United States produced 39.2

per cent., nearly twice the amount of the next largest producing country.

**Coke** is formed by heating bituminous coal with the exclusion of air until practically all the volatile matter has been distilled off. The gases given off are rich in compounds of carbon and hydrogen, and are very valuable for fuel and illuminating purposes. In addition, they contain many useful products, such as ammonia, benzene,  $C_6H_6$ , coal tar, etc. There are essentially two different methods of making coke. In one of these the coal is heated in heaps, much as the wood was in the older method for preparing charcoal. When made in this way all the valuable by-products are lost. The other method consists in the distillation of the coal in closed retorts. By this method the valuable by-products are conserved. Coke is largely used as a fuel in blast furnaces and many other metallurgical operations, since it produces a very high temperature, burns without smoke and contains a relatively small amount of sulfur. Coke and charcoal of course contain practically all the mineral matter which was present in the substance from which they were formed, and so leave a relatively large amount of ash.

**Relation Between the Allotropic Modifications.**—Although the various modifications of carbon differ so radically in their properties they are really composed of the one element carbon, and contain nothing else, as is shown by the following argument. When equal weights of pure diamond, graphite, or amorphous carbon are burned in oxygen, equal weights of carbon dioxide are produced in each case, and nothing besides carbon dioxide is formed in any case. The heat of combustion of the various modifications is different so that in this, as in other cases, the allotropic modifications differ in their energy content. Because of the non-volatility and insolubility of carbon, it is impossible to determine its molar weight. Its combining weight, however, is 12.00.

**Oxygen Compounds.**—Carbon forms two well known oxides, the monoxide  $CO$ , and the dioxide  $CO_2$ . The second of these compounds is by far the more important.

**Carbon Dioxide.**—Carbon dioxide,  $CO_2$ , is a gaseous substance whose molar weight is 44. It is colorless, has a very feeble taste and odor, is soluble in about an equal volume of water at

ordinary temperatures; its critical temperature is  $31^{\circ}$ , and its critical pressure is 73 atmospheres. The volume of a gram mole, 44 grams, of carbon dioxide at the critical temperature and pressure is 95 c.c. This is called its critical volume. Every liquid substance has these three critical magnitudes which differ as we pass from substance to substance. The critical phenomena were first studied in connection with carbon dioxide.

We learned in connection with oxygen, that a gaseous substance, above its critical temperature cannot be liquefied by any pressure however great; so a distinction can be made between a gas and a vapor; a gas being defined as an aeriform substance above its critical temperature, while a vapor is an aeriform substance below its critical temperature. Carbon dioxide then below  $31^{\circ}$  is vapor and may be liquefied by the application of sufficient pressure, while above  $31^{\circ}$  it is a gas, and cannot be liquefied by any pressure. Both gases and vapors are gaseous substances, so at ordinary temperatures carbon dioxide is a gaseous substance, although strictly speaking it is not a gas.

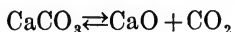
Liquid carbon dioxide is a common article of commerce. This country alone produced 36,000,000 pounds in 1905. It is sold in very strong cylinders. At a temperature of  $20^{\circ}$  its vapor pressure amounts to about 860 pounds to the square inch, so it may be easily seen that the cylinder should be well constructed and handled with care. The principal use for this carbon dioxide is in the manufacture of soda water and other carbonated beverages. The boiling-point, or rather subliming-point of carbon dioxide is  $-78.2^{\circ}$ ; the freezing-point is considerably higher than this  $-57^{\circ}$ ; so that at ordinary pressures liquid carbon dioxide cannot exist in open vessels. Liquid carbon dioxide is a colorless, very mobile substance, which is but slightly soluble in water. Its density is .922 at  $5^{\circ}$ , .864 at  $15^{\circ}$ , .783 at  $25^{\circ}$ . These figures show that liquid carbon dioxide, with rising temperature, expands more rapidly than any gas, in fact its coefficient of expansion is larger than that of any other known substance. Liquid carbon dioxide is not a conductor of electricity, does not act as a solvent toward most substances, and does not redden litmus paper; in short, it does not present any striking chemical properties.

The solid carbon dioxide may be formed by allowing the

liquid modification to flow out from the cylinder at any temperature below the critical temperature of the liquid. As soon as the liquid comes in contact with the air, the greater portion of it is at once turned into vapor. The heat necessary for this transformation is absorbed largely from the carbon dioxide itself, and so far cools a portion of this that it assumes the solid state, although its temperature in this condition is  $-78.2^{\circ}$ . The heat absorbed during the vaporization of a given quantity of any liquid is the greater the lower the temperature of volatilization. On this account the yield of solid carbon dioxide obtainable from a given weight rapidly increases as the initial temperature of the cylinder is lowered. If the cylinder is at  $31^{\circ}$  or higher, no solid whatever can be obtained. This is due to the fact that the heat of vaporization of a liquid at its critical temperature is zero, and consequently no cooling will result from its evaporation, and that above  $31^{\circ}$  the cylinder contains no liquid carbon dioxide.

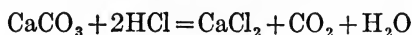
The solid carbon dioxide is a white snow-like substance which is very convenient for use as a cooling agent, since we can so easily get with it the definite temperature of  $-78.2^{\circ}$ . In order to secure better thermal contact with the substance to be cooled, the solid carbon dioxide is commonly mixed with ether. By diminishing the pressure upon the carbon dioxide, temperatures lower than  $-78.2^{\circ}$  may be obtained. In this way by causing it to evaporate in a vacuum, a temperature of  $-100^{\circ}$  may be reached.

Carbon dioxide occurs in nature in very large quantities. The air contains three to four parts of this substance to ten thousand parts by volume. It escapes in great volumes from volcanoes, mineral wells and springs, and at various places on the earth it issues in an almost pure state from fissures. It is formed during the breathing of animals and in the fermentation and decay of organic substances. It may be prepared by burning carbon or any carbonaceous material in an excess of oxygen or of air, by heating limestone, calcium carbonate,  $\text{CaCO}_3$ , or magnesite, magnesium carbonate,  $\text{MgCO}_3$ , which breaks down into calcium oxide,  $\text{CaO}$ , or magnesium oxide,  $\text{MgO}$ , and carbon dioxide,  $\text{CO}_2$ ,



or by the action of an acid upon a carbonate. The carbon

dioxide which is put on the market in the liquid form is very largely obtained from lime kilns and from the fermentation vats of the breweries. The ordinary laboratory method for its preparation is to place some pieces of marble, which is a very pure form of calcium carbonate, in a flask and allow hydrochloric acid to run slowly upon them. Under these conditions the carbon dioxide is given off in a steady stream,



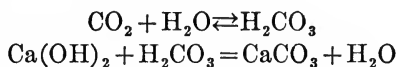
Being heavier than air and not very soluble in water, it may be collected either by the displacement of air or over water. Carbon dioxide is neither a supporter of combustion nor of animal life. Air containing 4 per cent. of carbon dioxide will extinguish a candle flame, but will support respiration for a short time. Since carbon dioxide is heavier than air and is being gradually given off by the earth, it often accumulates in old wells, cellars, cisterns, etc., in quantities sufficient to render it dangerous to persons entering such places. The presence of carbon dioxide in dangerous quantities may be easily detected by the lowering of a lighted lantern. If the flame is extinguished no one should enter until the excavation has been thoroughly ventilated.

The solubility follows Henry's law. Under a pressure of one atmosphere, a liter of water will dissolve one liter of carbon dioxide; under a pressure of 15 atmospheres, it will also dissolve a liter of carbon dioxide, but the gas contained in this liter would, if measured under a pressure of one atmosphere, occupy a volume of 15 liters. In preparing soda water, water is saturated with carbon dioxide at a pressure of about 15 atmospheres. When this solution is drawn out into the open air, it at once loses the greater part of the dissolved gas, since at ordinary pressure it can contain only one-fifteenth as much carbon dioxide as is held under the higher pressure. The escape of the gas produces the well known effervescence.

The solution of carbon dioxide in water has a feebly acid reaction and contains the very unstable substance, carbonic acid,  $\text{H}_2\text{CO}_3$ . This is a very weak dibasic acid which forms two series of salts, the normal and the acid carbonates. Because of the weakness of carbonic acid, the easily soluble normal salts are rather strongly hydrolyzed and are alkaline in reaction; and the

so-called acid salts are almost neutral in their reaction. The most abundant naturally occurring carbonate is that of calcium,  $\text{CaCO}_3$ . Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is manufactured in enormous quantities from sodium chloride, and is a very important chemical.

When one attempts to prepare carbonic acid from its salts by either of the general methods for the preparation of acids, the carbonic acid at once breaks down to water and carbon dioxide, which escapes in the gaseous state producing effervescence. This behavior is rather characteristic of carbonates and is often used as a rough test for them. The final test for the presence of carbon dioxide and of carbonates from which it may be produced is the formation of a white precipitate of calcium carbonate when carbon dioxide is brought in contact with lime water, which is a solution of calcium hydroxide in water. The carbon dioxide is first dissolved by the water forming carbonic acid, which then reacts with the calcium hydroxide for the formation of water and the difficultly soluble calcium carbonate,



Because of the fact that carbon dioxide will combine with water for the formation of carbonic acid, it is often called carbonic anhydride.

**Circulation of Carbon.**—During the breathing of animals oxygen is taken up from the air in the lungs forming an unstable compound with the hemoglobin of the blood. It is then carried to all parts of the body and gradually oxidizes the complex compounds contained therein, forming carbon dioxide as one of the products; this is carried by the blood to the lungs and there given up to the air and expired. The oxidation of these compounds is the source of the energy of the animals. In the dark practically this same process takes place in plants, but in the light those plants which contain green coloring matter in their leaves are able to bring about the reverse change, partially breaking up the carbon dioxide absorbed from the air, liberating a part of its oxygen in the free state and combining the residue with water for the formation of complex compounds of which the sugars, starches, and celluloses are prominent examples.

These compounds are food for plants as well as for all animals, which live directly or indirectly upon them. This decomposition of carbon dioxide and the building up of complex compounds from it takes place only under the simultaneous influence of chlorophyl, the green coloring matter of plants, and of light. It is accompanied by the absorption of a great amount of energy which is obtained from the light of the sun. The energy so absorbed is given out once more when these complex compounds burn, decay, or oxidize in the bodies of animals; and so the ultimate source of the energy of animals and of all engines, which are driven by the burning of wood and other vegetable products, is the light of the sun. Coal has been formed by the partial decomposition of vegetable organisms, and the energy obtained from it was originally absorbed by these organisms from the light of the sun; so the steam engine of to-day is really driven by the energy of the sunlight of thousands of years ago.

By this cycle of changes, carbon dioxide is successively taken up from and given back to the air, and thus there is in nature a sort of circulation of carbon. The energy, however, accompanying these transformations apparently does not move in any such cycle; that given out during the decomposition of the complex compounds is not available for the re-formation of these substances, and this change can take place only with the influx of a fresh supply of energy from the sun. We are to think of the energy relationships in the following way: A stream of energy comes to the earth in the sunlight; a very small part of this is absorbed by the green plants and stored as chemical energy in the form of complex carbon compounds, which are available for use as food, or combustibles, and furnish us with the greater part of the energy which we employ. After we have once made use of their energy, it is lost so far as we are concerned, since it is converted into bound energy and is no longer free. The supply of total energy remains constant, but the store of available energy, the free energy, is continually decreasing while the useless bound energy is increasing. The other sources of energy which man employs, water power and the wind, are really dependent upon the sun, so that we owe practically all of our stores of available energy to this body.

We have spoken of the energy obtained from the oxidation of

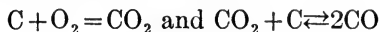


carbon and its compounds, as though it belonged to the carbon exclusively. This energy is developed during the combination of the carbon with oxygen and is just as much a property of the oxygen as of the carbon. Since oxygen is a gaseous substance and is universally present in the air, it may be obtained without cost, while the carbon compounds are rather local in their occurrence and can only be secured with expenditure of work. Therefore carbon compounds must be purchased, and consequently we have come to associate the possession of energy with the carbon.

**Photochemical Action.**—Chemical changes which take place under the influence of light are fairly numerous and are called photochemical changes. They may be divided into two classes: in one the light acts apparently catalytically. The combination of hydrogen and chlorine in the sunlight is an example of such an action. In this and similar cases, no energy is absorbed from the light. In the other class of photochemical changes, energy is actually taken up from the light. The changes taking place in the green plants are examples of this type of action. In any given photochemical change, the different rays going to make up white light are not equally effective. For example, in the case last mentioned, the red and yellow rays are practically the only ones that have any influence, while in the photochemical action upon a photographic plate, the blue and green rays are particularly active; and the red are almost without effect. Taking photochemical action as a whole, however, we find that every ray of light will act chemically, so we cannot speak of any particular rays as the chemical rays.

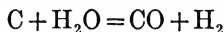
**Carbon Monoxide.**—Carbon monoxide is a gaseous substance which is formed when coal is burned in a limited supply of air. It may also be prepared by the action of carbon at a high temperature upon carbon dioxide. The carbon monoxide burns in the air with a pale blue flame, and it is the burning of this substance which produces the blue flames that are so commonly seen at the top of a hard coal fire. The chemical changes taking place in such a fire are mainly as follows: When the air first comes in contact with a hot carbon at the bottom of a firebox, carbon dioxide is formed, which, passing up through the body of the coal, is reduced to carbon monoxide; this burns when it comes in

contact with the air at the surface of the fire. The equations for the reactions are as follows,



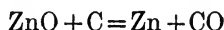
These reactions take place on a large scale in the manufacture of "producer gas" for fuel and power purposes, see p. 306, and also in the iron blast furnace.

When steam is passed over highly heated carbon, carbon monoxide and hydrogen are produced as shown in the equation

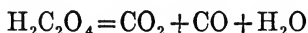


This is one of the reactions which takes place in the technically important process for making what is known as water gas. This will be discussed in some detail later, see p. 305.

Carbon is an excellent reducing agent and is much employed for this purpose in the extraction of metals from their oxides. When this change takes place at a high temperature, as is usually the case, carbon monoxide is formed. The equation for the reduction of zinc oxide is

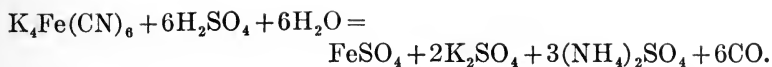


In the laboratory, carbon monoxide is often prepared by heating oxalic acid, a white crystalline substance, whose formula is  $H_2C_2O_4$ , in a glass flask with sulfuric acid. Under these conditions the oxalic acid decomposes into carbon dioxide, carbon monoxide and water,



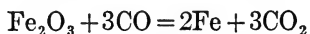
The carbon monoxide is obtained pure by passing the mixture of gases through a strong solution of potassium or sodium hydroxide, which takes up the carbon dioxide, forming the corresponding carbonates. A very convenient method for preparing pure carbon monoxide consists in the heating of formic acid, a colorless liquid whose formula is  $HCOOH$ , with concentrated sulfuric acid. The formic acid breaks down into water and carbon monoxide,  $HCOOH = CO + H_2O$ . In this reaction and that of oxalic acid the sulfuric acid apparently does nothing except take up the water formed.

Perhaps the most convenient laboratory method is to heat a mixture of potassium ferrocyanide,  $K_4Fe(CN)_6$ , and sulfuric acid,



**Properties.**—Carbon monoxide is a colorless, tasteless gas with a very faint, peculiar odor, very slightly soluble in water. Its molar weight is 28. The critical temperature is  $-140^\circ$  and the critical pressure 36 atmospheres; the boiling-point is  $-190^\circ$ . It is interesting to note that these magnitudes have practically the same values as the corresponding ones for nitrogen, which also has a molar weight of 28, the critical temperature of nitrogen being  $-146^\circ$ , its critical pressure is 36 atmospheres and its boiling-point  $-194^\circ$ . Carbon monoxide will combine directly with oxygen, chlorine, and many other substances. With oxygen, carbon dioxide is formed, while it combines with chlorine for the formation of a substance,  $\text{COCl}_2$ , called carbonyl chloride or phosgene. This combination takes place when carbon monoxide and chlorine are exposed to sunlight, or when a mixture of the two gases is passed over animal charcoal which acts as a catalyzer. Carbonyl chloride is a gaseous substance whose boiling-point is  $+8^\circ$ .

Carbon monoxide is able to remove oxygen from many oxides and hence acts as a reducing agent. The reduction of iron oxide to metallic iron by this gas takes place on an enormous scale in the blast furnace. The reaction may be represented by the following equation:



Carbon monoxide will unite directly with certain metals for the formation of compounds called carbonyls. This property is especially developed in the case of nickel which readily forms nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , a colorless, easily volatile liquid.

When carbon monoxide burns in the air a quantity of heat amounting to 286 KJ. is developed per gram mole. For this reason the gas is valuable as a fuel, and the water gas mentioned above, which consists essentially of carbon monoxide and hydrogen, is much used for this purpose.

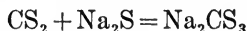
Great care must be exercised in working with carbon monoxide because of the fact that it is extremely poisonous. This apparently is connected with the fact that carbon monoxide

will combine with the hemoglobin of the blood for the formation of a very stable compound which is unable to take up the oxygen of the air. In this way the blood is deprived of its power of oxidizing the complex body substances, and the animal dies largely from lack of energy. So poisonous is carbon monoxide that 700 c.c. of the gaseous substance will be sufficient to kill an average man. The compound which carbon monoxide forms with the hemoglobin of the blood has a characteristic absorption spectrum and this property is made use of for the detection of the gas.

**Sulfur Compounds of Carbon.**—When charcoal is heated to a rather high temperature in the vapor of sulfur the elements combine for the formation of an easily volatile liquid substance, called carbon disulfide,  $CS_2$ . This substance is now manufactured on a large scale in electric furnaces. It is a colorless liquid whose boiling-point is  $46^\circ$ . It has a very high index of refraction for light. When perfectly pure it has a pleasant ethereal odor; the commercial article, however, contains impurities which give it a very disagreeable smell. It is an excellent solvent for sulfur, iodine, phosphorus, rubber, resins, and fats and hence finds extensive use in the arts and manufactures. When exposed to light it slowly decomposes and acquires a yellowish color. It is very combustible, burning to carbon dioxide and sulfur dioxide. The heat of formation of carbon disulfide is  $-106$  KJ. so that when this substance burns more heat is given out than would be evolved during the combustion of corresponding quantities of the separate elements. A mixture of carbon disulfide vapor and air is violently explosive and is remarkable for the fact that ignition takes place at temperatures as low as  $260^\circ$ . On this account even greater care must be taken in handling this substance than is used with gasoline.

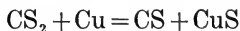
It will be recalled that sulfur belongs to the oxygen family of elements and on this basis we may consider carbon disulfide as corresponding to carbon dioxide. Carbon dioxide is an anhydride and will combine with water for the formation of carbonic acid or with oxides for the formation of carbonates. For example, calcium oxide,  $CaO$ , combines directly with carbon dioxide for the formation of calcium carbonate,  $CaCO_3$ . Corre-

spondingly, carbon disulfide will combine with sodium sulfide,  $\text{Na}_2\text{S}$ , forming sodium thiocarbonate,  $\text{NaCS}_3$ ,

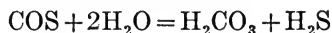


When sodium thiocarbonate is treated with an acid, thiocarbonic acid,  $\text{H}_2\text{CS}_3$ , is formed. This slowly breaks down into hydrogen sulfide,  $\text{H}_2\text{S}$ , and carbon disulfide, just as carbonic acid breaks down into water and carbon dioxide.

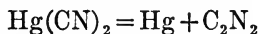
Carbon monosulfide,  $\text{CS}$ , analogous to carbon monoxide, is a gaseous substance which has been obtained in an impure state by passing carbon disulfide diluted with nitrogen over heated copper,



**Carbon Oxysulfide.**—Carbon oxysulfide,  $\text{COS}$ , may be regarded as a substance intermediate between carbon dioxide and disulfide. It is most easily formed by acting upon a thiocyanate with concentrated sulfuric acid. It is a gaseous substance, readily soluble in water, with which it slowly reacts for the formation of carbonic acid and hydrogen sulfide,



**Nitrogen Compounds of Carbon.**—At the very high temperature of the electric arc, carbon and nitrogen will combine directly for the formation of a gaseous compound, **cyanogen**,  $\text{C}_2\text{N}_2$ . This substance may also be obtained by heating mercuric cyanide,  $\text{Hg}(\text{CN})_2$ . This breaks down into metallic mercury and cyanogen, as shown in the equation,



This action is not unlike the decomposition of mercuric oxide and is carried out in the same way by heating the compound in a hard glass tube. Cyanogen is a colorless gas, having a peculiar pungent odor resembling that of peach kernels; it is exceedingly poisonous and burns in the air with a characteristic red-violet flame, forming carbon dioxide and nitrogen. During the formation of cyanogen, 309 KJ. of heat are absorbed, so the heat of combustion of this compound is much greater than that of carbon which it contains. The molar weight of cyanogen is 52, showing that the formula is  $\text{C}_2\text{N}_2$ , and not  $\text{CN}$ , which would correspond to

a molar weight of 26. The boiling-point of cyanogen is  $-21^{\circ}$ ; its critical temperature is  $124^{\circ}$  and critical pressure 62 atmospheres; its freezing-point is  $-34^{\circ}$ . At ordinary temperatures one volume of cyanogen is dissolved by four volumes of water.

Chemically, cyanogen resembles the halogens in many ways. It forms a series of salts called cyanides, which are similar to the chlorides, but contain the group CN, instead of chlorine. Silver cyanide, for example, is a difficultly soluble white substance, which is very much like silver chloride in its general properties. From these salts, **hydrocyanic acid** or prussic acid, HCN, may be easily obtained by the addition of a less volatile acid and distilling, according to the first general method for the preparation of acids. Hydrocyanic acid is a colorless, easily volatile liquid which boils at  $27^{\circ}$  and freezes at  $-14^{\circ}$ . It has a very strong odor which recalls that of peach pits or bitter almonds. It is one of the weakest acids, being only very slightly ionized when dissolved in water. On this account, the soluble cyanides react strongly alkaline when in solution in water, owing to hydrolysis. Hydrocyanic acid and the cyanides are extremely poisonous substances. Not only is hydrocyanic acid a poison toward animals, but it will also stop or "poison" the action of many catalyzers, and it is thought that perhaps the poisonous action of this substance on animals is due to its stopping the catalytic processes which are going on within them. Hydrocyanic acid is formed in nature from the action of water and a catalyzer or enzyme upon a substance known as amygdalin, which is present in bitter almonds and peach pits, glucose and oil of bitter almond being formed at the same time. It is this hydrocyanic acid which is the cause of the poisonous action of peach pits. It is also formed during many other changes which take place in the vegetable world, and the poisonous effects of some specimens of second growth sorghum upon cattle have been ascribed to its presence.

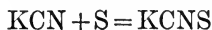
**Cyanates.**—Cyanides are good reducing agents, and when oxidized often form compounds called cyanates, potassium cyanate, KCNO, for example, is formed by cautiously oxidizing potassium cyanide, KCN. These compounds, so far as their formulæ are concerned, are like the hypochlorites and might be called hypocyanites, but since there are no higher compounds

corresponding to the chlorates, etc., they are called cyanates. The resemblance between the cyanates and the hypochlorites is still further shown by the fact that when cyanogen acts upon a solution of potassium hydroxide, a mixture of potassium cyanate and cyanide is formed, just as when chlorine acts upon potassium hydroxide we obtain a mixture of potassium hypochlorite and chloride. The equation for the above reaction is,



Cyanic acid, corresponding to these cyanates is very unstable. It is a colorless liquid with a strong smell resembling that of acetic acid, and readily passes over into cyanuric acid,  $\text{H}_3\text{O}_3\text{C}_3\text{N}_3$ .

**Thiocyanates.**—When a cyanide is heated with sulfur, the two substances combine for the formation of a thiocyanate. These correspond to the cyanates. The formation of potassium thiocyanate, KCNS, is shown in the following equation,



The thiocyanates are used as reagents for detecting the ferric salts with which they give an intense red coloration.

**The Hydrocarbons.**—Several hundred compounds of carbon and hydrogen have been described. For purposes of classification and as an aid in getting a comprehensive view of their relations, they have been divided into several series according to the composition and general properties of the substances. The principal series is that known as the Marsh Gas or Paraffin series, and the simplest member of this is marsh gas or methane. This series is distinguished by the fact that in all the compounds belonging to it carbon has a valence of 4—the highest valence which it is capable of taking on. For this reason, the members of this series are sometimes called the saturated hydrocarbons. Figure 29 gives the names and formulæ, and indicates the melting- and boiling-points of some of the more important of the lower members of the normal paraffins.

An inspection of this figure will show that the boiling- and melting-points of these hydrocarbons increase as they become more complex. It will be noticed too that the formula for each succeeding member of the series differs from that of the one which just precedes it by  $\text{CH}_2$ . A series of carbon compounds which

are related to one another in this way is called a **homologous series**. The members of such a series have similar properties which gradually change with the composition of the compound. The change in the boiling-point of the compounds shown in the figure is an illustration of this. Most of these hydrocarbons occur in nature in large quantities, the majority of them being found in crude petroleum, while methane and ethane are present in natural gas.

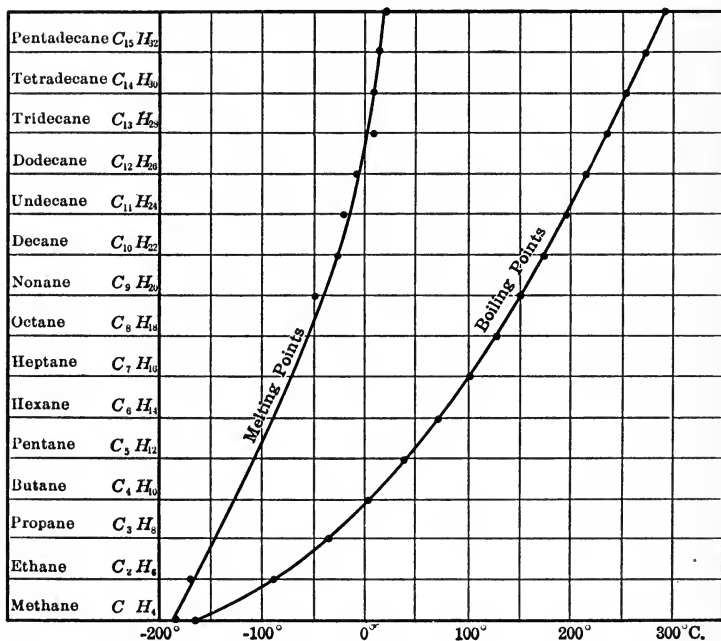


FIG. 29.

**Crude Petroleum.**—Crude petroleum or “oil” is found in many places in the United States, in Ontario, in Baku on the Caspian Sea, in Roumania, in India, and in Japan. The world’s annual production is more than 300,000,000 barrels of which the United States produces about 64 per cent. This oil is a mixture of a great many substances, but principally of hydrocarbons, and usually consists very largely of the hydrocarbons of the marsh gas series. In oil refining, advantage is taken of the fact



that the components have different boiling-points in order to secure their partial separation. For commercial purposes, no attempt is made to prepare pure substances from the oil, but the more volatile portions are distilled off and separated into fractions according to their density and adaptability for particular purposes. The following table gives the name, approximate components, density, and uses for some of the more common products.

SOME COMMERCIAL PETROLEUM PRODUCTS

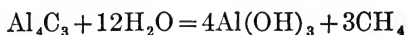
Trade name	Chief constituent	Density	Use
Rhigoline . . . . .	Pentane . . . . .	.6222	Solvent, automobiles.
Benzine . . . . .	Hexane . . . . .	.6511	“ “
Gasoline . . . . .	Heptane . . . . .	.722-.737	“ “
Naptha . . . . .	Octane . . . . .	.745-.824	Traction and stationary engines.
Kerosene . . . . .	Nonane, decane, etc.	.791-.824	Illuminating, fuel, and stationary engines.

The residue left after removing these substances is then distilled in a current of steam, which amounts to practically the same thing as distilling in a vacuum, since the water vapor carries the greater part of the pressure of the air. Some of the higher boiling products which come over under these conditions are used for lubricating oils, but must first be purified from the solid members of the series by cooling to a low temperature and filtering with the aid of filter presses. The solid substances so secured constitute what is known as **paraffin**, while the low melting product, which is salve-like at ordinary temperatures, is called **vaseline**. The final residue left in the retort is used as asphalt. Natural asphalt is a mixture of hydrocarbons which occurs in nature. A sort of natural paraffin known as ozocerite is found in small quantities. Just how these hydrocarbons are formed in nature is not known, but they have probably been produced, in most cases at any rate, by the partial decomposition of animal and vegetable organisms, although it is possible that they may have resulted from the action of water upon carbides, compounds of carbon with metals.

Most of the hydrocarbons are rather indifferent chemically. They show none of the properties of acids, bases, or salts, and fail to react with the majority of substances. They of course burn in oxygen, forming carbon dioxide and water, and react with chlorine or bromine for the formation of compounds. When heated to a very high temperature they all show a tendency to break down into hydrogen, carbon and simpler hydrocarbons containing a relatively smaller amount of carbon. The process is technically known as "cracking."

**Methane.**—Methane or marsh gas,  $\text{CH}_4$ , is the first member of the paraffin series. It is the principal constituent of natural gas. It is formed during the decay of vegetable matter in the absence of air, and hence rises to the surface from the bottom of ponds and marshes. It was this fact which gave to it its name, marsh gas. It is found in considerable quantities in coal, and since its mixture with air is explosive, it is one of the causes of the disastrous coal mine explosions. When found in mines it is often called "fire damp" by the miners, while the carbon dioxide, which is formed when it burns and is left in the mine after an explosion, is called "choke damp." In certain localities it is found in enormous quantities in porous strata lying some distance below the surface of the earth. When these are penetrated by a drill hole, a gas well is produced. The critical temperature of methane is  $-82^\circ$  and its critical pressure 56 atmospheres; its boiling-point is  $-164^\circ$ . Because of its very low critical temperature, the methane of natural gas does not exist in the depths of the earth in a liquid condition, but is present simply as a highly compressed gas, filling the pores of the rocks. The pressure upon the gas in some wells is as great as 100 atmospheres and consequently would be sufficient to liquefy the methane were it not for the fact that the temperature is too high.

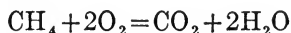
The origin of methane found in nature is as much in doubt as that of the other hydrocarbons, but the probabilities are that it was formed by the decomposition of organic matter. It is also made by the action of water upon aluminum carbide as is shown by the following equation,



and it is possible that a part of the methane has been produced by this reaction. In the laboratory the gas is usually prepared by distilling a dry mixture of sodium acetate and sodium hydroxide. The equation for the reaction is as follows,



Methane burns in the air for the formation of carbon dioxide and water. The flame has very little luminosity, consequently when it is desired to use it for illuminating purposes, it is burned in a sort of Bunsen burner and used to heat to incandescence a "mantle," composed of the oxides of certain rare earths. Because of the great amount of heat which is produced during the combustion, methane is very valuable for fuel and in the form of natural gas is much used for this purpose. As will be seen by the following equation,



one volume of methane will require two volumes of oxygen or ten volumes of air for complete combustion. The volume of the carbon dioxide formed will be equal to that of the methane consumed, while that of the water vapor will be equal to twice that of the methane. Because of the large quantity of carbon dioxide and water formed during the combustion of natural gas, every stove in which this fuel is consumed should be connected with a chimney, in spite of the fact that no smoke is produced. The quantity of water formed in the burning of natural gas is surprising. If one could condense all the water produced during the combustion of a thousand cubic feet of natural gas, more than 10 gallons of liquid water would be obtained. The explosive qualities of a mixture of gas and air are utilized as a source of energy in the gas engine.

When a mixture of chlorine and methane is exposed to sunlight the four combining weights of hydrogen are successively replaced by the chlorine forming the following series of compounds:

Methyl chloride.....	$\text{CH}_3\text{Cl}$
Methylene chloride.....	$\text{CH}_2\text{Cl}_2$
Chloroform.....	$\text{CHCl}_3$
Carbontetrachloride.....	$\text{CCl}_4$

The other product of each of these reactions is hydrogen chloride. These compounds are not salts and are not ionized when dissolved in water. Chloroform is perhaps the most important of these substances and is generally prepared by the action of bleaching powder upon ordinary alcohol. It is a colorless, easily volatile liquid which is used as a solvent and as an anesthetic. The iodine compound, iodoform,  $\text{CHI}_3$ , is a yellow, crystalline solid, which is a valuable antiseptic. Carbon tetrachloride is now being manufactured on a large scale, but not directly from methane. It is a valuable solvent and finds many applications as such, being used as a substitute for gasoline in dry cleaning, because it has the great advantage that it is not inflammable. In fact it is now being used as a fire extinguisher and is about the only thing beside carbon dioxide which will put out a gasoline fire.

The chlorine substitution products of methane slowly react with water for the forming of hydrochloric acid and carbon compounds containing oxygen.

**Radicals.**—A study of the derivatives of methane reveals the existence of a series of compounds which have the common characteristic that their formulæ can be so written that each contains a  $\text{CH}_3$  group,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{OH}$ ,  $(\text{CH}_3)_2\text{O}$ . When these compounds undergo certain transformations the  $\text{CH}_3$  group seems to pass unaltered from compound to compound and so acts like a chemical individual, being like the ammonium ion in this respect. A group which behaves in this way is called a radical, and this particular group,  $\text{CH}_3$ , is known as the methyl radical. A study of the chemistry of the carbon compounds shows that we have to do with a large number of such radicals. For example, each member of the paraffin series will form a monovalent radical, which contains one less combining weight of hydrogen per mole than the hydrocarbon from which it was formed. Ethane,  $\text{C}_2\text{H}_6$ , forms the ethyl radical,  $\text{C}_2\text{H}_5$ , propane,  $\text{C}_3\text{H}_8$ , yields the propyl radical,  $\text{C}_3\text{H}_7$ , etc. These radicals we have been considering so far are not ions, and have the remarkable property of being able to combine with almost any element or radical irrespective of the electrical character of the substance. For example, the ethyl radical will combine with sodium for the formation of sodium ethyl,  $\text{C}_2\text{H}_5\text{Na}$ , or with

chlorine for the formation of ethyl chloride,  $C_2H_5Cl$ , and yet sodium may be considered a typical electropositive element, while chlorine seems to be decidedly electronegative, at least in the chlorides. This tendency toward universal combination exhibited by these radicals is apparently one of the causes for the great variety of carbon compounds. The methyl radical, for example, will combine with chlorine, bromine, or iodine, forming methyl chloride, bromide, or iodide, with the hydroxyl, producing methyl alcohol,  $CH_3OH$ , and with oxygen for the formation of methyl ether,  $(CH_3)_2O$ . If no other substance is present for it to combine with, one methyl radical will combine with another for the formation of the compound  $CH_3-CH_3$  or  $C_2H_6$ , which is ethane, and this in turn will yield the ethyl radical,  $C_2H_5$ , which under the proper conditions will combine with a methyl radical for the formation of the compound,  $C_2H_5CH_3$ , or  $C_3H_8$ , which is propane, the third member of the group. Proceeding in this way, practically the whole series of paraffin hydrocarbons has been built up and consequently they all may be regarded as derivatives of methane.

**Types of Carbon Compounds.**—The principal carbon compounds with which we shall have to deal may be divided into a few well-marked types; the hydrocarbons, which we have already discussed, alcohols, ethers, aldehydes, acids, and esters. The following table gives the general formulæ for these compounds.

Type	General formulæ
Hydrocarbons.....	RH
Alcohols.....	ROH
Ethers.....	$R_2O$
Aldehydes.....	RCOH
Acids.....	RCOOH
Esters.....	RA

In this table "R" stands for any monovalent radical, and "A" for the anion of a monobasic acid.

**The Alcohols.**—The first member of the alcohol group, **methyl or wood alcohol**,  $CH_3OH$ , is one of the by-products obtained in

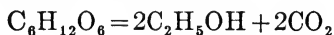
the destructive distillation of wood for charcoal. It is a colorless, mobile liquid, of a density of .796, which boils at 66°. When pure it has a pleasant odor, although that of the commercial article is very disagreeable. It burns with a smokeless, non-luminous flame, and is valuable as a fuel. It is a very good solvent and was extensively employed for this purpose before the introduction of denatured alcohol. It is decidedly poisonous and is largely used in the crude state to mix with ethyl alcohol for the production of the so-called denatured alcohol.

The molar weight and analysis of methyl alcohol show that it contains per mole one combining weight each of carbon and oxygen and four of hydrogen. Experience teaches that one of the hydrogens is different from the others, because sodium will replace only one, forming the methylate,  $\text{CH}_3\text{ONa}$ , and further that hydrochloric acid will react with the alcohol, yielding water and methyl chloride,  $\text{CH}_3\text{Cl}$ . To represent the action with sodium, one of the hydrogens must be written differently from the others, say  $\text{HCH}_3\text{O}$ ; but the action with the acid suggests a

H  
hydroxid, and the formula,  $\text{CH}_3\text{OH}$  or  $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{OH}$ , indicates

both actions, and the latter is called the structural formula for methyl alcohol. In a similar way, the properties of other compounds are studied, and structural formulæ devised to represent them.

**Ethyl alcohol**,  $\text{C}_2\text{H}_5\text{OH}$ , or grain alcohol as it is called, is formed by the action of an enzyme produced by yeast upon sugars  $\text{C}_6\text{H}_{12}\text{O}_6$ . The process is called fermentation and the equation for the reaction is as follows:



The enzyme acts as a catalyzer. The alcohol so formed may be largely separated from the water by distillation, the alcohol passing over first since its boiling-point is 78.3°. The alcohol of commerce contains about 95 per cent. by volume of alcohol and 5 per cent. of water. It is not possible to separate these two substances completely by distillation, since they form a minimum boiling mixture, boiling at 78.15° and containing 4.43 per cent. of water. (See hydrogen chloride and water.) Absolute alcohol

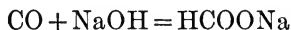
free from water may be obtained by adding unslaked lime to the 95 per cent. alcohol. The lime combines with the water to form calcium hydroxide, and after the action is complete, the absolute alcohol may be distilled off. The density of alcohol at 15° is .7940. As is well known, alcohol is a valuable fuel and an extremely useful solvent for many substances which are difficultly soluble in water. It is largely employed for the preparation of medicines. **Denatured alcohol** is 95 per cent. alcohol, mixed with some substance which cannot be readily separated from the alcohol and which will render it totally unfit for use as a beverage. A very commonly used formula is 89.5 per cent. grain alcohol, 10 per cent. wood alcohol and .5 per cent. benzine. Such alcohol is exempt from the payment of any internal revenue tax, and is consequently much cheaper than the pure article, and so finds extensive application in the arts.

**The Ethers.**—The general formula for these substances is  $R_2O$ . **Ethyl ether**,  $(C_2H_5)_2O$ , is the best known and by far the most important member of this group. It is prepared by mixing concentrated sulfuric acid and ethyl alcohol in such proportions that the liquid will boil at about 140°. The mixture is then distilled, when ether and water, together with some alcohol, pass over. If alcohol be run into the flask at such a rate that the boiling-point remains constant, a given portion of sulfuric acid will convert a large amount of alcohol into ether. The apparent equation for the reaction is,  $2C_2H_5OH = (C_2H_5)_2O + H_2O$ , and the sulfuric acid seems to act simply as a catalyzer. It is very probable that intermediate compounds are formed and that we are dealing with another case of transfer catalysis. Ethyl ether is a colorless, mobile, very volatile liquid, boiling at 34.6°. It is used as a solvent for iodine, fats, etc., and as an anesthetic.

**The Aldehydes.**—The general formula for the aldehydes is  $RCOH$ . These substances, in general, may be formed by the partial oxidation of the alcohols. The first member of the series is formaldehyde,  $HCOH$ . In this case hydrogen takes the place of the "R" in the general formula. Formaldehyde is produced by the incomplete combustion of methyl alcohol when the vapors of this substance mixed with air come in contact with platinum gauze or platinized asbestos. It is also formed to a certain extent by the incomplete combustion of natural gas, especially when the

flame of the latter substance plays against a cold copper surface. Formaldehyde is gaseous at ordinary temperatures, the boiling-point being  $-21^{\circ}$ ; it has a very pungent, irritating odor, is quite soluble in water and is put upon the market in a 40 per cent. solution, known as formalin. Both the solution and the gaseous substance are powerful germicides and are used as disinfectants. The aldehydes are good reducing agents, being oxidized to the corresponding acids, RCOOH.

**The Acids.**—The general formula for the organic acids is RCOOH. These substances are numerous and important. The first member of the series is formic acid, HCOOH. As was the case with formaldehyde, in the formic acid the hydrogen takes the place of "R" in the general formula. Formic acid may be prepared by the oxidation of formaldehyde, or from its salts, the formates by decomposing them with acids and distilling, using the first general method. As has been mentioned, formic acid will break down into water and carbon monoxide so that in a way this latter substance may be considered formic anhydride. However, this reaction is not reversible, so that formic acid cannot be prepared from water and carbon monoxide. Sodium formate, HCOONa, however, may be made by passing carbon monoxide over heated sodium hydroxide, the equation being



From this salt, the acid may be obtained as indicated above. It is a colorless liquid boiling at  $100.1^{\circ}$ , freezing at  $8.6^{\circ}$ . Like almost all other carbon acids it is a weak acid, although somewhat stronger than acetic acid which is the next member of the series. In spite of the fact that, as its formula indicates, it contains two combining weights of hydrogen per mole, it is a monobasic acid, only one of the hydrogens being ionizable. This fact that the hydrogens differ in their properties is expressed by writing them in different positions in the formula—HCOOH instead of  $\text{COOH}_2$ . As indicated by the general formula for the series, the organic acids contain the group COOH, and to this is ascribed their acid character, and the hydrogen of this group is supposed to be that which ionizes.

**Acetic Acid.**—Acetic acid,  $\text{CH}_3\text{COOH}$ , is the second member.

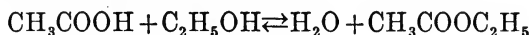


It is formed during the destructive distillation of wood, and is one of the valuable by-products of this process. Large quantities of the substance are produced by the oxidation of ethyl alcohol by the oxygen of the air with the aid of a certain form of bacteria, known as *B. Aceti*. The common name for this is mother of vinegar. The dilute solution of acetic acid, formed by the oxidation of the alcohol contained in cider, is known as vinegar. Vinegar usually contains 4 to 5 per cent. acetic acid. Pure acetic acid is a colorless liquid which boils at  $119^{\circ}$  and freezes at  $16.7^{\circ}$ . It mixes with water in all proportions. As has been mentioned repeatedly acetic acid is a weak acid, being only slightly dissociated. Although it contains four combining weights of hydrogen per mole, it is a monobasic acid, three of the four combining weights of hydrogen being present in the methyl radical, and these are non-ionizable.

**Oxalic Acid.**—Oxalic acid has the formula  $(\text{COOH})_2$  or  $\text{H}_2\text{C}_2\text{O}_4$ . This formula may be regarded as our general formula for acids in which the group  $\text{COOH}$  has taken the place of the "R," so that we really have in oxalic acid a combination of two acid groups. In accordance with this, it shows itself to be a dibasic acid.

The acid may be made by the oxidation of sugar with nitric acid. It is readily soluble in water and separates from the solution in the form of a white crystalline hydrate,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , and is usually sold in this form. The calcium salt of oxalic acid is very slightly soluble in water and on this account oxalic acid, or rather its ammonium salt, is largely used in the laboratory for the detection and determination of calcium.

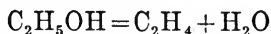
**The Esters.**—When an alcohol is acted upon by an acid, a reaction takes place which consists in the formation of water, apparently from a combination of the acidic hydrogen of the acid with the hydroxyl of the alcohol, and of an ester—a compound produced by the union of the radicals from the acid and the alcohol. The equation for the reaction between ethyl alcohol and acetic acid is as follows:



$\text{CH}_3\text{COOC}_2\text{H}_5$  is called ethyl acetate, and is an important member of the group of esters. This kind of a reaction takes place between practically every alcohol and every acid, so that we

have a large number of such compounds. The reactions are always reversible and consequently never complete unless special attention is taken to remove one of the products. The formation of esters resembles that of salts by the reaction of acids upon bases, but yet the action is essentially different in that the alcohols are not ionized, and hence are not bases, and that the esters formed are not salts, because they do not dissociate. These esters are pleasant smelling substances and it is to them largely that the flavors of our fruits and flowers are due.

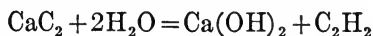
**Unsaturated Hydrocarbons.**—The methyl radical may be imagined as being formed from methane by the dropping of one combining weight of hydrogen from this substance. If two were removed the divalent radical  $\text{CH}_2$  would be produced. This radical is known as methylene and forms a long series of compounds similar to those of methyl, but differing of course because of the fact that the radical is divalent. The chloride, for example, is  $\text{CH}_2\text{Cl}_2$ . Under proper conditions two of these methylene radicals will combine for the formation of the substance  $\text{C}_2\text{H}_4$ , which is known as ethylene. This is the first member of a long series of hydrocarbons, known as the ethylene series. These compounds have the property of combining directly with two combining weights of hydrogen for the formation of members of the paraffine series. Because of the fact that they are capable of taking up more hydrogen they are called "unsaturated" hydrocarbons. They are also able to combine directly with two combining weights of a halogen per mole of hydrocarbon. Ethylene, the first member of the series, is formed by heating ethyl alcohol with sulfuric acid to a temperature of  $175^\circ$ . The apparent reaction is



but here again it probably goes in steps, intermediate compounds involving the sulfuric acid being formed. It is a colorless gaseous substance whose critical temperature is  $+9^\circ$ , it boils at  $-102^\circ$ , and it freezes at  $-169^\circ$ . Liquid ethylene is extensively used as a cooling agent. Ethylene is a valuable constituent of ordinary coal gas, since it burns with a strongly luminous flame, and contributes largely to the luminosity of the gas when burned with the ordinary lava tip.

**Acetylene.**—If we imagine three combining weights of hydrogen removed from methane, the trivalent radical CH would be produced. Two such radicals by their combination would form the substance  $C_2H_2$ , or acetylene. This compound is still more highly “unsaturated” than ethylene. It is the first member of another series of unsaturated hydrocarbons, known as the acetylene series. Acetylene is a colorless gas, which when perfectly pure has a pleasant ethereal odor, but which, owing to the presence of certain impurities, usually has a very disagreeable odor. It has within comparatively recent times become of considerable importance because of the facts that it burns in the air with an intensely luminous flame, and that when burned with oxygen in a properly constructed burner it will produce a very high temperature. Advantage is taken of this fact in the metal-working trades for the autogenous welding of metals and also for the rapid cutting of steel, etc., by burning a path through it.

Acetylene may be formed by the direct union of carbon and hydrogen at the temperature of the electric arc, but it is practically exclusively prepared at the present day by the action of water upon calcium carbide,  $CaC_2$ , the equation being as follows:



When mixed with air, acetylene is exceedingly explosive and the gas is particularly dangerous because any mixture with the air between proportions 3 per cent. and 82 per cent. acetylene will explode. These limits are wider than for any other gas. A mixture of natural gas and air, for example, explodes only when it contains from 5 to 13 per cent. of methane,  $CH_4$ . The critical temperature of acetylene is  $+35^\circ$ , the critical pressure 67 atmospheres. Its melting-point is  $-81^\circ$  and its subliming point is  $-87^\circ$ , so at atmospheric pressure it passes directly from the solid into the gaseous state without melting. Owing to the fact that its critical temperature is above that of the room, acetylene may be liquefied at ordinary temperatures by pressure alone, but the operation is dangerous because acetylene is a substance which is formed from its elements with the absorption of heat, and decomposes into them with the evolution of heat. The heat of formation is  $-243$  KJ. per mole. If then through any cause the acetylene should start to decompose, the heat thereby produced

would raise the temperature of the remaining substance, and so cause it to decompose more rapidly, thus producing more and more heat per second and making the reaction go faster and faster until a violent explosion occurs. This explosion may be very easily produced by setting off in liquefied or even compressed acetylene, fulminating mercury, a substance which is used for exploding dynamite. With this substance acetylene may be made to explode when it is under as low a pressure as two atmospheres. At ordinary atmospheric pressure, it is not explosive, unless mixed with oxygen or air. Acetylene is very soluble in an organic substance called acetone,  $(\text{CH}_3)_2\text{CO}$ , which belongs to a group of compounds called the ketones, which we have not discussed. This solution in acetone is not explosive and cylinders containing it under pressure are now largely used

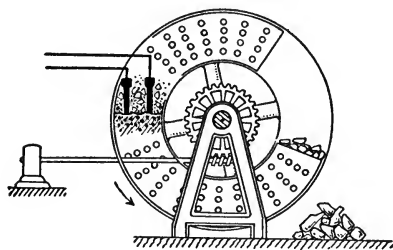
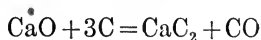


FIG. 30.

to supply acetylene for the lights on automobiles. One volume of acetone dissolves 25 volumes of  $\text{C}_2\text{H}_2$ ; one liter at 12 atmospheres dissolves enough acetylene to measure 300 liters at ordinary pressure. One of the most characteristic properties of acetylene is that when passed through an ammoniacal solution of a cuprous salt it yields a red precipitate of a carbide of copper,  $\text{Cu}_2\text{C}_2$ , known as copper acetylide. This is extremely explosive when dry. From this it will be seen that acetylene acts as a weak acid.

The **calcium carbide** used in making acetylene is made by heating lime (calcium oxide) and carbon to a very high temperature in an electric furnace (Fig. 30). The equation is,



**Fuel Gases.**—Gaseous fuels are of great importance for domestic and technical purposes because they are clean and very easily controlled. They are also finding a rapidly increasing use as a source of energy in gas engines, so that the subject of fuel gases is one of no little practical importance. Many different varieties

of gas are in use such as natural gas, coal gas, wood gas, oil gas, and the various types of water and producer gases. Natural gas has already been discussed. Wood and oil gases are of rather limited application, so that we will devote our attention at this point chiefly to coal, water and producer gas.

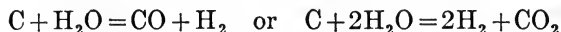
**Coal Gas.**—Coal gas is obtained by the destructive distillation of bituminous coal in closed fire clay retorts. Under these conditions most of the hydrogen and a part of the carbon of the coal is evolved in the form of combustible compounds. The composition of coal gas is variable, but the following is the result of the analysis of a representative coal gas. The relative proportions of the various constituents are expressed in per cents. by volume:

Hydrogen.....	57.08
Methane.....	33.99
Carbon monoxide.....	2.63
Unsaturated hydrocarbons.....	4.38
Nitrogen.....	0.15
Carbon dioxide.....	0.79
Oxygen.....	0.96
Carbon disulphide.....	0.02
	<hr/>
Total.....	100.00

Along with these gaseous substances a large number of other compounds are produced, such as tar, ammonia, benzene, hydrogen sulfide, etc. These are removed from the gas by the process of purification, and many of them are put to useful purposes. At first the coal gas was chiefly used for illuminating purposes, being burned from the ordinary lava tip. Its value under these conditions was largely dependent on the content of the unsaturated hydrocarbons. At the present day it is extensively used for heating, or for driving gas engines and a strongly luminous gas is not desirable for such purposes. So in the manufacture of the modern coal gas, the unsaturated hydrocarbon content is kept down, and when used as an illuminant it is burned with an incandescent mantle.

**Water Gas.**—When coal gas is made from bituminous coal, only a portion of the carbon of the coal is converted into gas. The remainder is left as coke, which, although a valuable fuel, is much

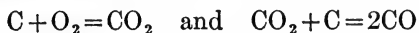
less convenient and valuable than the gas; so efforts have been made for a long time to devise some process whereby the whole of the carbon of the coal may be converted into combustible gas. This may be done by taking advantage of the fact that carbon and steam will react at a high temperature for the formation of either carbon monoxide and hydrogen, or of carbon dioxide and hydrogen, the first reaction taking place at a higher temperature than the second. The equations for these reactions are as follows:



The mixture of these gases is called water gas. The process for its manufacture is briefly as follows: coke or anthracite coal is charged into a suitably constructed furnace and set on fire and brought to a high temperature by blowing air through it. The current of air is then cut off and steam blown in, when both the above reactions take place. Heat is absorbed in each, and hence the temperature of the mass of carbon is rather rapidly lowered until finally the reaction practically comes to an end. The steam is then cut off and air blown through the carbon once more, taking care that the products of the combustion shall not be delivered into the gas holder for the water gas, since it would be unduly diluted thereby. As soon as the fuel has been sufficiently heated, the connections are changed once more, steam blown in, and the water gas collected. This alternation of processes is continued until the fuel is entirely consumed. The gas so obtained contains about 52 per cent. hydrogen and 40 per cent. of carbon monoxide. It burns with a practically colorless flame, producing a very high temperature, and is good for fuel and power purposes. For use as an illuminant it may be either burned with a mantle or enriched with unsaturated hydrocarbons obtained by decomposing petroleum products.

**Producer Gas.**—A fuel gas has also been obtained by taking advantage of the fact that when carbon burns with a limited supply of air, carbon monoxide is formed. This process is carried out technically by forcing air up through a rather deep bed of incandescent carbon. The carbon dioxide formed at the bottom of the fire, in passing up through the mass of carbon, is reduced to carbon monoxide and passes out of the apparatus

mixed with the nitrogen of the air (Fig. 31). The equations for its formation are as follows:



From this it may be seen that the volume of the carbon monoxide is twice that of the oxygen, so the gas produced in this way should contain 33 per cent. of carbon monoxide. In practice it contains 28 to 30 per cent. of this gas, the remainder being nitrogen and carbon dioxide. Since during this reaction considerable quantities of heat are evolved, it may be worked to advantage in conjunction with the reaction for the production of water gas. To do this a mixture of water vapor and air obtained by passing the latter through water heated to about 85°, is blown through the mass of heated carbon. The oxygen of the air reacts with the carbon for the formation of carbon monoxide thereby furnishing heat enough to carry on the reaction between the water and carbon for the formation of carbon dioxide and hydrogen. So much steam is used in this process that the temperature of the reacting mass is kept low enough so that practically all of the nitrogen of the coal is obtained as ammonia;

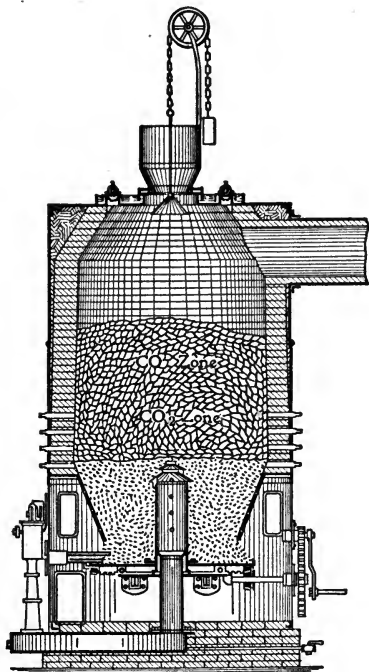


FIG. 31.

whereas in the coal gas manufacture only about one-third of the nitrogen is recovered. In this process common bituminous coal may be used, so that the gas produced is very cheap. The gas obtained in this way contains about 43 per cent. nitrogen, 2 per cent. methane, 28 per cent. hydrogen, 12 per cent. carbon monoxide, and 15 per cent. of carbon dioxide. It is especially valuable for fuel and power purposes, and is finding extensive and rapidly increasing use in the manufacturing industries.

A gas engine using producer gas will often deliver a horsepower for an hour, per pound to a pound and a half of coal used in the producer. The fuel efficiency of such a plant is much greater than that of a steam plant.

## FLAMES

**Flames** are produced by the rapid interaction of two or more gases whereby sufficient heat is generated to render the gases and their products luminous. In most of the cases to which the term is applied, one gas passes in a stream into a larger body of the other and the chemical action takes place at the point of contact of the two.

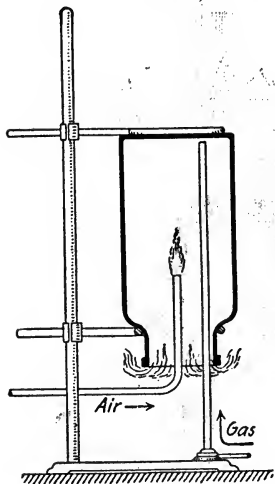


FIG. 32.

In the flames with which we are most familiar, the oxygen of the air is one of the active gases and the other is hydrogen, natural gas, coal gas, or some similar mixture; and since the flame is located at the opening whence the gas issues into the air, we very naturally speak of the gas as burning, but the air has just as much to do with the phenomenon as the other gas. As a matter of fact, it is a very simple matter to burn a stream of air in an atmosphere of coal or of natural gas. All that is necessary to do to show this is to place a wide-mouthed bottle, mouth downward (Fig. 32), upon a suitable support, and pass

into it a moderate stream of gas until the air is displaced, and then light the gas as it issues out of the mouth of the bottle. Now pass a glass tube from which a steady stream of air is escaping up into the bottle. As it goes up through the flame at the mouth of the bottle, the air will take fire, and continue to burn in the gas as long as the supply of the two is kept up.

All flames give off light, but they differ enough among themselves so that we may conveniently divide them into two classes; non-luminous and luminous. This classification is arbitrary, because there is every gradation between the typically non-luminous



ous flame of hydrogen and that of acetylene which is the most brilliant of all; that of methane stands near the dividing line. When infusible non-volatile solids are placed in non-luminous flames, they are heated to incandescence and give out light; a mixture of 99 per cent. thorium oxide, with 1 per cent. cerium oxide, is especially brilliant under these conditions, and it is this mixture which is used in the Welsbach mantles for incandescent gas lighting.

The luminous flames are nearly all produced by the burning of compounds of hydrogen and carbon, and there is much evidence in favor of the view that solid particles of carbon are formed in their interior, and that the greater part of the light is due to the incandescence of these particles. If a cold surface be placed in such a flame, these particles will deposit on it forming a layer of soot or lampblack. In fact, this is the way in which lampblack is made.

If the flame of an ordinary hydrocarbon gas, such as coal gas issuing from a circular opening, be examined, it will be found to consist of a number of conical sheaths or zones fitting one inside the other as indicated in the diagram (Fig. 33). In the relatively non-luminous sheath "a" water and carbon dioxide are formed, and the heat from this radiating inward decomposes the hydrocarbon toward the base of the flame forming hydrogen and acetylene, or hydrogen, methane and acetylene; as the gases pass upward the temperature rises and finally reaches a point where the acetylene rapidly decomposes into hydrogen and carbon. Since this is a reaction which takes place with the evolution of heat, the temperature of the particles of carbon is raised even above that of the rest of the flame, and this is the cause of the greater part of the light. These changes take place in the zone "b." As the carbon passes up through the flame, it gradually burns, first to the monoxide, then to the dioxide. In the interior of the flame, where the supply of oxygen is limited, the carbon is practically all burned to carbon monoxide before the hydrogen burns. The luminosity of a flame may be increased by putting both gases under greater pressure, or by heating the gas before it leaves the burner. On the other hand, anything



FIG. 33.

which will lower the temperature of the flame will decrease the light. This may be done by holding a cold object in the flame or by mixing some indifferent gas such as nitrogen with the combustible gas. This both dilutes the gas and makes more material to be heated, and hence makes the flame colder.

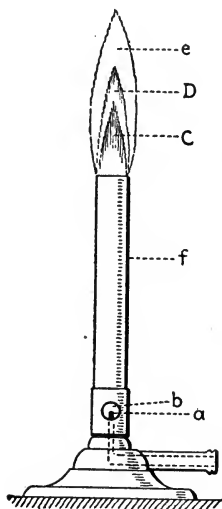


FIG. 34.

**Bunsen Burner.**—Robert Bunsen, a German chemist, invented the burner which bears his name, in order to burn coal gas with the clean smokeless flame, which is so desirable for chemical purposes. A diagram of the burner and its flame is shown in Fig. 34. The gas enters the burner through the jet "a," and, having a high velocity, it draws a certain quantity of air in at the holes "b" in the base of the tube "f." In passing up through this tube, the gas and the air mix. Three well-marked sheaths are formed in the flame. "C" is non-luminous, and so cold that a match head may be held in it for some time without igniting. In this, practically no chemical change takes place. "D" is bluish-green and very hot, especially at the upper tip, but not very luminous. In

it the hydrocarbons are transformed into carbon monoxide and hydrogen. In the outer layer "e" the hydrogen and carbon monoxide burn to water and carbon dioxide. The non-luminous flame of the Bunsen burner is smaller and hotter than a luminous flame burning the gas at the same rate.

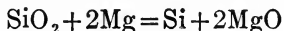
## CHAPTER XVII

### SILICON

**General.**—Silicon, the second member of the carbon group, occurs very abundantly in nature in the form of its oxide and various silicates. This element, next to oxygen, is present in the earth in the greatest quantity, forming as it does about one-fourth of the earth's crust. It was first recognized as a distinct element and prepared in the free state by Berzelius in 1823.

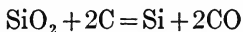
**Preparation.**—Silicon exists in at least two allotropic modifications, one crystalline, the other amorphous. Some evidence also points toward the occurrence of two distinct crystalline forms, corresponding to graphite and diamond.

Amorphous silicon may be prepared by passing its chlorine or fluorine compound over heated potassium or sodium, the halide of the metal is formed and silicon is liberated. This substance may be made more conveniently, however, by heating finely powdered quartz, which is silicon dioxide,  $\text{SiO}_2$ , with metallic aluminum or magnesium; the reaction which takes place with magnesium is represented by the following equation,



The magnesium oxide is removed by treating the resulting mixture with hydrochloric acid.

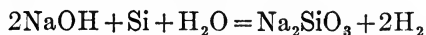
Crystalline silicon is now being prepared on a large scale at Niagara Falls by reducing the dioxide with carbon in an electric furnace of the arc type. It is used in the manufacture of steel.



**Properties.**—Amorphous silicon is a dark brown, friable substance without luster, is a non-conductor of electricity, and has a density of 1.8. If the temperature is raised somewhat it takes fire and burns. The combustion is not complete, however, as the silicon dioxide formed in the reaction acts as a protective

coating and prevents the free access of oxygen. The high temperature of the reaction also causes the unburned portion to change into the crystalline variety which is not combustible, so the residue will not burn even after the oxide has been removed. The crystalline silicon is very much more resistant chemically and is not attacked by oxygen even at red heat. It is dark steel gray in color and forms opaque octahedra possessing a metallic luster.

Both varieties melt at temperatures in the neighborhood of  $1500^{\circ}$  to a steel blue liquid which on solidifying always produces the crystalline variety. Silicon dissolves in hydroxides of the alkali metals with the evolution of hydrogen and the formation of the corresponding alkali silicates.



It is not soluble in any single acid but is in a mixture of nitric and hydrofluoric acids, forming silicon tetrafluoride, and is slowly oxidized by aqua regia to silicic acid.

**Silicon Dioxide.**—Silicon forms with oxygen one well-defined compound, silicon dioxide,  $\text{SiO}_2$ , which is analogous to carbon dioxide. The monoxide, the analogue of carbon monoxide, has been stated to exist and has been described as a brown powder, but as yet this has not been sufficiently confirmed. Silicon dioxide or silica, as it is commonly called, occurs very abundantly on the earth's surface both in the crystalline and the amorphous modifications. The purest form is rock crystal, which is colorless quartz. This compound when colored by different metallic oxides gives rise to smoky quartz, and other semi-precious stones. Flint occurs widely distributed in nature, and is rather impure amorphous silica; other forms of this variety are certain kinds of petrified wood, opal and jasper.

Silicon dioxide as prepared in the laboratory is ordinarily amorphous and it is very difficult to cause it to change over into the crystalline form, although this has been accomplished. On account of its extreme hardness and its transparency, rock crystal finds extensive use in the manufacture of fine lenses. Recently also laboratory utensils have been made from quartz. When heated before the oxy-hydrogen blowpipe it behaves like glass, in that it becomes pasty and does not pass directly from

the solid to the liquid state. In this condition it may be worked and blown into the desired shapes. Very great skill is required, however, since the temperature range between the solid state and the extreme liquid state is quite small. These vessels are very resistant chemically to nearly all reagents except the alkalis, and consequently they may replace the more expensive platinum in many operations. The temperature coefficient of this fused silica ware is very small, and a crucible heated to redness may be plunged into cold water without being broken.

**Silicic Acid and Silicates.**—Silicates are known which correspond to an even greater variety of silicic acids than there are phosphoric acids. We have for example, salts of orthosilicic acid,  $H_4SiO_4$ ; of meta silicic acid,  $H_2SiO_3$ ; diortho silicic acid,  $H_6Si_2O_7$ ; dimeta silicic acid,  $H_2Si_2O_5$ ; and finally the trisilicic acid,  $H_4Si_3O_8$ . When a soluble silicate is treated with an acid, the solution usually remains clear for a time; and then there is precipitated difficultly soluble silicic acid whose composition is rather variable but which tends to approach that of meta silicic acid,  $H_2SiO_3$ . When heated, this yields the dioxide and water.

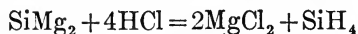
By proper manipulation, a colloidal solution of silicic acid may be prepared. A colloidal solution is one which appears perfectly homogeneous to the eye, and which will pass through a filter, but which has the same boiling- or freezing-point as pure water. When a beam of very strong light is sent through the solution and a microscope focused upon its path, a multitude of particles are seen so extremely minute that they cannot be perceived in any other way. A true solution is homogeneous even when examined in this way. This shows that the solute in a colloidal solution is not really in solution, but that it is merely very finely divided and in a state of suspension.

A few of the naturally occurring silicates will be mentioned at this point merely to show how important to us these compounds are. Clay, mica, asbestos, serpentine, feldspar, are the principal; while granite (a mixture of quartz, feldspar, and mica), basalt, porphyry, lava, pumice stone are also common silicate rocks. Sandstone consists principally of particles of silicon dioxide cemented together with calcium carbonate, iron oxide, or amorphous silica from silicic acid.

When exposed to the weather, the silicate rocks are gradually

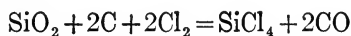
disintegrated under the combined action of water, carbon dioxide, changes of temperature, freezing and thawing, with the formation of clay (aluminum silicate), silica, and the carbonates of the metallic elements of the silicates. Under proper conditions, these products of disintegration will solidify into what are known as the sedimentary or secondary rocks, while the original silicates are called the igneous or primary rocks.

**Silicon Hydride.**—If in the preparation of silicon by means of metallic magnesium an excess of the metal is used, a compound magnesium silicide,  $\text{SiMg}_2$ , is formed. This compound reacts with hydrochloric acid yielding magnesium chloride and a gas which on contact with the air takes fire spontaneously, and burns, forming smoke rings of silicon dioxide.



This gas is silicon hydride,  $\text{SiH}_4$ , the analogue of methane, and like phosphine, if carefully purified loses the property of spontaneous inflammability, which property is probably, in this case also, due to the presence of some higher hydride.

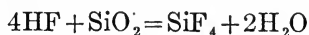
**Halogen Compounds.**—If amorphous silicon be treated with chlorine, or if a current of chlorine be passed over a mixture of finely powdered quartz and carbon which is strongly heated, the compound silicon tetrachloride,  $\text{SiCl}_4$ , is formed. Although in this latter reaction neither the carbon nor the chlorine alone is able to effect the decomposition of the silicon dioxide, their combined action can bring it about. The explanation for this is that, in the combined reaction, the substances formed possess much less free energy than those from either reaction alone. In other words, the action takes place with a greater fall of free energy, and the resulting state represents a condition of more stable equilibrium.



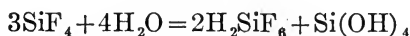
Silicon chloride is a colorless liquid whose boiling-point is  $59^\circ$ , and whose density is 1.5. It fumes strongly in the air since water readily decomposes it into silicic acid and hydrogen chloride.

If instead of chlorine, hydrogen chloride is passed over amorphous silicon, a compound of the composition  $\text{SiHCl}_3$  is formed and by analogy is called silico-chloroform.

Silicon unites with the other halogens to form similar compounds. The most important of these is the fluoride which is a gas at ordinary temperatures and is readily formed by treating silica or a silicate with hydrofluoric acid,



Silicon fluoride is decomposed by water, hence some dehydrating agent such as sulfuric acid must be added to remove that formed in the reaction. Silicon fluoride is most conveniently prepared by mixing together silicon dioxide and a fluoride, and adding concentrated sulfuric acid to the mixture. The reaction with water is different from that in the case of the other halogen compounds. Instead of silicic acid and hydrogen fluoride, we have the complex hydrofluosilicic acid formed according to the equation,



In the preparation of this substance, the gas must be passed into the water through an inverted funnel to prevent the clogging of the tube by the precipitated silica, or sufficient hydrofluoric acid may be added to prevent its separation.

The reaction of hydrofluoric acid on silicates is of special importance, for by means of it silicate rocks are brought into solution so that they may be analyzed; and it is technically used in the etching of glass, which is a mixture of metallic silicates. The surface of the glass is first covered over with a coat of paraffin or wax. The design to be etched is then scratched through the wax film, and the surface, with these parts exposed, is treated with the vapors or the water solution of hydrogen fluoride. The places where the glass has been dissolved may be filled with graphite or other preparations to make them show more distinctly. Scientific instruments of glass are graduated and marked by these processes.

**Carborundum.**—Carborundum is the trade name for silicon carbide, SiC. It is chemically resistant, very hard, will scratch ruby, and is used very largely as an abrasive. It is not attacked by acids but is gradually decomposed by fused alkalis forming the respective carbonate and silicate.

The manufacture of carborundum at present constitutes a con-

siderable industry, especially at Niagara, where cheap water-power is available. It is prepared by heating together in an electric furnace (Fig. 35), carbon, silicon dioxide and sawdust with common salt as a flux. The furnaces are constructed from fire brick, and are about 16 ft. long by 5 ft. wide and 4 or 5 ft. in depth. The walls are 2 ft. thick, and the ends and bed only are permanently constructed. On the ends are large iron plates which make contact with the copper wires on the outside, and on the inside with the carbon terminals. When the furnace is

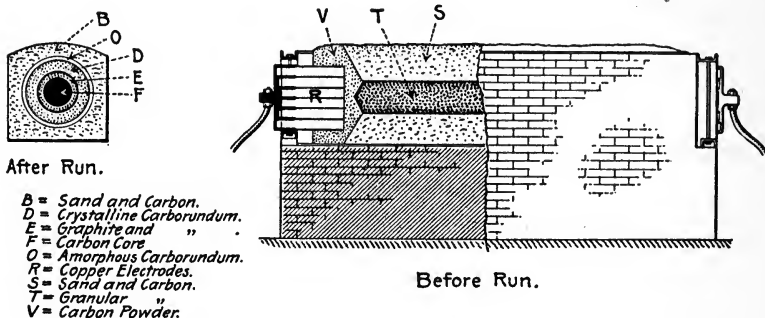


FIG. 35.

put in operation, these carbons are electrically connected by a carbon core which becomes intensely heated by the passage of an electric current and furnishes the heat necessary for the production of the requisite high temperature as well as that absorbed during the reaction. The electricity has no further effect on the process. To put the furnace in operation the sides are built up, the core placed in position in contact with the carbon terminals, the reaction mixture packed around it and the current turned on. When the run is complete the furnace is allowed to cool and the carborundum formed is removed. It is then crushed, treated with sulfuric acid to remove impurities such as iron oxide, washed and graded. The product is now ready to be worked up into abrasive wheels, hones and the like. For this purpose the carborundum is mixed with a suitable binding material such as kaolin and feldspar, moulded and baked at a high temperature.

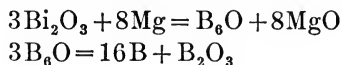


## CHAPTER XVIII

### BORON

**General.**—Boron is very similar to silicon in properties, both of the free element and of its compounds. The formulæ of these latter, however, together with some other considerations connect it quite closely with certain of the true metals. It occurs in nature as boric acid,  $H_3BO_3$ , the salts of this acid, and as the anhydride or boron trioxide,  $B_2O_3$ . The free element may be prepared in both the crystalline and amorphous varieties as in the case of silicon, and the methods are much the same as for that substance, viz., by the reduction of the oxide with a metal or the chloride with hydrogen.

Weintraub has recently prepared pure fused boron by reducing the trioxide with magnesium to the suboxide,  $B_6O$ , and then heating the latter to  $2000-2500^\circ$  in an electric furnace when it melts and loses all of its oxygen in the form of the trioxide.



The product is black, amorphous and very hard, scratches everything except diamond, but is rather brittle, and breaks with a conchoidal fracture. When cold, it is a very poor conductor of electricity, but at  $400^\circ$  it conducts 2,000,000 times as well as at room temperature. Its conductivity at ordinary temperatures is increased by dissolving in it carbon and other foreign substances; but the temperature coefficient is thereby reduced. Because of its great temperature coefficient, it is well adapted to the making of devices for the measurement of temperature and for the regulation of electrical machinery.

**Boric Acid.**—Boric acid, or boracic acid as it is commonly called, is formed by the action of water on the anhydride, boron trioxide. The limiting acid corresponding by analogy to orthophosphoric acid, is  $H_3BO_3$ , and while this acid exists free, all the

known salts are formed from "condensed" acids, *i.e.*, acids derived from  $H_3BO_3$  by the loss of water. In nature it occurs as somewhat yellowish scales. It is very soluble in hot water but much less so in cold. The aqueous solution reacts faintly acid. The acid may be purified directly by recrystallization, or better by first transforming it into its sodium salt, borax,  $Na_2B_4O_7$ . From this the acid may be obtained again by treatment with sulfuric or any other strong acid.

On being heated, the acid passes first into water and the trioxide, which at a higher temperature melts to a glass-like mass which is capable of dissolving metallic oxides. Upon this property depends the use of boric acid as a flux in hard soldering.

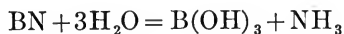
While the anhydride is fairly resistant to heat, the acid itself is volatile with steam. One of the methods for obtaining the acid depends upon this fact. In the volcanic districts, vapors containing boric acid escape from the earth. These are passed into water, condensed, and the boric acid finally becomes concentrated enough to crystallize out at lower temperatures. The acid is even more volatile with alcohol, due to the formation of an ester, and if this vapor is lighted, it burns with a green flame, furnishing a very delicate test for boric acid.

Of the many possible condensed acids, we shall mention only the metaboric, formed from  $H_3BO_3$  by the loss of one mole of water, according to the equation,  $H_3BO_3 = HBO_2 + H_2O$ ; and the tetraboric formed according to the equation  $4H_3BO_3 = H_2B_4O_7 + 5H_2O$ . In any water solution of boric acid, the ions of these different condensed acids exist in equilibrium.

The sodium salt of tetraboric acid,  $Na_2B_4O_7 \cdot 10H_2O$  or borax, occurs in California and in others of the western states and is also manufactured by decomposing the naturally occurring calcium borate,  $Ca_2B_6O_{11} \cdot 5H_2O$ , with sodium carbonate and bicarbonate and recrystallizing. Borax contains either 5 or 10 moles of water of crystallization depending upon the temperature at which it is crystallized. It effloresces in the air and if heated swells up then melts to a glassy substance which dissolves metallic oxides similarly to boric oxide. Some of these solutions have distinctive colors, and are used in blowpipe analysis and in making enamels. Borax and boric acid have fairly strong antiseptic properties and are used in medicine and as preservatives.

**Other Compounds.**—The chlorides and other halogen compounds of boron may be prepared in the same way as the corresponding compounds of silicon and are similar in their properties. Since boron is trivalent their general formula is  $BA_3$ , where A represents the halogen anion. The fluoride when dissolved in water forms the compound,  $BF_4$ , which is very much like hydrofluosilicic acid in its properties.

Boron readily combines with nitrogen to form boron nitride, BN, so unless special precaution is taken to exclude the air during the preparation of the free element, the latter is likely to be contaminated with the nitride. This compound is a white powder which when heated with water reacts to form ammonia and boric acid,



This offers possibilities for the preparation of nitrogen compounds from atmospheric nitrogen although this process, at the present, is not commercially successful.

## CHAPTER XIX

### THE ARGON GROUP

The gaseous substances helium, neon, argon, krypton, xenon and niton form an interesting group of non-metallic elements which is chiefly remarkable for the fact that no compound of a member of this group has ever been prepared. Another interesting point in connection with these substances is that the element helium is certainly one of the products of the spontaneous transmutations which the radio-active element radium undergoes.

The molar weights of these elements may be easily obtained from their gaseous densities but since they will not enter into combination with any substances, their combining weights cannot be directly determined. In fact, strictly speaking, they have no combining weights. But in spite of their inactivity we can arrive at a reasonable conclusion concerning their combining weights through the following line of argument. From what we know of relationships between the molar and combining weights of the gaseous elements, we may be very certain that the combining weight of one of these elements is either identical with its molar weight or is some simple fraction of the latter. The quantity of heat necessary to raise the temperature of one gram mole of a substance  $1^{\circ}$  is called its molar heat. Now the molar heat at constant volume, of the gaseous substances oxygen, nitrogen, hydrogen, carbon monoxide, nitric oxide, and hydrogen chloride, which contain two combining weights of the elements per mole is 20 to 21 joules, while the corresponding values for the compounds, carbon dioxide, nitrous oxide and water vapor, which have three combining weights of the elements per mole lie between 28 joules for water and 33 joules for nitrous oxide. From this it would seem that the molar heat of a substance amounts to roughly 10 to 11 joules per combining weight per mole. The molar heat of an element whose molar

weight was identical with its combining weight should then be somewhere in the neighborhood of 11 joules. This has been confirmed in the case of mercury. Both the combining weight and the molar weight of this element have been determined and found to be 200, so there is only one combining weight per mole. Its molar heat is 13. The molar heat of the members of the argon group is 12 to 13. From this we may safely conclude that in the case of each of these substances the combining weight is identical with the molar weight.

**Helium.**—The element helium has a combining and molar weight of 3.99. It is found in the air, of which it constitutes .000056 per cent. by weight or .00040 per cent. by volume. It is also found in the gases of many mineral springs and is present in relatively large quantities in natural gas. The gas at Dexter, Kansas, contains as high as 1.84 per cent. of helium. Outside of natural gas, the principal source of helium is the rare minerals containing the radio-active elements radium, uranium, thorium, etc., from which it may be obtained by simply heating the mineral in a vacuum or by dissolving it in dilute sulphuric acid or fused potassium acid sulfate. The helium is simply enclosed in the mineral and is not in combination. From the fact that it occurs in those minerals which contain radium, etc., it is probable that it is formed in the mineral by the transformation of the radio-active elements. The same source is indicated for the helium of natural gas by the fact that it contains radium emanation.

Helium was the last gas to be liquefied. This was done in July, 1908, by Kammerlingh Onnes. It is a clear, colorless liquid boiling at  $-268.5^{\circ}$  C. or  $4.5^{\circ}$  above absolute zero. Since its critical temperature is  $-268.0^{\circ}$  C. or  $+5^{\circ}$  A. it is a very difficult substance to liquefy. When the pressure under which it boiled was reduced to 1 cm. its boiling-point was lowered to  $3^{\circ}$  above absolute zero. This is probably about the lowest temperature which we will be able to reach unless some more easily volatile liquid than helium is discovered.

Helium under diminished pressure, glows brilliantly upon the passage of an electric discharge. Upon examining the light with a spectroscope the spectrum is found to consist of a number of bright lines, one in the yellow being especially strong (see frontis-

piece). Many years before helium was discovered on the earth this line was observed in the spectrum of the sun and ascribed to a then unknown element which was called helium from the Greek name for the sun "helios."

**Neon.**—Neon has a combining and molar weight of 20.2. It is found in the air to the extent of .00085 per cent. by weight or .00123 per cent. by volume. It occurs along with helium in the gases of certain mineral springs and in natural gas. The critical point of neon is below  $-210^{\circ}$  and its boiling-point lies somewhere between  $-243^{\circ}$  and  $-235^{\circ}$ . It is easily liquefied in a bulb surrounded by liquid hydrogen which boils at  $-253^{\circ}$ , and is separated from helium in this way. Neither helium nor neon is absorbed by cocoanut charcoal to any great extent, and a mixture of the two gases may be easily obtained from natural gas by absorbing the other gases in cocoanut charcoal cooled with liquid air.

**Argon.**—The combining and molar weights of argon, A, are 39.9. It occurs in nature in rather large quantities being present in the air to the extent of about 1.3 per cent. by weight or .937 per cent. by volume. It boils at  $-186^{\circ}$  and freezes at  $-189^{\circ}$ . Its critical temperature is  $-117^{\circ}$ . Argon was the first member of this group to be discovered, being found in 1894 in atmospheric nitrogen by Lord Rayleigh and Professor Ramsay who were seeking an explanation for the fact that atmospheric nitrogen was more dense than that from chemical sources. It is separated from nitrogen by combining the latter with metallic lithium, calcium, or magnesium at a high temperature, nitrides being formed. Its spectrum is shown in the frontispiece.

**Krypton and Xenon.**—These gases occur in the air, krypton to the extent of .028 per cent. and xenon to .005 per cent. They are obtained mixed with argon, helium, and neon by the removal of the nitrogen, etc., as indicated above. They are separated in the pure state by the fractional distillation of the crude argon. Krypton has a combining and molar weight of 82.92 and boils at  $-152^{\circ}$ . Its critical temperature is  $-73^{\circ}$ . Xenon has a molar and combining weight of 130.2, boils at  $-109^{\circ}$  and has a critical temperature of  $+15^{\circ}$ .

**Niton or Radium Emanation.**—Radium and its compounds very gradually give off an inert gas of the argon group which is

called niton or radium emanation. Although this is chemically inactive, it is highly radio-active, and changes into helium and other products at such a rate that one-half of it disappears every 3.8 days. Since it is formed so slowly from radium and decomposes so quickly, there is never very much of it available for investigation at any one time, and Sir William Ramsay who has studied it most fully has displayed great skill in its investigation. It has been shown in spite of the fact that it is formed from one element and changes into another, that it is fully entitled to be considered a distinct element. It has its own characteristic spectrum and set of other properties. Its molar and combining weights have been determined by Ramsay by weighing less than .0001 c.c. of the gas on a balance sensitive to less than 1/250,000 mgrm. These weights are doubtless identical and are 222.4. It boils at  $-62^{\circ}$  and freezes at  $-71^{\circ}$ . Niton is so highly radio-active that it shines in the dark, and gives out, in comparison with its mass, enormous quantities of heat. When brought in contact with chemical compounds, it very frequently decomposes them, but will not itself combine with anything. Niton is present in extremely minute quantities in air, soil, rocks, ground water, and the gases that issue from the earth. The quantity present in rocks is proportional to their radium content and furnishes the easiest method of determining the amount of radium in a rock. The rock is dissolved, the niton boiled off and passed into an electroscope; the quantity of niton and therefore of radium is estimated from the rate at which the gold leaves of the electroscope collapse.

#### INERT GASES IN ONE CUBIC METER OF AIR

Helium.....	4.	c.c.
Neon.....	12.3	c.c.
Argon.....	9370.	c.c.
Krypton.....	50.	c.c.
Xenon.....	128.	c.c.
Niton.....	Trace.	

## CHAPTER XX

### THE METALLIC ELEMENTS

**General.**—In the classification of the elements it has been customary for a long time to divide them into the metals and the non-metals. The latter we have been considering in the earlier part of this book, and it now remains to discuss the chemistry of the metals. The division of the elements into these two groups is very convenient, but is entirely arbitrary as is shown by the fact that certain elements have properties in common with each group and cannot be definitively located in either. In most cases, however, there is no difficulty in deciding to which class an element belongs because the metals in general have such strongly marked properties that they may be quickly recognized and if an element does not show these properties it is of course a non-metal.

**Characteristic Physical Properties of Metals.**—Metals have a metallic luster, are conductors of electricity and of heat and are generally malleable and tenacious. The **metallic luster** is shown by all metals in the massive state. It is due to the fact that they reflect nearly all the light which falls upon them: because of this, most of them are white in color; but gold and copper absorb a part of the light and hence show their well-known colors. When finely divided, most of the metals are black although some when in the very finest state of division show a remarkable variety of colors. (See colloidal silver, p. 470.) While all metals have metallic luster, this property is not confined to them, because many compounds notably the sulfides have it; and in addition the non-metallic element tellurium shows it distinctly.

As **conductors of electricity**, the metals are much superior to the electrolytes. The current has no direct effect upon them other than to raise the temperature, while it will be recalled that electrolytes are always decomposed by the current. Silver and copper are the best conductors of the metals and are about eight



times as good as iron or sixty times as good as mercury. While all metals conduct electricity without decomposition, a few of the non-metals also show this property, for example, carbon in the amorphous state, or as graphite, amorphous boron, tellurium and selenium under certain conditions.

The metals are better **conductors** of **heat** than the non-metals, but in this respect there is not as much difference between the two groups as in the case of the conduction of electricity.

Most, but not all of the metals, are **malleable** and may be rolled or beaten into thin plates. Gold excels all the others in this respect, and may be beaten in leaves not more than .0001 m.m. in thickness. But this property is not so characteristic of the metals as the preceding, because most of the metals lose their malleability at some temperature short of their melting-points, while arsenic, antimony, and bismuth are brittle over all temperatures at which they are solids.

Most metals are very **tenacious** and will resist a considerable force tending to pull a given piece apart. This property together with the malleability mentioned above renders them **ductile**, so that they may be drawn into wire. Steel is the most tenacious of the metals, and gold the most ductile; many of the metals such as arsenic, antimony, bismuth, are not very tenacious and because of their brittleness are not ductile.

When metals dissolve in most solvents they lose all of their metallic characteristics, and in general form salts, but they may dissolve in one another when fused together and retain the characteristic properties of metals. The same is true of solutions of the alkaline metals in liquid anhydrous ammonia. The solutions of metals in one another are called **alloys**. When solidification takes place, the component metals may crystallize out side by side in the pure state, or they may separate as a homogeneous solid solution, or they may form crystals containing the components of the system in definite, constant proportion, that is as a compound, or finally there may be presented various combinations of these possibilities so that the subject of alloys is quite complex. As the term alloy is now used, one or more of the constituents may be a non-metal, but the whole must present the general metallic properties. Alloys which contain mercury are called amalgams. Some of these are very important.

**Characteristic Chemical Properties of Metals.**—The most noticeable chemical property of the metals is that they form simple cations, but this property is not confined exclusively to them; because the non-metals, hydrogen and tellurium also form these ions. Closely connected with the tendency of the metals to form cations is the fact that their hydroxides are generally bases while those of the non-metals are almost invariably acids; but some of the hydroxides of the metals are very weak bases, and a few act both as bases and acids. From the above facts, it may be seen that there is no sharp distinction to be drawn between metals and non-metals, so the division is purely arbitrary; but is nevertheless convenient and practicable because in the great majority of cases no hesitation is felt in making the classification.

**The Ores of the Metals and Metallurgy.**—An ore is a mineral from which a metal may be profitably extracted on a commercial scale. The science of extracting metals from their ores is called metallurgy, and is an important branch of applied chemistry. Some of the metals which are easily reduced from their compounds and which are resistant to the action of air and of water are found free or native, but most of them are obtained from naturally occurring oxides, carbonates, silicates, sulfides, or more rarely from sulfates and chlorides. Something of the ores and their metallurgy will be given in connection with the discussion of the individual metals.

**Classification of the Metals.**—A study of the properties of the metals soon shows that they may be divided into groups of more or less closely related elements much as was done with certain of the non-metals. The relationship between these elements is rather tangled, however, and some of them have properties which would cause them to be placed in each of several groups and any arrangement which we make of them is more or less arbitrary. There is, however, a natural system for the classification of the elements which is called the periodic system and which includes both the metals and the non-metals. This system is based upon the observation that if the elements be arranged in the order of their combining weights, similar elements recur at regular intervals; and if the series be broken up into periods such that each period begins with a member of a definite family, the second position in each period will be filled by a member of a closely

related group of elements. The same is true for the third and following positions in the series. This may be illustrated as follows; arrange the elements in the order of their combining weights and we have,

Position,	1,	2,	3,	4,	5,	6,	7,	8
Period No. 1.	He.	Li.	Gl.	B.	C.	N.	O.	F.
Period No. 2.	Ne.	Na.	Mg.	Al.	Si.	P.	S.	Cl.
Period No. 3.	A.	K.	Ca.	Sc.	Ti.	V.	Cr.	Mn.

Choosing the members of the helium family as the elements which shall begin our periods, we find that the elements listed here fall into three periods of eight members each, and that the corresponding positions in each period are occupied by analogous elements. We can appreciate this especially for the last four members of the first two periods, since we are familiar enough with the properties of carbon and silicon to see their close relationship and similarly for nitrogen and phosphorus, oxygen and sulfur, fluorine and chlorine. That this same sort of relationship is continued over into the other periods and holds for the remaining positions in these periods, will be evident as we become more familiar with the properties of the elements. For example, sodium, potassium, etc., which occupy the second positions in the periods, form a part of a group of similar and very closely related metals as we shall soon see. In fact the relationship is fully as close as that between the halogens.

If the elements arranged in series in the order of their combining weights be broken up into periods in the way given above and these periods be placed vertically under one another, we obtain a table of the periodic classification or system of the elements. Such a table is given below. It is somewhat of a modification of one prepared by the Russian chemist, Mendelejeff in 1869, and very similar to a table published in 1870 by Lothar Meyer, a German chemist, who developed the idea independently of Mendelejeff.

An inspection of this table will show that chemically similar elements are found in vertical columns except in the case of the very last group in which the similar elements are found side by side.

In preparing this table, the principle of arrangement in the

## PERIODIC SYSTEM.

Type Compound	Group 0	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
Valence	0	+1	+2	+3	--4, +4	--3, +5	-2, +6	-1, +7	EO <sub>4</sub>
1	He, 4	Li, 7	Gl, 9.1	B, 11	C, 12	N, 14	O, 16	F, 19	.....
2	Ne, 20.2	Na, 23	Mg, 24.3	Al, 27.1	Si, 28.3	P, 31.0	S, 32.1	Cl, 35.5	.....
3	A, 39.9	K, 39.1	Ca, 40.1	Sc, 44.1	Ti, 48.1	V, 51.0	Cr, 52.0	Mn, 54.9	Fe, 55.8; Ni, 58.7; Co, 59
4	.....	Cu, 63.6	Zn, 65.4	Ga, 69.9	Ge, 72.5	As, 75	Se, 79.2	Br, 79.9	.....
5	Kr, 82.9	Rb, 85.4	Sr, 87.6	Y, 89	Zr, 90.6	Cb, 93.5	Mo, 96.0	.....	Ru, 101.7; Rh, 102.9; Pd, 103.7
6	.....	Ag, 107.9	Cd, 112.4	In, 114.8	Su, 119	Sb, 120.2	Te, 127.5	I, 126.9	.....
7	X, 130.2	Cs, 132.8	Ba, 137.4	La, 139.0	Ce, 140.3	Nd, 144.3	Sa, 150.4	Eu, 152	.....
8	.....	.....	.....	.....	.....	.....	.....	.....	.....
9	.....	.....	.....	Yb, 172	.....	Ta, 181.5	W, 184	.....	Os, 190.9; Ir, 193.1; Pt, 195.2
10	.....	Au, 197.2	Hg, 200.6	Tl, 204.0	Pb, 207.1	Bi, 208	.....	.....	.....
11	Nt, 222.4	.....	Ra, 226.4	.....	Th, 232.4	.....	U, 238.5	.....	.....

PERIODS

order of combining weights has been violated in two cases. Argon with a combining weight of 39.9 has been placed before potassium with a combining weight of 39.1 and tellurium is put before iodine although it has the larger combining weight. The reason for the first change is that potassium does not belong in the group of inert gases, but in with the other alkali metals in which group the argon would be entirely out of place while it goes very well with the other gases of the helium group. Tellurium and iodine are interchanged because the tellurium evidently belongs to the sulfur group and iodine to the halogen. Many researches have been undertaken to see if there was not some error in the determination of the combining weight of either tellurium or iodine but they have led to the conclusion that tellurium actually has a higher combining weight than iodine.

Another defect in the table is that there is no good place for hydrogen. Some have placed it at the head of the halogen family and others as the first member of the sodium group. But neither these nor any other suggestions which have been made seem to fit the case and the question of the proper location of hydrogen in the periodic system remains an open one.

There are other imperfections in the table which will become evident as we go along, but on the whole it furnishes a natural and very useful system for the classification of the elements, and it seems not unlikely that its apparent irregularities and defects will finally be found to have a great significance and to be very important.

Although each of the first eight vertical columns in the table is made up of very similar elements, a knowledge of their properties soon shows that each group is composed of two sub-groups, and that the members of each sub-group are found in the alternate rows or periods. This is brought out in the table by setting the rows or periods alternately to the right and left of the group. As a rule the members of each sub-group are more nearly like one another than they are like the members of the other sub-group within the family. The first member of each group usually has properties in common with both of the sub-groups and forms a connecting link between them.

Group O contains the members of the Argon group, the inert gases which seem to have no power to enter into combination,

and therefore may be considered to have a valence of zero. Neon is the only member of the second sub-group which is known.

Group I contains the monovalent alkali metals in one sub-group and the monovalent heavy metals, silver, copper and gold, in the other. The members of each sub-group are much alike, but while the two sub-groups have some properties in common, in general they differ markedly. The alkali metals are exceedingly active while copper, silver and gold are among the most inactive of the metals.

Group II contains divalent metals and again is divided into two well-marked sub-groups.

Group III is headed by the trivalent non-metallic element boron, but the rest of the members of the group are trivalent metals.

Group IV is composed of elements tetravalent with respect both to hydrogen and to oxygen. The first two elements are decidedly non-metallic in character, while the remainder are metals.

The elements of Group V are trivalent with respect to hydrogen, and pentavalent toward oxygen. Nitrogen and phosphorus are clearly non-metals. Arsenic is more of a non-metal than a metal, while vanadium although having properties in common with both classes is distinctly metallic in character.

Group VI contains elements divalent toward hydrogen and hexavalent toward oxygen. The members of the sub-group headed by chromium are distinctly metallic in character, while those of the other sub-group are non-metallic.

The elements of Group VII are monovalent toward hydrogen and heptavalent toward oxygen. They are all non-metallic with the exception of manganese.

Group VIII is a rather exceptional group in that it is composed of three sets of elements each set having three members whose combining weights, specific gravities and general properties are very similar. In this group, the elements which are most alike are found side by side, although there is also a distinct tendency toward similarity in the vertical columns.

It will be noticed that these sets of three elements come at the end of the third, fifth, and ninth series or periods of the elements.

A blank space in the table indicates that no element is known

whose combining weight and properties would give it this position. It is very probable that most of these elements will be discovered in the course of time. In the meantime it is possible to make a fairly definite prediction as to the properties of an element from those of the elements surrounding it in the table. This was done by Mendelejeff for the elements scandium, gallium, and germanium which were unknown at the time of the

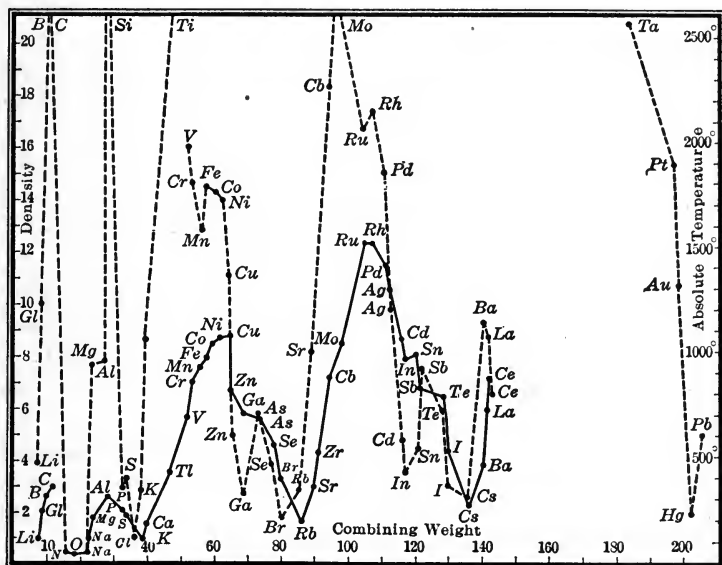


FIG. 36

publication of the table. Some idea of the accuracy of the predictions can be obtained by a comparison of the predicted properties of germanium with those which it was found to have. Since the then unknown element was the second member of the silicon sub-group, Mendelejeff called it eka-silicon. When it was discovered, it was named germanium so we will compare the predicted properties of eka-silicon with those found for germanium.

Eka-silicon, predicted	Germanium found
Comb. weight = 72.5	Comb. weight = 72.5
Specific gravity = 5.5	Specific gravity = 5.47
Oxide, $\text{EsO}_2$ . Sp. gr. = 4.7	Oxide, $\text{GeO}_2$ . Sp. gr. = 4.7
Chloride, $\text{EsCl}_4$ , liquid, boiling at a little below $100^\circ$ , sp. gr. = 1.9	Chloride, $\text{GeCl}_4$ , liquid, boils at $86^\circ$ , sp. gr. = 1.88
Ethide, $\text{Es}(\text{C}_2\text{H}_5)_4$ , liquid, boiling at $160^\circ$ , sp. gr. = 0.96	Ethide, $\text{Ge}(\text{C}_2\text{H}_5)_4$ , liquid boils at $160^\circ$ , sp. gr. a little less than water
Fluoride, $\text{EsF}_4$ , not gaseous.	Fluoride, $\text{GeF}_4 \cdot 3\text{H}_2\text{O}$ , white solid.

Not only are the chemical properties of the elements periodic functions of their combining weights, but the same is also probably true of all measurable physical properties with the exception of the specific heat which is inversely proportional to the combining weight for all solid elements of a combining weight higher than 35. This is very clearly shown by Fig. 36 which represents the relation between the density of the elements in the liquid or solid state and the combining weight and also that between the absolute temperature of fusion and the combining weight, the former being shown by the heavy lines and the latter by the dotted lines. Most other physical properties yield similar curves and indicate clearly that the properties are periodic functions of the combining weights.

It would be very interesting to know the proportions in which the various elements are present in the earth as a whole, but this is manifestly impossible since we have no way of getting at the composition of its interior. We can, however, get the analysis of the air, the ocean, and the rocks composing the outer 10 miles of the earth's crust, the lithosphere as it is called, and the following table prepared by Clark of the United States Geological Survey gives the results of some thousands of analyses.

All the abundant elements have a combining weight below 56 and the heavy metals appear to be present in very small quantities. The mean density of the earth is about twice that of the lithosphere and hence it has been supposed that the heavier elements have collected in the interior. Others ascribe the high density to the compression due to the weight of the overlying strata. This much is certain, however, that the elements cannot all be present in equal quantities by weight since their average density is greater than the mean density of the earth.



AVERAGE COMPOSITION OF LITHOSPHERE, OCEAN, AND  
ATMOSPHERE

	Lithosphere (93 per cent.)	Ocean (7 per cent.)	Average In- cluding nitro- gen
Oxygen.....	47.17	85.79	49.85
Silicon.....	28.00	.....	26.03
Aluminum.....	7.84	.....	7.28
Iron.....	4.44	.....	4.12
Calcium.....	3.42	.05	3.18
Magnesium.....	2.27	.14	2.11
Sodium.....	2.43	1.14	2.33
Potassium.....	2.49	.04	2.33
Hydrogen.....	.23	10.67	.97
Titanium.....	.44	.....	.41
Carbon.....	.19	.002	.19
Chlorine.....	.06	2.07	.20
Bromine.....	.....	.008	.....
Phosphorus.....	.11	.....	.10
Sulfur.....	.11	.09	.10
Barium.....	.09	.....	.09
Manganese.....	.08	.....	.08
Strontium.....	.03	.....	.03
Nitrogen.....	.....	.....	.03
Fluorine.....	.10	.....	.10
All other elements.....	.50	.....	.47
	100.00	100.00	100.00

## CHAPTER XXI

### THE ALKALI METALS



Group I of the periodic system is composed of the alkali metals, lithium, sodium, potassium, rubidium and cesium, and a distinct sub-group consisting of copper, silver, and gold. The alkali metals resemble one another closely, and hence may very properly be considered together. In many respects their properties are typical of the metals and a discussion of this class of elements may profitably begin with them. Copper, silver, and gold, however, differ so markedly from the alkali metals and have so many properties similar to those of metals belonging to higher groups, that it seems wise to leave their discussion to a later point.

Some of the more prominent properties of the alkali metals are given below in tabular form for sake of comparison.

Element	Combin. weight	Density	Melting-point	Boiling- point
Lithium.....	6.94	.59	186° C.	1400° C.
Sodium.....	23.00	.97	97.6°	878°
Potassium.....	39.10	.87	62.5°	758°
Rubidium.....	85.45	1.52	38.5°	696°
Cesium.....	132.81	2.40	26.5°	670°

It will be noticed that, as the combining weight increases, the melting- and boiling-points decrease and the density increases. Sodium, however, is somewhat irregular in its density, a fact which may be connected with the position of sodium in the periodic system as the first member of the copper sub-group since these metals all have high densities. This individuality of sodium seems to extend to its chemical properties since potassium, rubidium, and cesium resemble one another much more closely than they do sodium.

The alkali metals are chemically the most active of this class of elements and increase in activity as their combining weight increases. They will all decompose water, lithium very rapidly and cesium with the greatest violence. In each case, hydrogen and the hydroxide of the metal is formed. These hydroxides are soluble and are strong bases, and it is this fact that gives to the sub-group the name, the alkali metals.

None of these elements is ever found free in nature, a fact which might be anticipated from their great chemical activity. These elements differ markedly in their relative abundance in the earth's crust, the outer 10 miles of the earth, sodium being present to the extent of 2.43 per cent., potassium 2.49 per cent., lithium .005 per cent., rubidium and cesium in extremely small quantities. It will be seen from this that sodium and potassium do not differ much in their abundance, but owing to the fact that enormous quantities of sodium chloride have been deposited in the salt beds which are found widely distributed over the earth's surface, while only two such notable deposits of potassium salts are known, the sodium compounds are much more available and consequently much cheaper than the compounds of potassium. Since the sodium salts are fully as good as the potassium for all purposes which do not demand the presence of potassium ion, much larger quantities of the sodium compounds are manufactured and used than of potassium compounds. For this reason, the detailed discussion of the alkali metals will begin with that of sodium.

### SODIUM

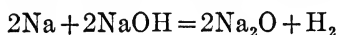
**History.**—Sodium compounds have, of course, been known from prehistoric times, but were not distinguished from the corresponding potassium compounds until the eighteenth century when Duhamel and a little later Marggraf clearly differentiated them. The element itself was first prepared by Sir Humphrey Davy in 1807, by the electrolysis of fused sodium hydroxide. This created a decided sensation, because up to that time sodium hydroxide had been regarded as an element.

**Occurrence.**—Enormous quantities of sodium compounds, chiefly the chloride, are found in sea water, and in places where

some of the sea water has been cut off from the rest of the ocean and evaporated, great beds of salt have been formed. It has been estimated that the ocean contains about 4,800,000 cubic miles of saline substances, and the salt beds about 300,000 cubic miles of salt. So it may be easily seen that the supply of this important substance is practically without limit.

Other important sodium compounds occur in nature in considerable quantities. These are the carbonate  $\text{Na}_2\text{CO}_3$  and the bicarbonate,  $\text{NaHCO}_3$ , the nitrate,  $\text{NaNO}_3$ , cryolite,  $\text{Na}_3\text{AlF}_6$ , borax,  $\text{Na}_2\text{B}_4\text{O}_7$ , and many of the silicates.

**Preparation.**—As mentioned above, metallic sodium was first prepared by Davy in 1807 by the electrolysis of fused sodium hydroxide. At that time, voltaic cells were the only source of electricity available for such purposes, and consequently the process was exceedingly expensive. For a long time after the discovery, sodium was prepared by the reduction of the carbonate or hydroxide by carbon at a high temperature, the sodium being distilled off and condensed. At the present day, electrical energy can be cheaply obtained, and sodium is prepared as Davy first made it. Sodium hydroxide is melted in an iron vessel and electrolyzed between iron or nickel electrodes. Sodium and hydrogen are liberated at the cathode and oxygen at the anode; the metallic sodium rises to the top of the bath and collects under an iron bell-like vessel from which it is dipped from time to time. The sodium hydroxide is replaced as it is used up, thus making the process continuous. It is very essential that the temperature of the bath be kept as near the melting-point of sodium hydroxide,  $300^\circ\text{C}$ ., as possible, since sodium reacts with the hydroxide as shown in the following equation:



This reaction becomes so rapid at  $325^\circ$  that practically no sodium is obtained, the metal being used up as fast as it is formed, but at  $300^\circ$  the yield is good. Thousands of pounds of sodium are now being made yearly by this process at Niagara Falls.

Many attempts have been made to prepare sodium by the electrolysis of fused sodium chloride, but the apparatus used has always been so short lived that the processes have not been successful.

**Properties.**—Sodium is a soft metal with a brilliant silvery white luster which is almost instantly lost upon exposure to the air owing to the formation of a film of oxide or hydroxide. By melting the metal and allowing it to solidify partially and then pouring off the liquid portion, it may be obtained in well formed octahedra. It melts at  $97.6^{\circ}$  and boils at  $878^{\circ}$ . The vapor has a blue color and is exceedingly active chemically. This makes it difficult to obtain the molar weight of sodium, but the results indicate that its molar weight is 23, the same as its combining weight. Sodium has the remarkable property of dissolving in liquefied anhydrous ammonia without forming a chemical compound. The solution is blue and conducts electricity like a metal, without decomposition. Upon evaporation, metallic sodium is left behind. The metal is also soluble in mercury, forming sodium amalgam. When this contains more than a small amount of sodium, it is solid and contains one or more compounds of the two elements. This amalgam is less active chemically than the metal itself, and finds extensive application, because for many purposes metallic sodium is too vigorous.

The principal chemical property of sodium is its great tendency to pass over into the ionic state or into some condition which is very closely related to this state such as a solid salt. In doing this, the sodium takes up positive electricity and hence is a strong reducing agent; consequently, it is used in the preparation of some of the metals and in making certain complex carbon compounds for use as dyes or medicines. The heat of formation of the sodium ion from the metal is 240 KJ.

When metallic sodium comes in contact with water, a very vigorous chemical reaction takes place with the formation of sodium hydroxide and hydrogen. If more than a very small piece of sodium is used, a violent explosion is liable to occur. When a small piece of sodium is thrown on water, it flies around on the surface of the liquid evolving hydrogen until the metal has all been changed into the hydroxide which remains for a moment, as a clear ball of the molten compound floating on the water. This is very hot, and the rush of steam which it produces from the water supports it and keeps it out of actual contact with the latter until it cools somewhat. When the sodium hydroxide actually touches the water it dissolves and the heat

generated produces a little explosion which spatters a portion of the hydroxide. Ordinarily, the hydrogen evolved does not become sufficiently heated to take fire, but if the motion of the globule of sodium be limited by thickening the water with starch, or placing a piece of filter paper on the surface of the water, the hydrogen catches fire and burns with a yellow flame, the color being due to the sodium.

Moist air acts rapidly upon sodium, but dry air at ordinary temperatures works so very slowly and the coating of oxide is such a good protector for the remaining metal, that large quantities of the metal are preserved in soldered tin cans or closely stoppered bottles. Small quantities of the metal are best kept under a petroleum oil which does not contain oxygen and is without action on the metal.

When heated in the air sodium burns with a yellow flame forming the oxide and peroxide.

The larger part of the sodium manufactured is used in the preparation of the peroxide and of the cyanide. The latter is used in the extraction of gold.

The combining weight of sodium is 23.00.

**Sodium Hydride.**—When sodium is heated to  $340^{\circ}$  in an atmosphere of hydrogen a crystalline compound, NaH, is formed. This decomposes at a high temperature and is insoluble in ammonia and organic solvents, but dissolves in water with the formation of sodium hydroxide and twice as much hydrogen as an equivalent quantity of the metal. Because of the great amount of hydrogen liberated per unit weight of the substance, it has been proposed to use it as a source of hydrogen for filling balloons.

In marked distinctions from most of the hydrogen compounds of the non-metals, sodium hydride has no acid properties.

**Sodium Chloride.**—Sodium chloride or common salt, NaCl, may be prepared by the interaction of moist chlorine and metallic sodium or by neutralizing sodium hydroxide with hydrochloric acid and evaporating.<sup>1</sup>

However, sodium chloride is never manufactured as indicated above, because of the fact that it occurs in nature in large quanti-

<sup>1</sup> It is remarkable that dry chlorine will not act on sodium even at the melting-point of the latter.

ties in easily worked beds of salt. From these the salt may be taken by ordinary mining operations when it is known as rock salt; or it may be obtained by boring down into the salt bed and running water down into the boring, allowing it to stand until it is saturated with salt, then forcing or pumping out the brine and evaporating it to secure the salt. This is usually done in long shallow iron pans heated from below by fires. In the more modern plants, the evaporation is accomplished in vacuum pans since this is more economical, making as it does, a saving of 50 per cent. on fuel and of 90 per cent. on labor. Large quantities of salt are obtained by the evaporation of brine from salt springs or from the ocean. In case the brine is dilute and fuel is dear, the evaporation is partially carried out by allowing the brine to trickle over a wall built of twigs to secure a large surface of exposure. Under these conditions the air takes up a good deal of water from the brine. Water from the ocean is usually concentrated by exposure to the heat of the sun in shallow basins constructed near the shore. The salt so obtained is called solar salt. The principle impurities contained in salt beds and brines are calcium sulfate and chloride, magnesium chloride and the bromides.

To remove these, the salt must be purified by crystallization. This cannot be done by preparing a hot saturated solution and allowing it to cool, since the salt is nearly as soluble in cold as in hot water, the solubility being 35.74 parts of salt to 100 parts of water at 0°, and 39.65 parts at 107.7° the boiling-point of the saturated solution. The salt is purified by boiling the solution which quickly causes the greater part of the calcium sulfate to precipitate, and then concentrating until most of the sodium chloride has crystallized out; but stopping the operation before the other impurities have begun to separate. Magnesium or calcium chlorides are particularly objectionable, since they cause the salt to deliquesce under ordinary atmospheric conditions. Pure sodium chloride will not deliquesce except in the very dampest weather of the summer.

The very pure sodium chloride required for chemical purposes is obtained by dissolving the salt in water, and saturating the solution with hydrogen chloride which precipitates out the greater part of the salt. The explanation of this will be given later.

Sodium chloride crystallizes in cubes which although they do not contain any water of crystallization usually have some enclosed water which causes the crystals to explode when the salt is heated. This phenomenon is known as decrepitation. The crystals melt at  $800^{\circ}$  and have a density of 2.16 at  $0^{\circ}$ . A saturated solution of salt when cooled to  $-10^{\circ}$  deposits crystals having the composition  $\text{NaCl}\cdot 2\text{H}_2\text{O}$ . These are unstable and decompose easily at temperatures slightly above that of their formation, but nevertheless may be obtained by the rapid spontaneous evaporation of a salt solution on a glass plate at  $+15^{\circ}$ . This being another instance of the phenomenon described by the law of successive reactions.

Sodium chloride as such has many familiar uses as a condiment, preservative, etc.; in addition, it is the source of practically all other sodium compounds and of the greater part of the chlorine and hydrogen chloride of commerce. For these reasons it is a very important substance. During the year 1910 the United States produced 4,250,000 tons of salt which was about one-fourth of the world's production.

**Sodium Bromide and Iodide.**—As would be expected from the close relationship between the members of the halogen group, sodium bromide and iodide are very similar to the chloride. Like the chloride they crystallize under certain conditions with two moles of water of crystallization and under other conditions as the anhydrous salts. These salts are isomorphous with the corresponding chlorides. The salt,  $\text{NaBr}\cdot 2\text{H}_2\text{O}$ , is transformed at  $50^{\circ}$  into a saturated solution of sodium bromide and the solid anhydrous salt. Under these conditions the four phases  $\text{NaBr}$ ,  $2\text{H}_2\text{O}$ ,  $\text{NaBr}$ , saturated solution and vapor will exist side by side, and since the system is made up of two components, sodium bromide and water, this point is a quadruple point and the temperature will not change until some one phase has disappeared.

The iodide,  $\text{NaI}\cdot 2\text{H}_2\text{O}$ , undergoes a similar change at  $67^{\circ}$ .

The solubility of the bromide is greater than that of the chloride and is in turn exceeded by that of the iodide, so it may be seen that the solubility increases as the combining weight of the halogen increases.

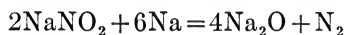
Both salts are used in medicine and the bromide in photography.

**Sodium Fluoride.**—Sodium fluoride,  $\text{NaF}$ , is much like the



chloride except that no compound corresponding to  $\text{NaCl}\cdot 2\text{H}_2\text{O}$  is known and that the salt combines with hydrofluoric acid to form the compound  $\text{NaFHF}$  for which there is no known corresponding chlorine compound. Sodium fluoride is much less soluble than the other sodium halides, since 100 parts of water will only dissolve 4 parts of the salt. It is used to a limited extent in medicine and as a preservative particularly in the distilleries and in the manufacture of yeast.

**Sodium Oxides.**—Sodium monoxide,  $\text{Na}_2\text{O}$ , may be prepared by heating metallic sodium with sodium nitrate or nitrite in the absence of air. The equation for the latter reaction is as follows:



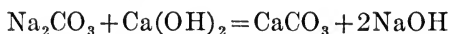
It is a gray substance which reacts violently with water for the formation of the hydroxide  $\text{NaOH}$ .

When heated in an excess of air to  $300^\circ$ , sodium is oxidized to sodium peroxide,  $\text{Na}_2\text{O}_2$ . To carry out the process, the sodium in thin pieces is placed in aluminum trays which are slowly passed in one direction through an iron tube heated to about  $300^\circ$  while a current of dry air, purified from carbon dioxide, is passed in the opposite direction. This brings the air from which the oxygen has largely been removed in contact with the fresh sodium and so moderates the reaction, while the nearly oxidized substance comes in contact with the fresh air and is fully oxidized.

We have here one reacting substance moving in one direction and the other in the opposite. This arrangement is often adopted in chemical work and is known as "the principle of counter currents." The sodium peroxide so prepared is about 93 per cent. pure and finds extensive use as an oxidizing agent and as a source of oxygen, since it reacts with water for the formation of sodium hydroxide and hydrogen peroxide which then breaks down into water and oxygen. Fused sodium peroxide, known as oxone, is put on the market for this purpose. A small quantity of a copper compound is added to the peroxide to catalytically decompose the hydrogen peroxide.

When sodium peroxide is heated with carbon to about  $300$  to  $400^\circ$ , sodium carbonate and metallic sodium are formed. This is convenient for experimental purposes but of course cannot be used industrially.

**Sodium Hydroxide.**—Sodium hydroxide may be prepared by the action of the metal upon water, and is so prepared when a very pure article is required. The hydroxide obtained by this method is of course too expensive for most purposes, and the bulk of the substance must be prepared in other ways. It may be made in a purely chemical way by adding calcium hydroxide in suspension in water, milk of lime as it is called, to an 8 to 10 per cent. solution of sodium carbonate and boiling for a time. Difficultly soluble calcium carbonate is precipitated and a solution of sodium hydroxide is left:



Sodium hydroxide is also prepared by the electrolysis of a solution of sodium chloride using mercury for the cathode. Under these conditions, sodium amalgam is formed which is removed from the electrolytic chamber and allowed to react with water when hydrogen and sodium hydroxide will be formed. The mercury freed from the sodium is returned to the electrolyzing chamber and retransformed into the amalgam. At the graphite anodes, chlorine is evolved. This process is carried out at Niagara Falls and other places where power is very cheap.

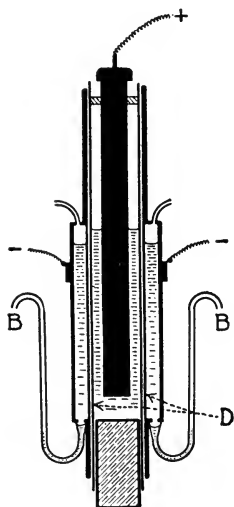


FIG. 37.

Another successful electrolytic process is that using what is known as the Townsend cell. This is shown in Fig. 37. The anode is graphite; D and D are asbestos diaphragms painted with a mixture of iron oxide, asbestos fiber, and colloidal ferric

hydroxide. The cathodes are two in number, and are made of perforated plates of iron directly in contact with the diaphragms. The anode chamber is filled with brine which percolates slowly through the diaphragms and sinks to the bottom of the cathode chambers, the remaining space in these chambers being filled with kerosene. From these, it passes off through the goose necks, B. When the current is passed through the cell, chlorine

is given off at the anode, and hydrogen and sodium hydroxide appear at the cathode. Since hydroxyl is an anion, it tends to travel toward the anode, but the brine is made to percolate through the diaphragms rapidly enough to sweep back the hydroxyl and hence prevent what would otherwise be a serious loss. The cathode solution contains both sodium hydroxide and chloride. As this is evaporated, the chloride becomes practically insoluble, and may be readily separated from the hydroxide.

Sodium hydroxide is a deliquescent white substance which is exceedingly soluble in water. Its solubility increases rapidly with the temperature, so rapidly in fact, that there is no solution which is saturated at its boiling-point. It is, of course, possible to saturate water with sodium hydroxide at  $100^{\circ}$ , but when this is done the boiling-point of the solution would be far above  $100^{\circ}$ ; and if heated to this new temperature the compound would be still more soluble and the solution would be unsaturated. The addition of more of the hydroxide to make the solution saturated would raise the boiling-point and this in turn would increase the solubility. In short, the point of saturation never catches up with the boiling-point, so a boiling solution of NaOH never deposits crystals of the compound, but simply gradually loses water until it becomes melted sodium hydroxide.

Several hydrates of sodium hydroxide have been prepared by cooling its concentrated solutions. They vary in composition from  $\text{NaOH}\cdot\text{H}_2\text{O}$  to  $\text{NaOH}\cdot 7\text{H}_2\text{O}$ .

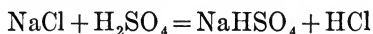
Sodium hydroxide is a very strong base and is generally used when such a substance is required as in the manufacture of soap, paper pulp, and in many other chemical processes. It is also commonly used in the laboratory when a solution containing the hydroxyl ion is needed.

**Sodium Carbonate.**—Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , has so many uses that it is almost indispensable to our civilization. It is found in nature in deposits and in solution in the lakes of the drier parts of the earth's surface. The United States has a number of such lakes, Mono Lake and Owens Lake in California, for example. The former contains 75,000,000 tons and the latter 40,000,000 tons of sodium carbonate. This is extracted at Owens Lake by solar evaporation, a double salt of the carbonate and the bicarbonate,  $\text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot 2\text{H}_2\text{O}$ , separating out which is

easily changed into the carbonate by heating to a moderate temperature, and can be produced at about half the expense of its manufacture from salt. High transportation charges, however, prevent its general use.

The ashes of sea plants contain sodium carbonate and this was formerly the chief source of the salt. At that time this compound was at least ten times more expensive than at present and this raised the price of many other things, notably glass and soap.

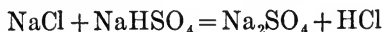
The oldest practical method for the preparation of sodium carbonate from the chloride is that known as the **Le Blanc process** having been brought out by Le Blanc a French apothecary in 1791, in competition for a prize offered by the French Academy for the discovery of such a process. An Englishman named Collison took out a patent in 1782 for practically the same method and actually made some of the carbonate so that he really deserves the credit for the invention rather than Le Blanc. The method involves essentially three steps. The first consists in the conversion of sodium chloride into sulfate,  $\text{Na}_2\text{SO}_4$ , by heating with sulfuric acid in a shallow cast iron pan a mixture of two moles of salt with one mole of "chamber" sulfuric acid. A rapid reaction takes place until half of the salt has been decomposed forming sodium acid sulfate and hydrogen chloride as shown in the following equation:



At the close of the operation, the evolution of hydrogen chloride comes to an end and the mixture turns solid. It then contains sodium acid sulfate and half of the original sodium chloride. This mixture is raked out of the pan and to the hearth of a reverberatory furnace where it is kept well stirred by rakes and heated to a high temperature by being brought in contact with the flames and hot gases from the fire end of the furnace. Such a furnace together with the decomposing pan is shown diagrammatically in Fig. 38, p is the decomposing pan, h the hearth, f and f the fires and c, c the flues by which the hydrogen chloride and the products of combustion escape.

The furnace is called a reverberatory furnace because the flames are deflected by the roof and caused to play upon the hearth.

On the hearth of this furnace the sodium acid sulfate reacts with the sodium chloride as shown below,



The sodium sulfate so obtained is called salt cake.

The second step consists in the reduction of the sodium sulfate to sulfide,  $\text{Na}_2\text{S}$ , by powdered coal; and the third, of the transformation of the sulfide to carbonate by heating with calcium carbonate in the form of chalk, or powdered limestone.

These two reactions are carried out at one operation by heating a proper mixture of sodium sulfate, slack coal and limestone, either in a reverberatory or in a rotary cylindrical furnace through

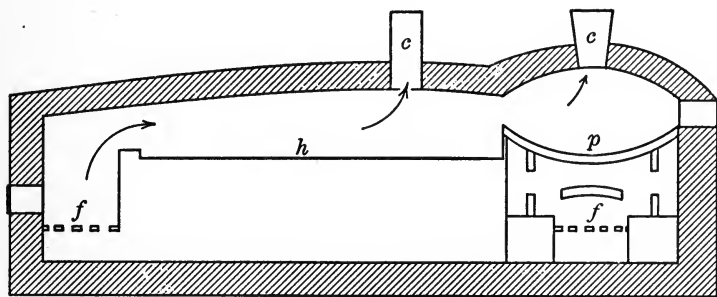
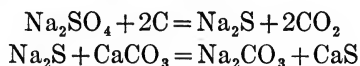
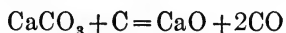


FIG. 38.

which the flames from the fire box pass. The latter form of furnace saves the great amount of hand labor required to keep the charge stirred on the hearth of the reverberatory furnace. The equations for the reactions are,



The end of the operation is indicated by the appearance of flames of carbon monoxide colored yellow by sodium compounds upon the surface of the mixture. This gas is formed by the interaction of the excess of calcium carbonate and carbon, which is always present in the original mixture, according to the equation,

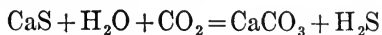


The product of this fusion is black in color and is known as

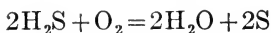
black ash. It usually contains less than 45 per cent. sodium carbonate, 30 per cent. calcium sulfide, 8 to 10 per cent. calcium oxide and 5 per cent. coal, also a large number of other substances. The calcium sulfide is difficultly soluble in water while the sodium carbonate dissolves easily. Hence, the latter is extracted from the black ash by water, using the principle of counter currents by allowing the fresh water to come in contact with the ash from which nearly all the sodium carbonate has been dissolved while the nearly saturated solution acts upon the fresh black ash. In this way, practically all the carbonate is removed from the ash and a nearly saturated solution is obtained. This solution is then evaporated in shallow pans by the waste heat from the furnaces, and the salt separates as the monohydrate,  $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ , which is called "crystal carbonate." The crystals are removed from the solution as they are formed and dried at a higher temperature forming the anhydrous salt,  $\text{Na}_2\text{CO}_3$ , known as soda ash. By dissolving this in hot water and allowing it to crystallize at ordinary temperatures, the deca-hydrate,  $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$ , crystallizes out. This is known as soda crystals, sal soda, and washing soda. It dissolves more rapidly than soda ash and is largely used for domestic purposes, but contains so much water that it does not pay to ship it far.

The residue left after the extraction of the sodium carbonate from the black ash contains calcium sulfide which represents the sulfur of the sulfuric acid. This sulfur must be recovered for two reasons, first competition is very strong in the soda industry and second if the sulfide were exposed to the air and weather it would be gradually dissolved and pollute the neighboring streams, and since under the action of the carbon dioxide of the air and water, hydrogen sulfide would be evolved, these streams would be very offensive.

There are several ways in which this sulfur may be recovered. One of the best is to suspend the residue in water and pass in carbon dioxide from lime kilns when hydrogen sulfide is formed according to the following equation:



This hydrogen sulfide is then burned to water and sulfur in a limited supply of air,

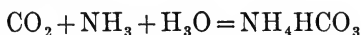


The hydrogen chloride evolved in preparing the salt cake is of course saved and either marketed as hydrochloric acid or made into bleaching powder.

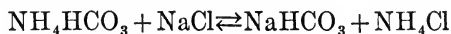
The **Solvay** or **ammonia soda process** was invented in 1838 by Dyer and Hemming and so far improved mechanically by Solvay between 1861 and 1872 that it was made into a commercially successful method and hence has his name. It furnishes an excellent example of the fact that good chemistry has to be combined with good mechanics to make a commercially successful chemical process.

The process consists essentially in saturating an ammoniacal brine containing about 257 gm. of salt and 76.5 gm. of ammonia per liter with carbon dioxide. The saturation is carried out at about 30 to 45°, but at the end of the operation the temperature is lowered to ordinary temperatures. When the solution becomes well saturated solid sodium bicarbonate,  $\text{NaHCO}_3$  begins to separate out and continues to do so until a little more than two-thirds of the sodium chloride has been transformed.

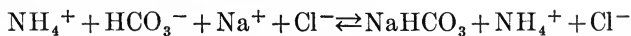
While the mechanical details of the process are so complex that some of the larger works on technical chemistry should be consulted for them, its chemistry is simple. The carbon dioxide, ammonia, and water combine to form a solution of ammonium bicarbonate,  $\text{NH}_4\text{HCO}_3$ ,



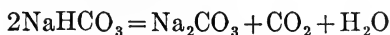
This then reacts with the sodium chloride to form sodium bicarbonate which is precipitated, and ammonium chloride which remains in solution. The equation is,



or written in the ionic form

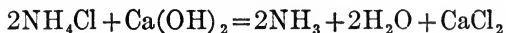


The sodium bicarbonate is then filtered off, washed, and heated to change it into the carbonate,



The carbon dioxide so obtained furnishes a portion of that required in the process, but the greater part of the gas comes from

the burning of limestone in special designed lime kilns. The ammonium chloride which is left in the solution from which the sodium bicarbonate has separated is worth about eight times as much as the sodium carbonate which it helps to prepare, consequently the ammonia must be recovered and used again. This is done by adding slaked lime to the mother liquor and boiling off the ammonia formed, absorbing it in fresh brine and so keeping it in circulation. The equation is,



The calcium chloride so obtained is mixed with undecomposed sodium chloride and finds but little application.

The Solvay process produces much purer sodium carbonate than the Le Blanc process and is for many locations the cheaper. In 1910, 2,000,000 tons of soda ash were made, for the greater part, by the Solvay process. A possible rival for both these methods is found in a process which is based upon the fact that sodium carbonate may be prepared by passing carbon dioxide into sodium hydroxide solution which is made by the electrolysis of sodium chloride.

**Properties of Sodium Carbonate.**—The deca-hydrate forms large transparent crystals from which the vapor pressure of water is rather high and which consequently effloresces easily, passing over into the monohydrate. This, in turn, in very dry air or at a higher temperature loses water and becomes anhydrous. A meta-stable hepta-hydrate,  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ , may also be prepared.

The deca-hydrate melts at  $35.5^\circ$ , and upon further heating, deposits the monohydrate which becomes less soluble as the temperature is raised, while the deca-hydrate becomes more soluble with rising temperature up to its melting-point; therefore sodium carbonate is most soluble at  $35.5^\circ$ . Sodium sulfate behaves in a similar manner and the phenomena will be discussed in detail in connection with this substance.

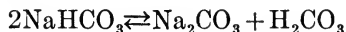
Anhydrous sodium carbonate is a white opaque substance and melts at  $826^\circ$ . It dissolves in water with the evolution of heat. A solution of sodium carbonate is fairly alkaline, due to the hydrolysis since carbonic acid is a weak acid. For solutions of ordinary concentration, something like 1 to 2 per cent. of the carbonate is hydrolyzed.



**Uses of Sodium Carbonate.**—Sodium carbonate is used in making glass, soap, in the softening of water, in washing and bleaching of linen and cotton fabrics, washing wool, paper making, dyeing and dye manufacture, the making of sodium salts, as a reagent in the laboratory to furnish the carbonate ion, and for many other important and useful purposes.

**Sodium Bicarbonate.**—Sodium bicarbonate,  $\text{NaHCO}_3$ , which is also called sodium acid carbonate, sodium hydrogen carbonate, primary sodium carbonate, monosodium carbonate, baking soda, saleratus, or by the housewife simply soda, occurs in nature along with sodium carbonate. Mono Lake, for example, contains 17,000,000 tons of the bicarbonate. It is obtained in the manufacture of sodium carbonate by the Solvay process or by acting upon the monohydrate with carbon dioxide.

It is a white crystalline powder which decomposes into sodium carbonate, water, and carbon dioxide, when heated to a moderate temperature. Its solubility at  $20^\circ$  is 9.60 parts of the salt per 100 parts of water and increases with the temperature. A solution of the bicarbonate is neutral toward phenolphthalein and alkaline toward methyl orange. This shows that the hydrocarbonate ion,  $\text{HCO}_3^-$ , is but very slightly dissociated into hydrogen and the carbonate ion, in fact the solution contains a little carbonic acid.



When the solution is boiled the carbonic acid breaks down into water and carbon dioxide, which escapes in the form of bubbles. As fast as the acid is decomposed more is formed, so that by boiling a solution of sodium bicarbonate the greater part of the salt may be transformed into the carbonate. The action is incomplete, however, since the carbonate formed is hydrolyzed, making the solution decidedly alkaline, thus decreasing the concentration of the hydrogen ion until finally no more carbonic acid can form and the evolution of carbon dioxide ceases. The more dilute the solution is the more the salt is decomposed.

**Sodium Nitrate.**—Sodium nitrate,  $\text{NaNO}_3$ , occurs widely distributed in nature in small amounts and is found in enormous quantities in certain deposits in the desert regions of Chile. These deposits are scattered over an area a few miles in width and 500

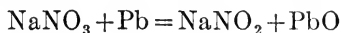
miles long. The rich nitrate stratum is composed of volcanic rock and great pebbles cemented together by the salts. It varies in thickness from a few inches to 26 ft. and contains on an average 17 to 25 per cent. of sodium nitrate. This deposit is covered with a few feet of barren or at least much less productive material. The crude nitrate always contains considerable sodium chloride, nitrate and perchlorate of potassium and sodium iodate with occasionally some chromate. The iodine is an important by-product and runs from .06 to 5 per cent. of the nitrate, 2 per cent. being a satisfactory iodine content. The nitrate is purified by dissolving it out of the crude material with hot water and allowing the solution to crystallize.

The mode of formation of these deposits is an interesting geological puzzle. The presence of the perchlorate iodate and chromate indicate a powerful oxidizing agent. It has been suggested that perhaps this agent was ozone.

It is estimated the available supply in Chile is 245,000,000 tons and the yearly production is about 2,000,000 tons. So the supply will last for some time to come.

Sodium nitrate crystallizes in rhombohedra which melt without decomposition at 317° and have a density of 2.26. It is very soluble in water and deliquesces which makes it unfit for the better grades of gunpowder. It is used in the manufacture of nitric and sulfuric acids, of potassium nitrate, as a preservative for meats, and in making sodium nitrite, but the greater part is used as a nitrogen fertilizer.

**Sodium Nitrite.**—Sodium nitrite,  $\text{NaNO}_2$ , is made by heating sodium nitrate with lead or iron and recrystallizing the product,



It melts at 271° and is very soluble in water though less so than the corresponding potassium salt. It is largely used in the manufacture of organic dyes.

**Sodium Sulfate.**—The deca-hydrate of sodium sulfate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  has been known for centuries under the name of Glauber's salts, having been first described by Glauber in 1658. The salt may also be obtained as the hepta-hydrate,  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , and in the anhydrous state. In the latter form it occurs in nature.

As has been mentioned, sodium sulfate is made as the first step

in the Le Blanc process for the preparation of sodium carbonate and also in the manufacture of nitric acid from sodium nitrate.

The solubility relations between the different forms of sodium sulfate are interesting and instructive, being in many ways typical of all salts which crystallize with different numbers of moles of water of crystallization.

The two hydrates and the anhydrous salt are each distinct substances and as such, each has its own solubility at any given temperature, which in general is different from that of either of the others, as is shown by the curves in the following Fig. 39.

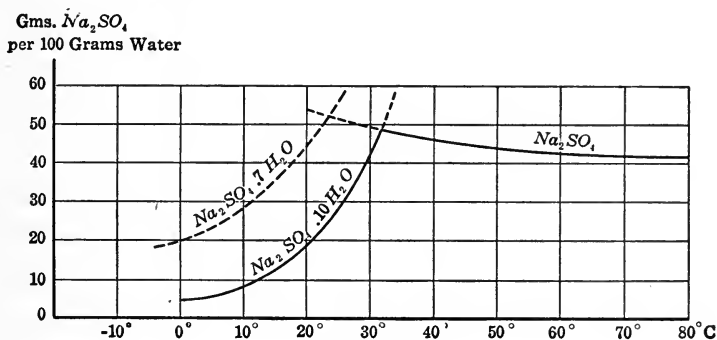


FIG. 39.

These curves show, for example, that at 20° a solution in equilibrium with Na<sub>2</sub>SO<sub>4</sub>, 10H<sub>2</sub>O will contain per 100 gm. of water 19.4 gm. of the salt calculated as Na<sub>2</sub>SO<sub>4</sub>, while those in equilibrium with Na<sub>2</sub>SO<sub>4</sub>, 7H<sub>2</sub>O or with the anhydrous salt contain respectively 44 gm. and 54 gm. of Na<sub>2</sub>SO<sub>4</sub> per 100 gm. of water. These figures demonstrate that the solubility of a salt cannot be expressed by a definite number unless there is given in addition to the temperature and pressure at which the measurement is made the particular solid phase with respect to which the solution is in equilibrium. A solution in equilibrium with a given substance is said to be saturated with respect to that substance. Since a solution saturated with anhydrous sodium sulfate contains a great deal more sodium sulfate per given weight of water than one saturated with the deca-hydrate, Na<sub>2</sub>SO<sub>4</sub>, 10H<sub>2</sub>O, it follows that the expression saturated solution does not mean that the solvent has taken up all of the solute

that it can contain but simply that the solution is in equilibrium with that particular solid phase. In the entire absence of a given solid phase of a solute a certain quantity of a solvent may contain in solution a much larger quantity of that solute than it can retain in the presence of that solid phase. Such a solution is said to be supersaturated with respect to that phase and is in a meta-stable condition, becoming unstable either when it reaches a certain degree of supersaturation or when brought in contact with some of the solid phase or with a substance isomorphous with it.

Sodium sulfate is especially prone to form supersaturated solutions and if a solution be prepared which is saturated or nearly saturated with the salt at about  $32^{\circ}$ , but which does not contain the smallest trace of the deca-hydrate, be cooled to ordinary temperatures in a flask closed with a plug of cotton all the salt will remain in solution, although it contains about twice the solute which a saturated solution of the deca-hydrate would contain. If now even a very small piece of a crystal of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  be introduced into the liquid, crystallization will at once take place and continue until the solution is no more than saturated. Sodium sulfate is such a common substance that it is almost universally present in dust and the cotton plug is used to exclude the latter, and so prevent the crystallization of the salt.

Supersaturation is very similar to superheating or supercooling of a liquid, each takes place in the absence of the phase into which the substance may pass.

On cooling a supersaturated solution of sodium sulfate prepared as described above to about  $10^{\circ}$  crystals of the heptahydrate  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  spontaneously separate. If now this solution containing the crystals of the heptahydrate be warmed to room temperatures, it will dissolve a part of the crystals and remain saturated with respect to  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ . Such a solution would contain less  $\text{Na}_2\text{SO}_4$  than one saturated at the same temperature with the anhydrous salt, but more than one saturated with the deca-hydrate and hence would be at the same time unsaturated with respect to the anhydrous salt and supersaturated with respect to the deca-hydrate. So if there were introduced into the solution some of the anhydrous salt, the latter would dissolve

and the solution would become supersaturated with respect to the hepta-hydrate, a further quantity of which would crystallize out. On the other hand, the introduction of even the smallest fragment of a crystal of the deca-hydrate to a saturated solution of the hepta-hydrate containing crystals of the latter would bring about the separation of crystals of the deca-hydrate which would cause the solution to become unsaturated with respect to the hepta-hydrate whose crystals would dissolve while those of the deca-hydrate grew.

An inspection of the figure will show that the curves for  $\text{Na}_2\text{SO}_4$  and for  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  cut at about  $25^\circ$  and hence that these two salts will be in equilibrium with each other and have the same solubility at this temperature. Below  $25^\circ$  the anhydrous salt is the more soluble and its saturated solution is meta-stable toward the hepta-hydrate, while above this temperature the hepta-hydrate is the more soluble and is meta-stable toward the anhydrous salt. This is another illustration of the fact that the meta-stable substance is the more soluble. The curve for the hepta-hydrate lies above that for the deca-hydrate and the two curves do not cut. This shows that at all temperatures the saturated solution of the hepta-hydrate is meta-stable toward the deca-hydrate. The solubility curves for the deca-hydrate and the anhydrous salt cut at about  $32.4^\circ$  and hence at this temperature the two salts are in equilibrium and have the same solubility. At all temperatures below this point the anhydrous salt is the more soluble and is meta-stable toward the deca-hydrate, while above this point the deca-hydrate is the more soluble and is meta-stable. In the curves, meta-stable equilibrium is shown by the dotted and the stable by the solid lines.

The two hydrates of sodium sulfate dissolve in their almost saturated solution with the absorption of heat and consequently in accordance with the law of mobile equilibrium, becomes more soluble with rising temperature while the anhydrous salt dissolves with the evolution of heat, and hence should and does decrease in solubility with rising temperature.

If one should determine the solubility curve of the deca-hydrate without taking any special precautions, it would run up in a smooth curve until  $32.4^\circ$  was reached, when it would suddenly shoot off in quite a different direction or a "break" would

appear in the curve, but just as the "break" took place, the solid phase changed to the anhydrous salt; in fact, the appearance of such a break in a solubility curve is a certain indication of a change in the nature of the solid phase.

When the deca-hydrate is heated to about  $32.4^{\circ}$  it partially liquefies and deposits some of the anhydrous salt. There will then be present three phases,  $\text{Na}_2\text{SO}_4$ ,  $10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$ , and solution, and since the system has two components,  $\text{Na}_2\text{SO}_4$  and water, there will be one degree of freedom because the sum of the phases and the degrees of freedom must be four, and either the temperature or pressure may be chosen when the other becomes fixed. If the pressure be made one atmosphere by carrying out the operation in open vessels, the temperature becomes fixed and is  $32.370^{\circ}$ . This is very near the temperature of the quadruple point of the system,  $\text{Na}_2\text{SO}_4$ ,  $10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$ , solution, and vapor, which is  $32.6^{\circ}$  and 30.8 mm. of mercury.

The salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , forms large monoclinic crystals which effloresce rather easily upon exposure to the air, thus showing that the vapor pressure of the water from the salt is greater than the partial pressure of the water vapor in the air. The vapor pressure of the hydrated salt is not definite at any given temperature so long as there is no other solid or liquid phase present in equilibrium with this, because the system will be one of two components, water and the anhydrous salt; and therefore if there are only two phases present, the hydrate and the vapor, there will be two degrees of freedom and the pressure of the vapor may have very different values at one and the same temperature. But if another solid phase be present and in equilibrium with the hydrate, say the anhydrous salt or another hydrate, the number of degrees of freedom is reduced to one and there is a definite pressure of the water vapor at each temperature. So as soon as the deca-hydrate has slightly effloresced and formed a little of the anhydrous salt, the vapor pressure of the water from the crystals becomes fixed and since it is generally higher than the partial pressure of the water in the air, the salt usually effloresces. In all these ways, sodium sulfate is typical of the other salts, and what has been said here applies with a little alteration to all cases where there is more than the one modification of the salt.

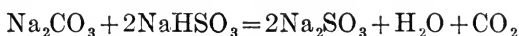
Sodium sulfate is used in medicine as a cathartic and also in the manufacture of glass and of sodium carbonate.

**Sodium Acid Sulfate.**—Sodium acid sulfate,  $\text{NaHSO}_4$ , or sodium bisulfate as it is often called, is formed in the first stage of the preparation of the sulfate from the chloride, or by the action of sulfuric acid on the neutral sulfates. It crystallizes from water in large triclinic prisms and when heated to a moderate temperature it loses water and is changed into the pyrosulfate,  $\text{Na}_2\text{S}_2\text{O}_7$ , which when heated still higher, decomposes into sulfur trioxide and the normal sulfate. Because of this property, it is fused with certain oxides and silicates to convert them into soluble sulfates as a preliminary to their analysis. It is more effective for this purpose than sulfuric acid because the latter cannot be heated above its boiling-point,  $330^\circ$ . Solutions of  $\text{NaHSO}_4$  react decidedly acid owing to the dissociation of the  $\text{HSO}_4^-$  ion into  $\text{H}^+$  and  $\text{SO}_4^{--}$ .

**Sodium Sulfite.**—Sodium sulfite,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , is prepared by dividing a solution of sodium carbonate into two equal parts and saturating one with sulfur dioxide when carbon dioxide and acid sodium sulfite will be formed,



The remainder of the carbonate solution is then added and carbon dioxide and the neutral sulfite will be produced,



When the hepta-hydrate is heated, it changes into the anhydrous salt and a saturated solution of the salt, the relations being very much like those for the sulfate.

In addition to the acid and neutral salts mentioned above, a compound having the formula,  $\text{Na}_2\text{S}_2\text{O}_5$ , known as sodium disulfite or sodium meta-bisulfite is made in rather large quantities for use in photography, as is also the neutral sulfite.

When exposed to the air, the sulfites take up oxygen and are changed to sulfates. This process is generally retarded by the presence of small quantities of certain organic substances such as alcohol or sugar which here act as negative catalyzers. The use of the sulfites in photography depends largely upon their power of reacting with oxygen since they are added to the

“developers,” which are strong reducing agents to protect them from the oxidizing action of the air.

Sodium sulfite is also used as an antiseptic or preservative and as an “antichlor” to reduce any chlorine which may be left in the goods after bleaching with this substance.

**Sodium Sulfide.**—Sodium sulfide,  $\text{Na}_2\text{S}$ , is prepared on a large scale by the reduction of the sulfate with powdered coal at a high temperature as was done in the preparation of sodium carbonate by the Le Blanc process. It dissolves in water and the solution has an alkaline reaction owing to hydrolysis which results in the formation of some of the hydrosulfide,  $\text{NaHS}$ , or rather of the hydrosulfide ion,  $\text{HS}^-$ . The salt crystallizes with nine moles of water as  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , and is capable of taking up sulfur to form various polysulfides of which the compounds  $\text{Na}_4\text{S}_6$ ,  $14\text{H}_2\text{O}$ , and  $\text{Na}_2\text{S}_5$  are the best known.

Small quantities of these sulfides are used in the laboratory as reagents, but the salts find extensive use in the manufacture of some kinds of glass and in the removal of hair from hides.

**Sodium Thiosulfate.**—Sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$ , is an important salt which may be made by boiling a solution of the sulfite with sulfur. The latter is taken up much as oxygen is by the sulfites, and thiosulfates are regarded as sulfates in which one combining weight of sulfur has taken the place of a combining weight of oxygen. The salt is obtained as a by-product of the Le Blanc process. The residue of calcium sulfide left in this process slowly oxidizes in the air to the thiosulfate, and when this is treated with sodium carbonate, calcium carbonate and sodium thiosulfate result.

The penta-hydrate is very soluble and readily forms supersaturated solutions. It melts at  $48^\circ$  and if protected from dust will remain liquid at ordinary temperatures until brought in contact with some of the solid salt. This liquid may be regarded as either the supercooled hydrate or supersaturated solution.

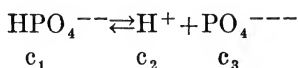
The salt is used as an “antichlor” and as a fixing agent in photography, a use which will be discussed in connection with the silver salts.

**Chlorine Oxygen Compounds of Sodium.**—The methods of preparation, properties, and uses of sodium hypochlorite,  $\text{NaClO}$ ,



and chlorate,  $\text{NaClO}_3$ , have already been given under the oxygen compounds of chlorine and will not be repeated here.

**Sodium Phosphates.**—Three sodium salts of orthophosphoric acid are known, monosodium phosphate,  $\text{NaH}_2\text{PO}_4$ , disodium phosphate,  $\text{Na}_2\text{HPO}_4$ , and trisodium phosphate,  $\text{Na}_3\text{PO}_4$ . The disodium salt,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , is the most familiar of these. It is made by neutralizing a solution of phosphoric acid with sodium hydroxide or carbonate and allowing it to crystallize. The salt is easily soluble and effloresces readily. It is used in medicine as a laxative and in the laboratory as a soluble phosphate reagent to furnish the hydrophosphate  $\text{HPO}_4^{--}$ , and the phosphate,  $\text{PO}_4^{---}$ , ions. Solutions of  $\text{Na}_2\text{HPO}_4$  are practically neutral in reaction, from which it follows that the ion  $\text{HPO}_4^{--}$  is but very slightly dissociated into the hydrogen and phosphate ions, so that the concentration of the latter is very small. For this reason, if the solution is to be used as a source of the phosphate ion,  $\text{PO}_4^{---}$ , sodium or ammonium hydroxides are added to it. The explanation for this is as follows. The reaction,



is reversible and according to the law of mass action,  $c_3 c_2 / c_1 = a$  constant. The addition of a base to the solution will decrease the concentration of the hydrogen ion and with it the product of  $c_2$  and  $c_3$  and this will of course have to be followed by a decrease in  $c_1$ , the concentration of the hydrophosphate ion. But the hydrophosphate ion decreases in concentration by changing into hydrogen as ion, which is used up by the base, and the phosphate ion which accumulates in the solution. So a solution of disodium phosphate to which sodium or ammonium hydroxide has been added contains a much larger amount of the phosphate ion than a pure solution of the salt and is used when the properties of the phosphate ion are sought.

The trisodium salt,  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , is made by adding an excess of sodium hydroxide to a solution of the disodium salt and evaporating to crystallization. Its solution in water is very alkaline and the salt is practically completely hydrolyzed into  $\text{Na}_2\text{HPO}_4$  and  $\text{NaOH}$ . It is used to soften or break "hard water." It does

this by precipitating the calcium and magnesium of the water as phosphates.

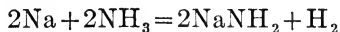
The monosodium salt is very soluble in water and the solution is acid toward litmus and phenolphthalein, but nearly neutral toward methyl orange, which is not as sensitive toward hydrogen as ion as the other indicators.

The sodium salts of the other phosphoric acids are not of much importance, except perhaps the metaphosphate,  $\text{NaPO}_3$ , which fuses easily and in this state dissolves many oxides and then solidifies to glass-like masses having characteristic colors. For this reason it is used in blowpipe analysis.

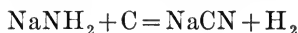
**Sodium Tetraborate.**—Borax or sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , has been described under boric acid, see p. 318. Like the metaphosphate, when melted it dissolves metallic oxides, and gives characteristically colored glass-like substances. Because of this, it is used in blowpipe analysis. It is also used as a flux in hard soldering. Because of the weakness of boric acid a solution of borax is hydrolized enough to be alkaline. On this account it is used to a slight extent in households to soften water, but this is a very costly method.

**Sodium Silicate.**—A salt having the composition  $\text{Na}_2\text{SiO}_3$  can be made by fusing together sodium carbonate and silicon dioxide. It is soluble in water and is called water glass. It is used in fire proofing wood, in making a kind of artificial stone or sand brick, being mixed with sand and lime for this purpose, and in the household for preserving eggs.

**Sodium Cyanide.**—Sodium cyanide is being made on a large scale for use in the extraction of gold, for which purpose it has some advantages over potassium cyanide; since a given weight of sodium cyanide has in it a larger amount of cyanogen, the essential thing for the purpose, than the same weight of potassium cyanide. The salt is made by passing ammonia over metallic sodium heated to  $300^\circ$  to  $400^\circ$  in an iron vessel when sodium amide,  $\text{NaNH}_2$ , is formed,



This sodium amide is then brought in contact with charcoal heated to dull redness when sodium cyanide and hydrogen are produced,



Like all other soluble cyanides sodium cyanide is very poisonous.

**Sodium Acetate.**—Sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ , is a very easily soluble salt which melts in its water of crystallization at  $58^\circ$ ; and if a little water be added to the molten salt, a solution is formed which may be cooled to ordinary temperature without crystallization. It is then very much supersaturated with the trihydrate and crystallizes upon the addition of a fragment of this salt.

Sodium acetate is used in the laboratory to decrease the acidity of a solution without making it neutral or alkaline. This is useful in analytical chemistry because of the fact that many precipitates will form in weakly acid solutions which are soluble in more highly acid solutions. To make the conditions favorable for the formation of such a precipitate in a solution which contains a strong acid, such as hydrochloric, all that is necessary is to add to the solution sodium acetate in sufficient quantity. The greater part of the hydrogen ion from the strong acid combines with the acetate ion to form undissociated acetic acid, because acetic acid is a weak acid and thus the acidity of the solution is decreased.

**Analytical Properties of Sodium.**—Like the salts of all other metals, the solutions of sodium salts show one set of properties in common, and this is really what is meant when it is said that they contain sodium as ion. In general, the statement of the analytical properties of an ion consists in giving a list of the more common ions with which it will form difficultly soluble compounds. There is, however, no very difficultly soluble compound of sodium, so this element must be recognized in some other way. For this, advantage is taken of the fact that the colorless flame of the Bunsen burner is colored intensely yellow by very small quantities of sodium and when this flame is viewed through a spectroscope, two bright yellow lines are seen if the instrument is very powerful or the two may appear as one in the smaller instruments (see frontispiece). This is an exceedingly delicate test and will detect .000000003 grm. of sodium. It is given by practically all substances and one must judge as to

whether sodium is present as an inconsiderable trace or as an essential constituent from the length of time which the flame color lasts as well as its intensity.

When the light from a powerful arc lamp is examined with a spectroscope a very bright continuous spectrum is seen. If the light from the arc passes through a Bunsen burner flame colored yellow by a sodium compound before it enters the spectroscope, black lines appear in exactly the position of the bright sodium lines when viewed in the absence of the arc light. In fact, the black lines may be made to change into bright ones simply by diminishing the intensity of the arc. This and other similar experiments lead to the conclusion that an incandescent gas will take up from a more intense source of light just that kind of light which it gives out, and when the more intense source of light is a solid, this will produce dark lines on a bright background. The dark lines come just where the incandescent gas alone would give bright lines. The solar spectrum consists of a bright background crossed by a very great number of dark lines many of which are identical in position with bright lines given by terrestrial substances when in the incandescent gaseous state. From these facts it is supposed that the sun consists of an intensely heated core surrounded by an atmosphere of gases which while incandescent are much cooler than the core and which contain many of our well known terrestrial elements. The presence of sodium for example, is clearly indicated by the fact that there are dark lines in the solar spectrum which exactly coincide with the bright lines of the sodium flame (see frontispiece).

In this way the presence of something like forty terrestrial elements in the sun has been ascertained. Among these may be mentioned hydrogen, helium (first discovered in the sun and then found in the earth), calcium, carbon, chromium, cobalt, iron, magnesium, manganese, nickel, silver, sodium, potassium, and vanadium.

#### POTASSIUM

**History.**—The history of potassium is identical with that of sodium. Its compounds were known to the ancients, but were not distinguished from those of sodium until the eighteenth century.

The metal was first prepared by Sir Humphrey Davy in 1807 at the same time and by the same method as the preparation of sodium.

**Occurrence.**—Potassium is never found free in nature, but occurs widely distributed in small quantities in the silicate rocks which compose the greater part of the earth's crust. On an average, potassium constitutes 2.49 per cent. of the lithosphere. This is about the same as the sodium content of the rocks. The silicates when acted upon by water and carbon dioxide slowly decompose and their potassium and sodium content passes into solution. One would expect then that the rivers flowing down into the sea would carry approximately equal quantities of sodium and potassium salts, but this is not the case, since the sodium greatly predominates. The explanation for this is found in the fact that soils have the power to hold back the potassium salts by what is known as adsorption.

Whenever a solid is introduced into a solution, there is a change in the concentration of the solution which is in immediate contact with the solid. With some solutions, the concentration is increased at the surface of the solid, with others it is decreased. If the concentration is increased, the substance is said to be adsorbed. Potassium salts are adsorbed by the soils while the sodium salts are not, and hence the latter easily find their way to the ocean. Because of this, the ocean contains relatively more of sodium salts than of potassium.

In spite of this disproportion between the sodium and potassium content of the ocean, it might be expected that the conditions which would give rise to the great deposits of salt would produce smaller deposits of potassium compounds. But since the potassium content of the sea is so small in comparison with that of the sodium, the ancient seas would have had to become nearly completely dry before any potassium salts would be deposited. This would put such salts at the very top of the deposits where they would be extremely liable to be dissolved and washed away. So far as can be reasoned out from our present conditions, such deposits could only be formed when a great body of sea water dried up completely in a desert region and the deposits became covered so deep by dirt blown in from the surroundings that they were protected from any further action of water. At any rate the

condition would be quite exceptional, and as a matter of fact only two large deposits of potassium salts are known; that in the neighborhood of Stassfurt, Germany, and a smaller one at Kalusz in Austria. The climate of these regions is now far from that of a desert, but there is some evidence that it was such at the time of the formation of the deposits. The discovery of beds of potassium salts in this country has frequently been reported of late, but their importance has not as yet been demonstrated.

**Potassium Compounds and Plants.**—Growing plants seem to have an imperative need for compounds of the alkali metals, potassium and sodium. Those which grow on the land take up potassium compounds from the soil to such an extent that their ashes formerly constituted the chief source of these compounds. The plants growing in the sea and many of those along the seashore are rich in sodium salts. It seems to be largely a matter of habit and availability which determines the compounds that the plant takes up. This is shown by the fact that if plants which when grown near the seashore are rich in sodium compounds are transplanted inland they gradually lose in sodium and gain in potassium until practically all of the former has disappeared. The reverse change takes place in plants taken from the interior to the coast. In the sea, of course, the sodium compounds are present in unlimited quantities, while on shore because of the adsorption of potassium, land plants find these compounds the more available. Some sea plants, notably the giant kelps of the Pacific, take up potassium compounds in such quantities that they may become an important factor in meeting the needs of this country for these very important substances.

There is then a direct connection between the soluble potassium content of a soil and its fertility, for of course, plants can only feed upon soluble substances. The soils usually contain large amounts of insoluble potassium compounds chiefly silicates, which slowly decompose under the action of the water and carbon dioxide, giving rise to soluble potassium salts and thus tending to keep up the supply of the latter in the soil. But if the land is kept under cultivation and the greater part of the crop removed as is often the case, soluble potassium compounds cannot be formed as rapidly as they are needed, and the fertility of the soil must decrease. The remedy is obviously to restore everything

possible to the soil, and to make up the deficiency in potassium by use of some of the Stassfurt salts as fertilizers. These are, of course, expensive and it is to be hoped that large beds of potassium salts will be discovered in this country. We have unlimited quantities of naturally occurring silicates or feldspars which are rich in potassium, and some experiments seem to indicate that these when very finely ground are of some value, at least for certain plants, as potassium fertilizers.

Animals have need for considerable quantities of sodium compounds chiefly for the chloride which constitutes the greater part of the salts in the body fluids, but their demand for potassium is rather small. Herbivorous animals get with their food much larger quantities of potassium and smaller quantities of sodium than they need. Now the elimination of the unnecessary potassium seems to be unavoidably accompanied by the excretion of the useful sodium compounds, and this accounts for the great appetite for sodium chloride shown by herbivorous animals. Carnivorous animals get their sodium and potassium in the proper proportions in their food and hence do not care especially for salt.

**Preparation of the Element.**—Metallic potassium may be prepared by the same methods that were used in the preparation of sodium including the electrolysis of the fused hydroxide, the method which is used on such a large scale to liberate sodium.

Potassium oxidizes more readily than sodium, so a layer of petroleum oil is placed in the cathode chamber to protect the potassium from oxidation when it rises to the surface of the hydroxide after having been liberated by the current. The demand for potassium is not large and only small quantities are made, because sodium which is much cheaper will do nearly everything that potassium can do, and since the combining weight of potassium is 39.1 while that of sodium is 23.00, 39.1 parts of potassium would be required to do the work which would be done by 23.00 parts of sodium at a much lower cost.

**Physical Properties.**—Potassium is a silver white metal which very quickly tarnishes upon exposure to moist air. It is waxy at ordinary temperatures, melts at  $62.5^{\circ}$  and boils at  $758^{\circ}$ ; the vapor is blue in color and the molar weight is apparently identical with the combining weight, 39.1. The metal is soluble in liquid ammonia, and the solution which has a blue color is a

conductor of the first class for electricity. Potassium easily forms an alloy with mercury which is much like the corresponding sodium amalgam. It may be made by bringing the metals together, or by electrolyzing a solution of a potassium salt with a mercury cathode. Like sodium amalgam, it decomposes water more slowly than the pure metal forming hydrogen and potassium hydroxide.

Sodium and potassium form an alloy which is interesting because if it does not contain too much sodium it is a liquid at ordinary temperature.

**Chemical Properties.**—The chemical properties of potassium are practically the same as those of sodium except that potassium is somewhat more active, so that when thrown upon water the potassium gets hot enough to set fire to the hydrogen which is evolved and which burns with a violet flame, this being the color given to flames by potassium compounds.

In fact, the entire chemistry of potassium is so similar to that of sodium that in most cases it will be necessary to add to what was given under sodium merely the slight points of difference presented by the potassium compounds.

The heat of formation of potassium as ion is 259 Kj.

**Potassium Hydride.**—Potassium hydride, KH, is prepared in the same way as the sodium hydride and is very similar to it in its properties.

**Potassium Oxides.**—Potassium forms two compounds with oxygen, a monoxide,  $K_2O$ , which dissolves in water to give potassium hydroxide and a peroxide,  $K_2O_4$ , which differs from the peroxide of sodium in composition, but like it, dissolves in water for the formation of the hydroxide, hydrogen peroxide and oxygen.

**Potassium Hydroxide.**—Potassium hydroxide, KOH, or caustic potash is so similar to sodium hydroxide that practically everything which was said concerning that compound might be repeated here as a description of potassium hydroxide. It may be prepared by the electrolysis of potassium chloride or by acting upon a dilute boiling solution of the carbonate with calcium hydroxide (milk of lime), calcium carbonate being precipitated and potassium hydroxide left in solution. It is exceedingly soluble, and crystallizes from the solution with varying amounts



of water of crystallization forming  $\text{KOH}\cdot\text{H}_2\text{O}$ ,  $\text{KOH}\cdot 2\text{H}_2\text{O}$ ,  $\text{KOH}\cdot 4\text{H}_2\text{O}$ ,  $2\text{KOH}\cdot 5\text{H}_2\text{O}$ ,  $2\text{KOH}\cdot 9\text{H}_2\text{O}$ . As is the case with sodium hydroxide, there is no solution of potassium hydroxide which is saturated at its boiling-point; so in the manufacture of the compound, the solutions are evaporated until nothing but molten  $\text{KOH}$  is left. This is then poured into moulds and comes on the market in round white brittle sticks.

Its chemical properties are almost identical with those of sodium hydroxide for they mainly depend upon the properties of the hydroxyl which is the same in each, and differs only in so far as the potassium ion is different from sodium. It is a very strong base and is used as such, but wherever possible sodium hydroxide is used in its place. The reason for this is that the sodium hydroxide is cheaper and less of it is required to do a given amount of chemical work because of the smaller combining weight of sodium.

Potassium hydroxide is very deliquescent, and its solutions take carbon dioxide from the air forming the carbonate which is also deliquescent.

Sodium hydroxide and its solutions behave like potassium hydroxide, but sodium carbonate is efflorescent rather than deliquescent. If then it is desired to remove both carbon dioxide and water from air or other gas, potassium hydroxide is chosen because its surface will remain moist and active, while sodium hydroxide would soon become covered with solid sodium carbonate and cease to be effective.

The chief technical use for potassium hydroxide is in the manufacture of soft soap and of oxalic acid.

**Potassium Chloride.**—Potassium chloride,  $\text{KCl}$ , is found in the potassium deposits of Stassfurt and is known as sylvite. It is also found there as double salts with magnesium chloride,  $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ , known as carnallite and with magnesium sulfate,  $\text{MgSO}_4\cdot\text{KCl}\cdot 3\text{H}_2\text{O}$ , kainite. The greater part of the potassium chloride of commerce is made from carnallite. The crude carnallite is crushed and heated with a solution of magnesium chloride left from previous operations. In this the carnallite easily dissolves, while the admixed sodium chloride and magnesium sulfate are left behind. The solution is now cooled when the greater part of the potassium separates as the chloride which

is removed and purified. Further cooling of the solution results in the re-formation of a little carnallite which is put through the process once more.

Potassium chloride is easily soluble in water, 100 parts of water dissolving 35.5 gm. of KCl at 25° and unlike sodium chloride it increases markedly in solubility with rising temperature. It crystallizes in anhydrous cubes which have a density of 1.951 at 23° and melt at about 780°. It is the source from which most of the other potassium compounds are made.

**Potassium Bromide.**—When bromine is dissolved in potassium hydroxide solution, water and potassium bromide and bromate are formed.



If this solution be evaporated to dryness and the residue gently heated, the bromate will decompose into bromide and oxygen. By recrystallization, pure bromide may be obtained. Of course, if the bromate is desired, it may be separated from the bromide by crystallization. The greater part of the bromide of commerce is made by first preparing a solution of a bromide of iron by heating together water, bromine and iron filings and then precipitating the iron with a solution of potassium carbonate. By filtering and evaporating the solution, the pure salt may be obtained.

Potassium bromide crystallizes in anhydrous cubes which are isomorphous with the chloride. Its density is 2.7 and its melting-point is 750°. Its solubility is greater than that of the chloride since 100 gm. of water dissolve 67.7 gm. of the bromide at 25°, the solubility increases with the temperature.

Potassium bromide is used in medicine as a sedative. Since it is a habit-producing drug, it must be employed with caution. It is also used in photography and in the laboratory when a soluble bromide is needed as a source of bromine as ion.

**Potassium Iodide.**—Potassium iodide, KI, may be prepared by either of the methods used for the bromide. It crystallizes in colorless anhydrous cubes having a density of 3.05 and melting at 705°. It is very soluble in water, 100 gm. of the latter dissolve 148 gm. of KI at 25°. Iodine is much more soluble in a solution of potassium iodide than in water forming the salt KI<sub>3</sub>, which apparently gives the ions K<sup>+</sup> + I<sub>3</sub><sup>-</sup>.

Potassium iodide is used in medicine, in photography, and in the laboratory when a soluble iodide is wanted as a source of iodine as ion.

**Potassium Fluoride.**—Potassium fluoride, KF, is a white crystalline salt of comparatively slight importance. It is made by neutralizing a solution of hydrofluoric acid with potassium hydroxide or carbonate. It is very soluble in water and is deliquescent. In the presence of an excess of hydrofluoric acid, it gives an acid salt, KF·HF which is a white crystalline solid. When the acid salt is heated to a dull red heat, it decomposes into potassium fluoride and hydrofluoric acid. This is made use of in the preparation of anhydrous hydrofluoric acid.

The fluorides are very poisonous, but have been used as preservatives, and in etching glass.

**Potassium Chlorate.**—Potassium chlorate, KClO<sub>3</sub>, is the most important of the oxyhalogen salts of potassium. The methods for its preparation, and its uses have already been discussed on p. 157.

**Potassium Perchlorate.**—When potassium chlorate is cautiously heated, a part of it is converted into the perchlorate, KClO<sub>4</sub>. This is a white crystalline substance which is not very soluble in water. Because of this, it is formed when perchloric acid is added to a solution of a potassium salt. It is almost insoluble in alcohol and therefore potassium is sometimes quantitatively determined by precipitation as the perchlorate in alcoholic solution. As described on p. 163, the perchlorate decomposes at a high temperature into the chloride and oxygen.

**Potassium Bromate.**—Potassium bromate, KBrO<sub>3</sub> and potassium iodate, KIO<sub>3</sub> are not very important compounds, but are most important of the salts of the corresponding acids. They may be made by the action of the free halogens upon potassium hydroxide. Potassium iodate may be more readily prepared by heating finely powdered potassium iodide with potassium chlorate until the latter begins to decompose. A reaction then takes place with formation of the iodate and chloride,



The iodate, like the bromate, is only slightly soluble in water and so may be readily separated from the chloride.

**Potassium Nitrate.**—Potassium nitrate,  $\text{KNO}_3$ , saltpeter, has been known for thousands of years being found as a white efflorescence in the neighborhood of human habitation in hot countries. The salt is formed by the action of oxygen of the air under the influence of nitrifying bacteria upon the nitrogenous materials and wood ashes, containing potassium carbonate, which accumulates in such conditions. India was the chief source of the salt for a long time, it being obtained there by a caste of the natives who made a business of going around the villages gathering the soil wherever it showed signs of the presence of the salt and leaching it out using the principle of counter currents. The solution was then allowed to evaporate and the salt purified by crystallization. At the present day the greater part of the salt is made by bringing together equivalent quantities of sodium nitrate and potassium chloride, and a little water. The mixture is then heated to a fairly high temperature. Under these conditions a large amount of sodium chloride separates. The solution is then filtered while still hot and allowed to cool when potassium nitrate and a little sodium chloride crystallizes out. The mixture is purified by washing with the mother liquors of previous recrystallizations, which removes the greater part of the sodium chloride and then recrystallizing.

This process may be easily understood after an inspection of Fig. 40, which gives the solubility curves of  $\text{KNO}_3$ ,  $\text{KCl}$ ,  $\text{NaCl}$ , and  $\text{NaNO}_3$ , the four possible salts resulting from the mixture of  $\text{KCl}$  and  $\text{NaNO}_3$ .

It will be seen from these, that at high temperatures  $\text{KNO}_3$  is the most soluble and  $\text{NaCl}$  the least so of the four salts, so in the hot solution  $\text{NaCl}$  separates. Upon cooling the solution,  $\text{KNO}_3$  becomes the least soluble and crystallizes out. The separation of the  $\text{NaCl}$  in the cooled solution can be understood from the fact that its solubility decreases somewhat as the temperatures fall, and also that as potassium nitrate crystallizes out, more sodium chloride must be formed in the solution, which will cause the separation of the corresponding amount of the salt in the solid state. It is evident that the separation of sodium chloride upon cooling might be easily avoided, and yet the greater part of the potassium nitrate be obtained in a fairly pure state if a little water were added to the hot solution, after the

removal of the solid NaCl at the high temperature. This would make the solution unsaturated with respect to NaCl, but leave it supersaturated with  $\text{KNO}_3$ .

Potassium nitrate is a white crystalline salt easily soluble in water with the absorption of heat, and having a bitter cooling taste. Its density is 2.1 and it melts at  $340^\circ$ . When heated to a high temperature, it decomposes, giving oxygen as one of its products. It was used by Scheele as one of the sources of this substance at the time of his discovery of the element. The crystals are anhydrous but tend to enclose portions of the solu-

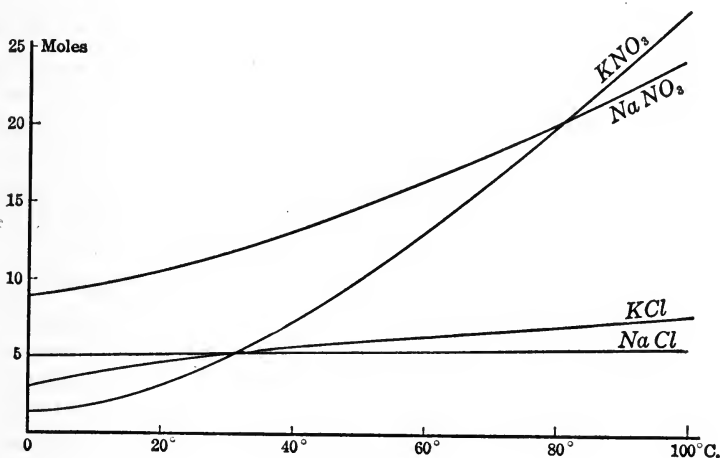


FIG. 40.

tions from which they were formed. Because of this, large crystals are generally impure, and when a pure salt is desired, the solution is kept well stirred as it cools to encourage the formation of small crystals.

Potassium nitrate is used in the laboratory, in medicine, in preserving meats to which it imparts a red color, and in the manufacture of fireworks and gunpowder. This last use absorbs by far the greater part of the  $\text{KNO}_3$  of commerce.

The composition of gunpowder varies somewhat but is near 75 per cent. potassium nitrate, 10 per cent. sulfur, 14 per cent. charcoal, and 1 per cent. water. The solid ingredients are pulverized separately, mixed together, moistened and ground until

thoroughly incorporated. The mixture is then subjected to great pressure and afterward broken up into fragments which are sorted into sizes by sifting. The grains are polished or given a glaze by rattling them in a barrel, dried to remove the water added during the various operations, and finally dusted by passing the powder over very fine sieves.

Gunpowder contains two easily combustible substances, sulfur and charcoal in intimate contact with a very good oxidizing agent, potassium nitrate. At a somewhat elevated temperature, these react very rapidly with the production of the gases nitrogen, carbon monoxide, carbon dioxide, hydrogen, marsh gas, hydrogen sulfide and a number of solid substances chief among which is potassium carbonate. The great amount of gas produced together with the high temperature of the reaction, about 2200° C., produces great pressure which would reach above 6400 atmospheres or 47 tons per square inch if the products of the explosion occupied the volume of the gunpowder before the explosion. To this high pressure the well-known effects of gunpowder are due.

Sodium nitrate is much cheaper than the potassium salt, and is used in making the lower grades of powder for blasting, but cannot be used in the better kinds because it is deliquescent.

**Potassium Nitrite.**—Potassium nitrite,  $\text{KNO}_2$ , is made in the same way as the corresponding sodium salt and has nearly the same uses. It is so soluble that it is purified with difficulty and hence is more expensive and is not used as much as sodium nitrite.

**Potassium Carbonate.**—Potassium carbonate,  $\text{K}_2\text{CO}_3$ , which is called potash or pearlash was formerly the most important of the potassium salts as it was the source of other potassium compounds, but since the discovery of the Stassfurt deposits it has largely lost its position. In former times, it was obtained from wood ashes by leaching them, using the principle of counter currents, but it is now chiefly obtained from the potassium sulfate of the Stassfurt deposits by a modification of the Le Blanc process for the preparation of soda, or from potassium chloride by taking advantage of the fact that when carbon dioxide under pressure is passed into potassium chloride solution containing magnesium carbonate in suspension, a double salt having the

formula  $\text{KHCO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}$  is deposited at temperatures below  $24^\circ \text{C}$ . This salt is decomposed by hot water, forming  $\text{MgCO}_3$  which is precipitated, carbon dioxide which passes out of the solution, and a solution of potassium carbonate from which the salt may be obtained.

Considerable quantities are obtained from the fatty substance known as suint which forms about half the weight of sheep's wool, the potassium having evidently been obtained by the sheep from their food and excreted in this way. The potassium is present in the wool as potassium sudorate which is converted into the carbonate at a high temperature.

Potassium carbonate is also obtained from the residue of beet sugar manufacture, and some is still extracted from wood ashes.

Potassium carbonate is a white solid melting at about  $880^\circ$ ; it is deliquescent and hence is very soluble in water, 100 parts of the latter dissolve at  $26^\circ$ , 113.5 parts of the carbonate. The solution is alkaline in reaction because of hydrolysis and the formation of  $\text{HCO}_3^- + \text{OH}^-$ .

It is used in making soft soaps, hard glass, and for the preparation of other potassium salts.

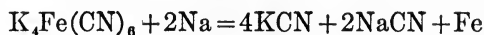
**Potassium Bicarbonate.**—Potassium bicarbonate,  $\text{KHCO}_3$ , potassium acid carbonate or primary potassium carbonate as it is called, like the corresponding sodium compound, is much less soluble than the normal carbonate and may be prepared by passing carbon dioxide through a strong solution of the carbonate. While less soluble than the carbonate it is still easily soluble, 100 parts of water at  $25^\circ$  dissolve 36 parts of the salt. Its solution is slightly alkaline, and is partially decomposed on boiling, into a solution of the carbonate and carbon dioxide, the reaction being like that for sodium bicarbonate (p. 349). When the dry salt is heated to  $190^\circ$  it is entirely decomposed into the carbonate, carbon dioxide, and water.

**Potassium Cyanide.**—Potassium cyanide,  $\text{KCN}$ , is an important salt which is manufactured by heating potassium ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ , with potassium carbonate when the following reaction takes place,



The salt  $\text{KCNO}$  is potassium cyanate and cannot be easily

separated from the cyanide. If the ferrocyanide is heated alone, a carbide of iron and nitrogen are formed besides the potassium cyanide. This process gives pure KCN but wastes cyanogen. By heating a mixture of dry potassium ferrocyanide with sodium, a mixture of potassium and sodium cyanides is obtained which is as good for most purposes as potassium cyanide and is sold as such. The equation is,



Potassium cyanide is now made by the action of ammonia upon a fused mixture of potassium carbonate and charcoal. The reaction is apparently much like that for the preparation of sodium cyanide from the metal, ammonia and charcoal; for metallic potassium may be formed by the action of carbon on the carbonate.

Potassium cyanide is very soluble in water and the solution is intensely and very rapidly poisonous. Hydrocyanic acid is a very weak acid so solutions of potassium cyanide react alkaline owing to hydrolysis. The hydrocyanic acid formed can be readily detected by its odor.

Potassium cyanide is used in large quantities in gold mining and in electroplating with gold and silver. It is used in the laboratory wherever a solution containing the cyanogen ion is required and also as a reducing agent. When it acts in the latter capacity, potassium cyanate KCNO is formed. When heated with sulfur, the latter is taken up forming a thio compound, analogous to the cyanates, known as potassium thiocyanate, KCNS, which is used in analytical work. This salt is sometimes, though incorrectly, called potassium sulphocyanide.

**Potassium Sulfate.**—Potassium sulfate occurs in nature in schoenite  $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$  and several other Stassfurt salts. It is obtained from schoenite by adding potassium chloride and a little water, on heating, the comparatively difficultly soluble potassium sulfate crystallizes out and magnesium chloride is left in solution.

Potassium sulfate crystallizes in anhydrous rhombic pyramids which look as if they belong to the hexagonal system. It is only moderately soluble in water, 100 parts of the latter dissolve 12.04 parts of the salt at 25°.



It is used in the preparation of potassium carbonate and of alum,  $KAl(SO_4)_2 \cdot 12H_2O$  but chiefly as a fertilizer.

**Potassium Acid Sulfate.**—Potassium acid sulfate  $KHSO_4$  is made in the same way and used for the same purposes as the corresponding sodium salt and has practically the same properties as the latter.

**Potassium Persulfate.**—Potassium persulfate,  $K_2S_2O_8$ , is prepared by electrolysis of a cold acid solution of potassium acid sulfate, using a large current and a very small anode. Under these conditions, the anion,  $HSO_4^-$ , is liberated at the anode and two combining weights unite to form persulfuric acid,  $H_2S_2O_8$  which then dissociates giving hydrogen and the persulfate ion, the latter gives a difficultly soluble compound with potassium as ion,  $K_2S_2O_8$ , potassium persulfate, which soon begins to crystallize from the solution. The salt is a white crystalline solid which is now on the market for uses as an oxidizing agent.

**Potassium Sulfide.**—Potassium sulfide and polysulfides  $K_2S$  and  $K_2S_n$  are so very much like the corresponding sodium salts that nothing more need be said here.

**Analytical Properties of Potassium.**—Solutions of potassium salt all have certain properties in common which are expressed by saying that they contain potassium as ion.

This is very fortunate for having once learned a few of the more striking of these common properties, the properties of potassium as ion, we can easily tell whether or not a given salt contains potassium. If the salts were not ionic in their behavior, it would have been necessary to learn a complete set of properties for each salt before it could have been recognized. The most useful analytical properties of an ion are the ones which are the most characteristic to our senses. For sodium, there are the flame and spectroscopy tests; for potassium, there are these same tests but they are less delicate than for sodium. Potassium compounds impart to the flame of the Bunsen burner a violet coloration which is easily masked by a little sodium unless the flame is viewed through a blue glass which cuts off the yellow sodium light and allows the violet of the potassium to be seen. The spectrum of potassium consists of a fairly strong line toward the extreme red end of the spectrum, a much fainter red line near the orange and a weak line well out in the violet end of the spec-

trum. In between these lines is a host of faint lines so close together that in the smaller instruments they are not seen separately, but appear as a band of light from the orange to the violet (see frontispiece). None of the potassium lines is anywhere near as intense as the sodium line and hence the spectroscopic test for potassium is far less delicate than that for sodium.

Potassium in the ionic condition differs from sodium in that it will combine with a number of different ions to form compounds which are sufficiently difficultly soluble in water to make them useful for the detection and determination of this element. Naturally for such a purpose the less soluble a salt the more useful it is, since the delicacy of the test and the accuracy of the determination depend directly upon this property.

Potassium cobaltinitrite,  $K_3Co(NO_2)_6$ , is the least soluble of the potassium salts, and is thrown down as a yellow precipitate when a solution of sodium cobaltinitrite,  $Na_3Co(NO_2)_6$ , which contains the cobaltinitrite ion  $Co(NO_2)_6^{---}$ , is added to a neutral or slightly acid solution of a potassium salt unless the latter be very dilute. This is a sensitive test for potassium, but is not as characteristic as the spectrum since ammonium, rubidium, and cesium compounds give very similar precipitates with the cobaltinitrite. But ammonium compounds are easily removed and rubidium and cesium occur so rarely that practically the test is a very good one for potassium.

Potassium cobaltinitrite has a small but definite solubility which is diminished by the presence of an excess of either potassium or of cobaltinitrite as ion. In fact, it is a general rule that the solubility of a salt is diminished by increasing the concentration of one of its component ions.

Potassium chloroplatinate,  $K_2PtCl_6$ , is rather difficultly soluble, 100 parts of water dissolving 1.26 parts of the salt. It is formed by the union of the potassium and chloroplatinate ions  $PtCl_6^{--}$ , when chloroplatinic acid,  $H_2PtCl_6$ , is added to a fairly strong solution of a potassium salt. The precipitate consists of small glistening yellow octahedra. The salt is less soluble in the presence of an excess of either ion, and its solubility is also markedly decreased by the addition of alcohol, so that this substance may be used to make the test more delicate. Many other

substances are difficultly soluble in alcohol so that this liquid must be used with caution. The test is far less sensitive than the preceding, and is no more characteristic since again ammonium, rubidium, and cesium give very similar compounds.

Potassium as ion will also give rather difficultly soluble precipitates with picric acid,  $C_6H_2(NO_2)_3OH$ , perchloric acid,  $HClO_4$ , hydrofluosilicic acid,  $H_2SiF_6$ , and tartaric acid,  $H_2C_4H_4O_6$ , the precipitates being potassium picrate,  $C_6H_2(NO_2)_3OK$ , potassium perchlorate  $KClO_4$ , potassium fluosilicate,  $K_2SiF_6$ , or potassium hydrogen tartrate  $KHC_4H_4O_6$ . The conditions which affect the solubility of this latter compound are so typical of those of other compounds that they are worthy of a careful study.

When a strong solution of tartaric acid is added to a rather concentrated solution of a potassium salt, say the chloride or nitrate, the solution becomes supersaturated with respect to potassium hydrogen tartrate,  $KHC_4H_4O_6$ . This supersaturation may be so great that the solution will spontaneously deposit crystals, or it may persist until the solution is shaken vigorously or until a minute crystal of the salt is added. Of course after crystallization has once started it will continue until the solution becomes exactly saturated with the salt. After this point has been reached the addition of various reagents will produce interesting changes in the solubility of the substance. For example, the addition of a few drops of sodium hydroxide solution will cause a marked increase in the quantity of precipitate showing that the solubility of the potassium hydrogen tartrate has been decreased, but the addition of an excess of sodium hydroxide will cause the entire precipitate to disappear showing that an excess of this reagent increases the solubility of the potassium salt.

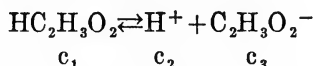
Further, the addition of either sodium acetate or of a very soluble potassium salt will decrease the solubility of the hydrogen tartrate, and cause a marked increase in the quantity of precipitate formed in the solution described above.

The addition of a very moderate amount of one of the stronger acids such as hydrochloric, nitric, or sulfuric to a solution containing a precipitate of potassium hydrogen tartrate will increase the solubility of the latter and cause the precipitate to disappear.

Acetic acid on the other hand has but little effect. Tartaric acid is a weak acid and this behavior of its potassium salt is typical of all difficultly soluble salts of weak acids, so that a general law may be put forward which says:

*The Difficultly Soluble Salts of Weak Acids Dissolve upon the Addition of Stronger Acids.*—The converse of this is not true, the difficultly soluble salts of strong acids are not dissolved by weak acids nor are they as a rule dissolved by strong acids.

Various more or less satisfactory explanations for these phenomena may be given, but the most useful and instructive is that offered by a combination of the theory of electrolytic dissociation with the law of mass action. According to the theory, an electrolyte in solution is partially broken up into ions as shown below for acetic acid,

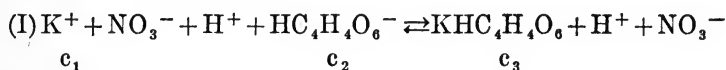


This is to be regarded as a reversible reaction and so subject to the law of mass action. Hence if  $c_1$  represents the concentration of the undissociated acetic acid and  $c_2$  and  $c_3$  that of the hydrogen and acetate ions respectively, equilibrium will result when,

$$\frac{c_2 \times c_3}{c_1} = K$$

If this be tested by experiment, the various concentrations being calculated from the electrical conductivity of the solution, the result will be found to agree closely with the theory as expressed in the mathematical relation just given. This is true not only for acetic acid but also for all other weak acids and for weak bases. It is true too, for dilute solutions of the more highly dissociated substances, the strong acids and bases and the salts, but apparently does not hold for the more concentrated of these substances. This may be due to the conductivity being an imperfect measure of the concentration of the ions in such solutions, or to some other influence being superimposed upon those which are measured. Fairly satisfactory explanations of these deviations can be given, but are not of interest at this point because these deviations from the simple theory and law given above are not such as would alter any conclusion which we

might reach as to the kind of change which would follow the addition of any given reagent, but would simply affect the calculation as to the extent of such change. For qualitative purposes then, the theory of electrolytic dissociation and the law of mass action may be combined and treated as though they exactly describe the actions of the substances. With this preliminary, the discussion of the action of the various reagents upon potassium hydrogen tartrate as precipitated from solutions of potassium nitrate by solution of tartaric acid may be taken up in detail. The equation for the main reaction and equilibrium is as follows:

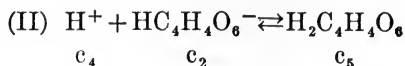


The equilibrium here is between the potassium ion, the hydrogen tartrate ion, and the undissociated potassium hydrogen tartrate. The concentration of these substances being represented respectively by  $c_1$ ,  $c_2$ , and  $c_3$ , the mass law equation becomes,

$$\frac{c_1 c_2}{c_3} = K$$

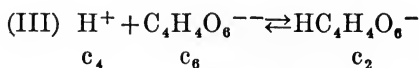
It cannot be too strongly emphasized that  $c_3$  represents the concentration of that portion of the potassium hydrogen tartrate which, while undissociated, is actually present in the solution in the dissolved state. It does not in any way represent that which is present as a precipitate. The only connection between  $c_3$  and the precipitate is found in this, that when the solution is in equilibrium with some of the precipitate, *i.e.*, is saturated, the equilibrium will be between the undissociated  $KHC_4H_4O_6$  in solution and that in the precipitate; and in this case, as in all others where there is equilibrium between the same substances in two phases, the equilibrium is determined by the ratio of the concentration of the substances in the two phases and not by the absolute amount of either phase. Therefore, since the concentration of the  $KHC_4H_4O_6$  is fixed and constant in the solid phase,  $c_3$ , that of this substance in solution must be fixed and constant also. From which it would follow that the product of  $c_1$  times  $c_2$  would be constant for this saturated solution, and this point should be appreciated and kept thoroughly in mind.

In addition to equilibrium I, given above, there are two others which are of importance in this connection.



The condition for equilibrium being,  $\frac{c_4 c_2}{c_5} = K'$

and



Equilibrium resulting when,  $\frac{c_4 c_6}{c_2} = K''$

Now it must be remembered that all three of these equilibria are present at the same time in a solution which contains potassium nitrate and tartaric acid, and that anything which alters one changes each of the others.

The addition of a few drops of sodium hydroxide to the solution will affect first equation II by decreasing  $c_4$  through the formation of water, but a decrease in  $c_4$  will be followed by a decrease in  $c_5$  and this will result in an increase in  $c_2$ . But  $c_2$  comes in the equilibrium I and its increase at once produces an increase in  $c_3$ . However, the solution was saturated with potassium hydrogen tartrate and hence the increase in  $c_3$  makes it supersaturated and results in the increase in the precipitate mentioned in the list of facts which were to be explained.

The action of sodium acetate can now be easily understood since it acts like the hydroxide to decrease the concentration of the hydrogen as ion.

An excess of sodium hydroxide, it will be recalled, redissolved the precipitate of potassium hydrogen tartrate; the explanation for this apparently contradictory behavior is as follows: As the hydroxide is added, water is formed decreasing  $c_4$  and causing the undissociated tartaric acid to break up as shown in II until all the tartaric acid is transformed then the further addition of hydroxide will result in the breaking up of the hydrotartrate  $HC_4H_4O_6^-$  as shown in equation III; so by decreasing  $c_4$  through the addition of NaOH,  $c_2$  will be first increased and then decreased. But since  $c_2$  is one of the factors in equation I, a decrease in  $c_2$  will

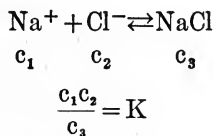
affect I, and will have to be followed by a decrease in  $c_3$ . But if  $c_3$  is decreased, the solution will become unsaturated and some of the precipitated substance will have to go into solution. So it may be easily seen why the solubility of potassium hydrogen tartrate is increased by the addition of an excess of sodium hydroxide.

The increase in solubility of  $\text{KHC}_4\text{H}_4\text{O}_6$  upon the addition of strong acids can be easily explained by considering the effect of the increase in the concentration of the hydrogen ion,  $c_4$ , upon II. If  $c_4$  is increased, to keep the fraction  $c_4c_2/c_3$  constant,  $c_3$  will have to increase which can only happen at the expense of  $c_2$ , so  $c_2$  will decrease. But in I a decrease in  $c_2$ , as we have seen, is followed by a decrease in  $c_3$  and this in turn by the solution of the precipitate. The failure of acetic acid to redissolve the precipitate can be understood, because acetic acid is so weak that it does not materially increase  $c_4$  and therefore does not decrease  $c_2$  and  $c_3$ , and hence leaves the solubility practically unaltered.

While potassium hydrogen tartrate is a fairly important substance, great quantities of it being used in the more expensive baking powders for example, it is not important enough to justify the time expended upon this discussion were it not for the fact that it is typical of most other substances, and that a thorough understanding of what is going on here will enable the student to deal easily with all other cases.

Under sodium chloride it was mentioned that this salt would be precipitated from its saturated solution by the addition of hydrogen chloride.

This may be understood by considering the following equilibrium:



If now hydrogen chloride be passed into the solution,  $c_2$  will be increased, and this will of necessity be followed by an increase in  $c_3$ , and a decrease in  $c_1$  to correspond; but an increase in  $c_3$  makes the solution supersaturated, and brings about the precipitation of the salt. A strong solution of hydrochloric acid may be used

instead of the gaseous hydrogen chloride with similar results. Potassium chloride will be precipitated in the same way and for the same reason by passing hydrogen chloride into its solution.

### RUBIDIUM AND CESIUM

The methods of spectroscopic analysis were developed by Bunsen and Kirchoff about 1859 to 1860 and were immediately utilized by them in the search for new elements. In this they were successful for in 1860 they announced the discovery of a new alkali metal whose spectrum was characterized by two bright blue lines and hence was named Cesium, Cs, from *cæsius*, the Latin word for the blue of the clear sky. Again, in 1861, they discovered another alkali metal whose spectrum consisted of two very strong lines in the violet and a number of others in the red, yellow and green portion of the spectrum. Two of the red lines are deeper red than the potassium lines, and hence the element was called Rubidium, Rb, from *rubidius* the Latin word for the darkest red color.

These two elements occur very widely distributed in nature in extremely minute quantities, but rubidium is more abundant than cesium. Bunsen obtained these elements from the mother liquors of the salt wells at Durkheim, and some idea of their rarity may be obtained from the fact that 9 gm. of rubidium chloride and 7 gm. of cesium chloride were obtained from 44,200,000 gm. of the mineral water. Their present source is the mother liquors from the extraction of potassium at Stassfurt.

Rubidium and cesium are always found in connection with lithium, sodium, and potassium. They are so like one another and so very much like potassium that it is a difficult matter to separate them not only from each other but also from potassium. They both form difficultly soluble compounds with the cobalt-nitrite, chloroplatinate, hydrotartrate, and other ions which give difficultly soluble potassium salts. In fact they can only be separated by taking advantage of the small difference which exists in the solubility of the compounds.

Metallic rubidium and cesium may be obtained by heating their corresponding hydroxide with powdered magnesium.

Rubidium is a brilliant silver white metal which melts at  $38.5^{\circ}$  and boils at  $696^{\circ}$ . It has a density of 1.52 and acts upon water



even more vigorously than potassium. The hydroxide so formed, RbOH, is at least as strong as that of potassium. The combining weight of rubidium is 85.45.

Metallic cesium has a silver white color, melts at  $26.4^{\circ}$  and boils at  $670^{\circ}$ . Its density is 2.4. It is even more active chemically than rubidium. Cesium hydroxide, CsOH, is a very strong base, and its salts are isomorphous with those of potassium and rubidium. The combining weight of cesium is 132.81. Both cesium and rubidium but especially cesium shows a tendency toward the formation of compounds of the type,  $MA_3$  or  $MA_5$  in which M stands for the metal and A for a combining weight of halogen. It is a difficult matter to decide as to whether the rubidium and cesium in these compounds have higher valencies than one, or whether the anion is of the type of that formed by potassium iodide and iodine,  $I_3^-$  and the question is still open.

Potassium, rubidium and cesium evidently form a triplet of very closely related elements. The difference between the combining weight of potassium, 39.1 and that of rubidium 85.45 is 46.35 which is just about that between rubidium and cesium which is 47.36. The same sort of relation exists between the triplet formed by chlorine, bromine, and iodine, and here too the difference in combining weight is about the same being roughly 45. In a good many ways the properties of these three elements vary in a regular manner with the combining weight as may be seen from the following table.

As the combining weight of the metal increases.

The chemical activity of the metal increases.

The solubility of the hydrotartrate increases.

The solubility of the sulfate increases.

The solubility of the chloride increases.

The solubility of the chlorplatinatate decreases.

The solubility of the alum decreases.

The boiling and melting points of the metals decrease.

#### AMMONIUM

In the discussion of ammonia  $NH_3$  it was pointed out that this substance would combine directly with acids for the forma-

tion of ammonium salts. For example ammonium chloride,  $\text{NH}_4\text{Cl}$  is formed by the union of ammonium and hydrogen chloride,

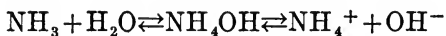


Ammonium chloride when dissolved, acts as though it were dissociated into chlorine as ion and the complex cation  $\text{NH}_4^+$ , called the ammonium ion. This ion forms a long list of salts and is so very similar to potassium in its properties that it would be entirely out of place not to discuss it here in connection with this element. Most of the ammonium salts are isomorphous with the corresponding compounds of potassium, and usually cannot be distinguished from them in color or general appearance. This taken together with the fact that the ammonium ion gives difficultly soluble compounds with the same reagents that the potassium ion does, makes it a rather easy matter to mistake the ammonium ion for the potassium.

The sources and methods of preparation of some of the ammonium compounds have already been mentioned in connection with the discussion of the compounds of nitrogen, pp. 227-228.

**Ammonium Hydroxide.**—As was given in connection with the discussion of ammonia, ammonium hydroxide is formed when ammonia dissolves in water, and may be obtained at low temperatures as a solid which melts at  $-79^\circ$ . Its solution shows comparatively weak basic properties indicating a small concentration of hydroxyl.

The equilibria in the ammonia solution may be represented as follows:

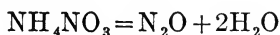


and the weakly basic character of the solution may be due either to the ammonium hydroxide being a weak base, or the conditions of equilibrium being such as to make the concentration of the ammonia large in comparison with that of the ammonium hydroxide so that there is not much of the latter present at any one time to ionize. As a matter of fact it does not make much difference which if either of the views is the correct one, since the point of practical importance is that ammonium hydroxide acts like a weak base.

**Ammonium Chloride.**—Ammonium chloride or sal ammoniac,  $\text{NH}_4\text{Cl}$ , is one of the more important of the ammonium salts. It is easily soluble in water, and crystallizes in cubes or octahedra. Its solutions are slightly acid due to hydrolysis. When heated to about  $350^\circ$ , it decomposes into ammonia and hydrogen chloride which pass off as gases, and recombine when they reach a cooler place, forming ammonium chloride, hence ammonium chloride is volatile. Most other ammonium salts undergo similar decomposition when heated giving ammonia and the acid. Ammonium chloride is made by heating together ammonium sulfate obtained from the gas works and sodium chloride; the ammonium chloride volatilizes and sodium sulfate is left behind. It is used in making dry cells and some other kinds of electrical batteries, as a reagent in the laboratory, in soldering and in medicine. Some idea of the extent of the use of ammonium chloride in batteries may be gathered from the fact that 50,000,000 dry cells are made in this country every year.

**Ammonium Bromide and Iodide.**—Ammonium bromide,  $\text{NH}_4\text{Br}$ , and ammonium iodide,  $\text{NH}_4\text{I}$ , are white salts although the latter tends to turn brown from iodine liberated by the oxygen of the air from  $\text{HI}$  set free by hydrolysis, the latter being due to the weakness of  $\text{NH}_4\text{OH}$ . These salts are isomorphous with the potassium salts and are used in medicine.

**Ammonium Nitrate.**—Ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , is a white crystalline salt which is interesting because of the fact that it has four solid forms with transition points at  $35^\circ$ ,  $83^\circ$  and  $126^\circ$ . Its melting-point is  $160^\circ$ . At temperatures somewhat higher than its melting-point ammonium nitrate decomposes into nitrous oxide and water;

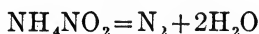


In this respect, it differs from most of the other ammonium salts since it does not yield ammonia and the acid. The difference is presumably due to the oxidizing action of the nitric acid on ammonia. The nitrous oxide is a powerful oxidizing agent; for this reason the nitrate is used in some powders, in fact under exceptional conditions it is explosive without any admixture.

Ammonium salts are largely used as reagents because it is a simple matter to free the solution from any excess of them. A

convenient way to do this is to add to the solution an excess of nitric acid and evaporate to dryness. As the concentration proceeds the ammonium nitrate formed gradually decomposes, and soon the ammonium compounds are destroyed. Another way to accomplish the same results is to evaporate to dryness and then heat until the ammonium salts are volatilized.

**Ammonium Nitrite.**—Ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , is very unstable and is of importance mainly because it easily decomposes giving nitrogen and water;

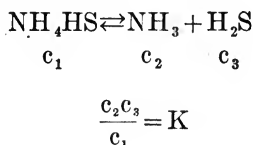


**Ammonium Sulfate.**—Ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , is in some ways the most important of the ammonium salts. It is obtained in the recovery of ammonia in the gas works, and is the starting-point for the preparation of most of the ammonium compounds. It is extensively used for this purpose, but more as a nitrogen fertilizer, something like 500,000 tons of it being used for manurial purposes each year.

It is a white crystalline salt isomorphous with potassium sulfate.

**Ammonium Persulfate.**—Ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , is made in the same way as potassium persulfate and resembles it closely.

**The Sulfides of Ammonia.**—Ammonium hydrosulfide,  $\text{NH}_4\text{HS}$ , is formed when equal volumes of ammonia and hydrogen sulfide are brought together. It is a crystalline substance which decomposes into its constituents until there is a perfectly definite relationship between the partial pressure of the various gaseous substances, which relationship is that indicated by the law of mass action,



But the concentration of a gaseous substance is proportional to its partial pressure, and hence the relation follows that equilibrium will result when,

$$\frac{p_2 p_3}{p_1} = \text{constant}$$

where  $p_1$ ,  $p_2$ , and  $p_3$  are the partial pressures of the gases whose concentrations are  $c_1$ ,  $c_2$ , and  $c_3$ .

Since  $\text{NH}_4\text{HS}$  is a solid,  $c_1$ , the concentration of  $\text{NH}_4\text{HS}$  in the vapor which is in equilibrium with it is constant and therefore  $c_2 \times c_3$  is constant also and consequently  $p_2 \times p_3$  is constant. The addition of either ammonia or hydrogen sulfide will drive back the dissociation of the sulfide as may be easily seen.

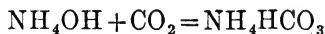
The salt is readily soluble in water and gives the ammonium and hydrosulfide ions.

Two volumes of ammonia and one of hydrosulfide will unite to form ammonium sulfide  $(\text{NH}_4)_2\text{S}$ . This is much less stable than the acid salt and passes quickly into the latter with the loss of ammonia. When dissolved in water, it is largely hydrolyzed giving ammonium hydroxide and the hydrosulfide ion,  $\text{HS}^-$ .

Solutions of these salts may be made by passing hydrogen sulfide into ammonium hydroxide solution. They are used as reagents to furnish the sulfide ion  $\text{S}^{--}$  and hydrosulfide  $\text{HS}^-$  which are necessary for the precipitation of such sulfides as require a higher concentration of sulfur as ion than is furnished by hydrogen sulfide, the sulfides of manganese and zinc for example.

A solution of ammonium sulfide will dissolve sulfur, and thereby acquires a yellow color and is then known as yellow ammonium sulfide. It contains polysulfides and is used as a reagent.

**Ammonium Carbonate.**—When an excess of carbon dioxide is passed into a solution of ammonium hydroxide, ammonium bicarbonate,  $\text{NH}_4\text{HCO}_3$ , is formed.



This is a fairly stable white crystalline salt which is soluble in water. The solid has a slight odor of ammonia and tends to decompose into ammonia, water and carbon dioxide. This reaction is quite rapid at moderately elevated temperatures and is made use of by bakers who use the bicarbonate as a leavening agent much as the housewife uses baking powder. For this purpose, the bicarbonate has the distinct advantage over the

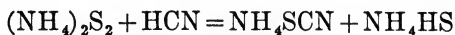
baking powder that it leaves practically no foreign substance in the food.

An excess of ammonium hydroxide will convert the bicarbonate into the carbonate  $(\text{NH}_4)_2\text{CO}_3$  but this is very unstable and soon decomposes.

Commercial ammonium carbonate is made by subliming a mixture of the sulfate and powdered calcium carbonate. It is a mixture of the bicarbonate and carbamate,  $\text{NH}_4\text{CO}_2\text{NH}_2$ . The latter is formed when ammonia combines with carbon dioxide.

**Ammonium Oxalate.**—Ammonium oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is made by neutralizing oxalic acid with ammonium hydroxide. It is a white crystalline salt soluble in water and much used as a reagent.

**Ammonium Thiocyanate.**—Ammonium thiocyanate is made by the interaction of yellow ammonium sulfide and hydrocyanic acid,



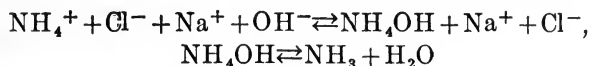
It is very easily soluble in water and is exceedingly poisonous. It is much used as a reagent.

**Microcosmic Salt.**—Sodium ammonium hydrogen phosphate  $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  is used in blowpipe analysis. When heated it loses ammonia and water and goes over into sodium meta phosphate which gives beads having characteristic colors with many of the oxides.

**Analytical Reactions of Ammonium.**—The ammonium ion forms difficultly soluble compounds with the cobaltinitrite, chloroplatinate, and hydrotartrate ions. These compounds cannot be distinguished by the eye from the corresponding potassium compounds. Ammonium compounds, however, do not give a flame test or spectrum when introduced in the Bunsen flame.

A very sensitive and characteristic test for ammonium compounds is based upon the fact that when a soluble base like sodium hydroxide is added to an ammonium salt, undissociated ammonium hydroxide is formed owing to the weakly basic character of this substance. As soon as the ammonium hydroxide is formed it breaks down into water and ammonia. The latter may be easily detected by its odor or by its action on moistened

red litmus which is turned blue when held in the vapors over the solution. The reactions in the solution, are as follows:



The ammonia then vaporizes and dissolves in the water on the litmus where the following reactions take place



and it is this hydroxyl which turns litmus blue.

Of course potassium compounds can do nothing like this so it is very easy in this way to distinguish between the two sets of compounds.

**Ammonium Amalgam.**—The great similarity between the ammonium ion and the potassium ion suggests that if free ammonium  $\text{NH}_4$  could be obtained it would be metallic in character. Attempts to prepare free ammonium have so far been unsuccessful, but an amalgam of this substance and mercury can be made either by electrolyzing most ammonium salts (the nitrate will not do), using a mercury cathode or by the action of sodium amalgam on an ammonium salt solution.

Below  $-85^\circ$  the amalgam is a hard stable substance, but at ordinary temperatures it is very spongy and consists largely of a mass of bubbles due to the decomposition of the dissolved ammonium into hydrogen and ammonia. That ammonium has metallic characteristics is shown by the fact that it dissolves in mercury which will not dissolve anything else that is not a metal.

## LITHIUM

The existence of the element lithium was first recognized by Arfvedson in 1817. It is very widely distributed and is obtained from petalite  $\text{LiAl}(\text{Si}_2\text{O}_6)_2$  and lepidolite or lithium mica. The metal was first prepared by Bunsen and Matthiessen in 1858 by the electrolysis of the fused chloride. It is a solid metal with a silver white luster, melts at  $186^\circ$  and boils above  $1400^\circ$ . Its density is .594 so that it floats on the petroleum used for its preservation.

The combining weight of lithium is 6.94 making it the third

element in the order of combining weights. It is active chemically but less so than the other members of the alkali group. It reacts rapidly with water but the metal does not melt and the hydrogen is not inflamed. It burns when heated in air, hydrogen, chlorine, bromine, iodine, sulfur, or nitrogen. This last property is interesting and somewhat important because there are not many things which will combine so readily with nitrogen. Lithium nitride,  $\text{Li}_3\text{N}$ , is formed.

Perhaps the most significant properties of lithium are that its phosphate,  $\text{Li}_3\text{PO}_4$ , and its carbonate,  $\text{Li}_2\text{CO}_3$ , are rather difficultly soluble in water, 100 grm. of water will dissolve 0.04 grm. of the former and 1.31 grm. of the latter. It is also noteworthy that the bicarbonate  $\text{LiHCO}_3$  is more soluble than the carbonate. With every other alkali metal, the bicarbonate is less soluble than the carbonate and the phosphate is easily soluble. The phosphates and carbonates of the members of the next group in the periodic system are difficultly soluble and the bicarbonates are more soluble than the corresponding carbonates. This shows that lithium has properties that make it a sort of connecting link or transition element between the two groups. That it really belongs to the alkali metals and not with the Group II is shown by the fact that it is monovalent while the members of Group II are divalent.

Glucinum the first member of Group II is like lithium in that it has properties which connect it with both Group II and with Group III.

In many ways it would have been more logical to have opened the discussion of the metals with that of lithium, but its postponement until this point just before taking up Group II is justified by the properties mentioned above.

**Lithium Carbonate.**—Lithium carbonate  $\text{Li}_2\text{CO}_3$  is commercially the most important lithium salt. It has been used in medicine under the notion that it will dissolve uric acid. The source of this idea is the fact that lithium urate is more soluble than the sodium salt, but the tendency is always for the formation of the least soluble salt and even if lithium urate were formed, sodium urate would be precipitated by the sodium salts universally present in the body fluids. The use of lithium salts in medicine for this purpose is not founded upon good chemistry and clinical



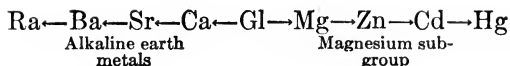
experience seems to indicate that it is no more valuable than the other alkalis.

**Lithium Chloride**—Lithium chloride is used in making artificial mineral waters and for making red fire and other fireworks.

**Analytical Properties of Lithium.**—Lithium is very easily detected by the fact that it imparts a bright red color to the Bunsen flame and that its spectrum contains a very strong red line which is visible even when the lithium is present in exceedingly small quantities. It is separated from other alkali metals by taking advantage of the fact that its chloride is soluble in a mixture of alcohol and ether in which the chlorides of the other alkali metals are but very slightly soluble. It does not form difficultly soluble compounds with the cobaltinitrite or chloroplatinate ions. While it does form such compounds with the phosphate and carbonate ions. It thus differs materially from the other alkali metals. The spectrum of lithium is shown in the frontispiece.

## CHAPTER XXII

### GROUP II



**General.**—The first member of Group II in the periodic system is glucinum. As mentioned under lithium, glucinum has properties which connect it both with Group II and with Group III and therefore its discussion will be postponed until a later point. The other members of the group fall naturally into two well-marked sub-groups; the one called the alkaline earth metals and comprising the common metals, calcium, strontium, and barium, and the very rare element radium; and the other sub-group called the magnesium family containing glucinum, magnesium, zinc, cadmium, and mercury. All the members of the group are divalent, but mercury also forms a series of compounds in which it is monovalent.

Calcium, strontium, and barium form a triplet of very closely related elements, and for a long time have been grouped together under the name of the alkaline earth metals. The discussion of the group will be opened with that of these metals since they are in many ways more closely connected with the alkali metals than are the members of the magnesium sub-group.

### THE ALKALINE EARTH METALS

#### CALCIUM

The compounds of calcium have been known and used from the very earliest times, but the element itself was first prepared, although in an impure state, by Davy in 1808. The pure metal was not secured until 90 years later when Moisson prepared it by the electrolysis of the fused iodide and by the reduction of this salt with sodium.

**Occurrence.**—Calcium compounds are very abundant and are

widely distributed over the earth's surface in the form of silicates, carbonates (limestone), sulfates, fluoride, phosphates, borates, etc. The element is present in the sun and certain of the fixed stars as shown by their spectra.

Compounds of calcium are indispensable for the growth and life of plants and animals. The bones and teeth of animals are composed largely of calcium phosphate but contain some carbonate and fluoride in addition.

**Preparation of the Element.**—Calcium is prepared now on a fairly large scale by the electrolysis of the fused chloride, the anode consisting of carbon and the cathode of an iron rod. The calcium, as it is liberated, clings to the end of the rod and the latter is gradually withdrawn from the fused salt, causing the calcium to build up an irregular cylinder of the metal. It is essential that the temperature of the fused calcium chloride be kept as low as possible; for this purpose, calcium fluoride is sometimes added to the bath, since it dissolves and lowers the melting-point of the chloride.

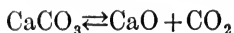
**Properties.**—Calcium has a silver white luster, melts at  $800^{\circ}$  and volatilizes below its melting-point in a vacuum. It may easily be obtained in the form of crystals. It has a density of 1.55 and is malleable, although somewhat harder than lead. It tarnishes rapidly in moist air at ordinary temperatures, but may be turned and polished in the air if kept hot.

Calcium decomposes water, forming hydrogen and calcium hydroxide,  $\text{Ca}(\text{OH})_2$ . It acts vigorously on acids. When heated in the air, it burns brilliantly and also combines rapidly at higher temperatures with nitrogen, chlorine, sulfur, silicon, and phosphorus. With nitrogen, calcium nitride,  $\text{Ca}_3\text{N}_2$ , is formed. When calcium is heated in a closed vessel, both the oxygen and nitrogen are removed and a very high vacuum results.

The combining weight of calcium is 40.07.

**Calcium Hydride.**—Calcium combines directly with hydrogen to form calcium hydride,  $\text{CaH}_2$ , a white crystalline substance which reacts with water, forming the hydroxide and hydrogen.

**Calcium Oxide.**—Calcium oxide, or lime, is a very important substance as everyone knows. It does not occur in nature, but is readily prepared by heating marble or limestone to a high temperature when the following reaction takes place,



This reaction is reversible and the conditions governing it will be considered in detail under calcium carbonate.

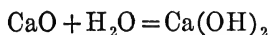
This process is carried out in furnaces called lime kilns. The more modern types of these kilns consist of a tall shaft of brick work with the interior somewhat egg-shaped in cross section. Limestone and coal or coke are charged in at the top in alternate layers and pass slowly down through the furnace, the fuel being consumed in the passage and furnishing the heat and high temperature necessary for the "burning" of the limestone to lime. The "burned" lime or calcium oxide is removed at the bottom, thus making the process continuous. As much air as possible is passed through the kiln to decrease the partial pressure of the carbon dioxide and so favor the decomposition of the carbonate as will be explained under the carbonate. The lime produced in this country in 1910 was 3,481,780 tons.

Calcium oxide is a white substance having a density of 3.3. It shows some signs of melting when heated in the oxyhydrogen blowpipe and under such conditions gives a very bright light which is known as the calcium or lime light.

The melting-point of lime is about 1900° and it not only melts easily at the temperature of the electric furnace, but even boils. When the vapors of the oxide condense, crystals of calcium oxide are formed. Calcium oxide is not reduced by sodium or by carbon except at temperatures of the electric furnace. The calcium obtained by the reduction with carbon unites with more carbon to form the carbide,  $\text{CaC}_2$ .

Lime has a great tendency to combine with water for the formation of the hydroxide,  $\text{Ca}(\text{OH})_2$ . Because of this, it is used in drying ammonia and certain other gases and in dehydrating alcohol. Its most important use, however, is in the preparation of mortar and cement.

**Calcium Hydroxide.**—Calcium hydroxide or slaked lime,  $\text{Ca}(\text{OH})_2$ , is made by the action of water on calcium oxide or quicklime as it is sometimes called. The equation is,



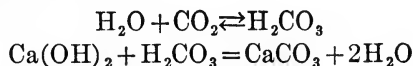
The action is slow in starting but evolves considerable heat,

so that after the reaction has once begun the temperature rises and it then goes on rapidly. When large quantities of lime slake at a time in contact with wood, the temperature often rises high enough to set fire to the wood. In this way buildings containing lime in storage are sometimes set on fire by water in times of floods.

Lime made from pure limestone slakes easily and is called "fat" lime, while that from stone containing clay or magnesium carbonate slakes slowly and is called "poor" lime.

Calcium hydroxide is a white powder whose density is 2.08 and which therefore occupies a larger volume than the lime from which it was formed. It is slightly soluble in water, 600 parts of the latter being required for one of the hydroxide at ordinary temperatures, and about twice as much water at the boiling-point since the solubility of the hydroxide decreases with rising temperature. The solution is decidedly alkaline in character since calcium hydroxide is a strong base, although not as strong as sodium hydroxide. The solution of the hydroxide is called lime water and is used as a reagent for the detection of carbon dioxide.

The gas suspected to contain carbon dioxide is bubbled through clear lime water. If  $\text{CO}_2$  is present the lime water soon becomes milky owing to the precipitation of the slightly soluble carbonate. This constitutes the test for carbon dioxide. The equations for the reactions are as follows,



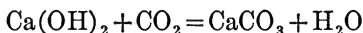
Lime water also finds many other uses.

Because of its cheapness, calcium hydroxide is largely used wherever a base is desired, unless the properties of the calcium ion interfere. If the presence of much water is objectionable, a suspension of the hydroxide in water called milk of lime is used. That part which is actually in solution reacts first and then more dissolves so that ultimately it may all be used.

Slaked lime is used in the manufacture of sodium and potassium hydroxides, ammonia, bleaching powder, mortar, the softening of water, the purification of illuminating gas, the removal of hair from hides, and for many other purposes.

Air-slaked lime is lime which has been exposed to the air until it has fallen to powder from the water and carbon dioxide taken up from the air; it contains calcium oxide, hydroxide, and carbonate.

**Mortar.**—Mortar is made by mixing together 1 part of slaked lime made into a paste with water and 3 parts of sand. The water gradually evaporates and the mixture sets in a few days sufficiently to give some stability to the building. In this setting process, the calcium hydroxide decreases greatly in volume and renders the mass porous. The sand is added largely to decrease the shrink and to make the mortar more porous. After setting, the mortar gradually absorbs carbon dioxide from the air and is converted into calcium carbonate,

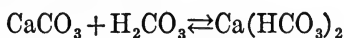


The carbonate crystallizes as it is formed and the crystals interlace and bind the sand and the masonry together. When this hardening process is complete the mortar is very hard and strong, but it takes place so very slowly that years and even centuries are required for its completion. The hardening does not take place under water nor in very damp places. Under such conditions hydraulic cement must be used. Such cements will be discussed under aluminum.

**Calcium Carbonate.**—Calcium carbonate occurs very abundantly in nature as limestone, marble, and chalk. The latter is made up of the fragments of the shells of marine organisms, while limestone and marble are composed of interlaced crystals of a form of calcium carbonate known as calcite. The only difference between the two is that marble is the more distinctly crystalline. Calcite crystals have a density of 2.70 to 2.75, but there is another form of crystalline carbonate known as aragonite having a density of 2.92 to 3.28. Calcite is the stable form and pseudomorphs of calcite after aragonite are often found. Aragonite changes rapidly into calcite at about 500°, but very slowly at ordinary temperatures so that specimens of aragonite are found in nature which must be thousands of years old, but which have not had time to change into calcite. Calcite is sometimes found in very large clear crystals and is then known as Iceland spar. Calcium carbonate is difficultly

soluble in water and is precipitated whenever a soluble carbonate is added to a solution of a calcium salt.

The freshly precipitated carbonate is amorphous, and like all such substances is more soluble than the crystalline modification into which it passes after a time. At ordinary temperatures the change takes place slowly and calcite is formed, but at the boiling-point the transformation is rapid and aragonite is produced. The difference in solubility between the crystalline modification and the amorphous is comparatively great; and whenever in analytical work calcium is precipitated as the carbonate, care should be taken to boil the solution until the precipitate becomes crystalline. The solubility of calcite is so slight that a liter of water will dissolve only 12 mgrm. of the salt, but the solubility is greatly increased by carbon dioxide dissolved in the water owing evidently to the formation of the bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$ ,

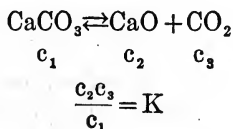


Underground waters are more or less heavily charged with carbonic acid, and hence dissolve some of the calcium carbonate with which they come in contact.

Calcium bicarbonate is quite unstable and exists in solutions only when they contain an excess of carbonic acid. Therefore it is decomposed and the carbonate is precipitated when its solution is boiled or exposed to air, since in either event the greater part of the carbonic acid will be driven out of the solution.

The precipitation on boiling is the cause of the formation of a part of the scale which collects in boilers and in tea kettles, and the precipitation on exposure to air is the main cause of the formation of stalactites on the roofs of caves and of stalagmites on the floors where the underground water drips down from the roof upon them.

As mentioned under calcium oxide the carbonate decomposes at a high temperature into the oxide and carbon dioxide. The equation for the reaction is,

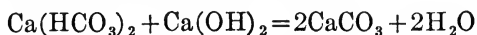


This reaction is reversible, and applying the law of mass action the conclusion is reached that as  $c_2c_3/c_1 = \text{constant}$  and since  $\text{CaCO}_3$  and  $\text{CaO}$  are solids,  $c_1$  and  $c_2$  are constant, that therefore  $c_3$ , the concentration of the  $\text{CO}_2$  is constant for equilibrium at any one temperature. The concentration of a gaseous substance is proportional to its pressure, so it follows that the carbon dioxide in equilibrium with the  $\text{CaO}$  and  $\text{CaCO}_3$  at any given temperature will always have a certain fixed pressure.

The phase law will give the same information. The system is one of two components, say  $\text{CaO}$  and  $\text{CO}_2$ . The number of phases plus the degrees of freedom will then be four, but here there are three phases, the solids,  $\text{CaCO}_3$ ,  $\text{CaO}$  and the gas  $\text{CO}_2$ . There will then be one degree of freedom and hence the pressure of carbon dioxide will be fixed and definite at any given temperature.

The decomposition of the calcium carbonate is accompanied by the absorption of heat, and therefore in accordance with the law of mobile equilibrium the pressure of the carbon dioxide increases with rising temperature. It reaches atmospheric pressure at about  $900^\circ$ , and this is the temperature at which calcium carbonate will decompose in an open vessel in an atmosphere of pure carbon dioxide; but in a stream of air or any other gas which will keep the partial pressure of the carbon dioxide low by sweeping it away as fast as it is formed, the decomposition will take place at a much lower temperature. This comes into play in the lime kiln for there the limestone is heated in a current of gases in which the partial pressure of carbon dioxide is far below that of the atmosphere, and consequently the temperature of decomposition is comparatively low.

Waters containing calcium and magnesium salts are called **hard waters**, and that part of the hardness which is due to calcium bicarbonate is called temporary hardness because it may be removed by boiling for a time. It may also be removed by adding to the solution the proper amount of calcium hydroxide to change the bicarbonate into carbonate,



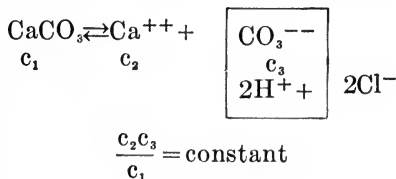
The rest of the hardness is called permanent hardness, although it too may be overcome by proper chemical treatment



as will be described in connection with the discussion of magnesium.

Calcium carbonate although so slightly soluble in water readily dissolves in acids. This of course is another case of a difficultly soluble salt of a weak acid being dissolved by a stronger acid.

The main equilibrium may be represented as follows:



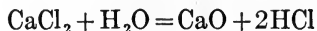
The addition of hydrochloric acid will decrease  $c_3$  through the union of the hydrogen ion with the carbonate ion for the formation of carbonic acid which breaks down into carbon dioxide and water. The decrease in  $c_3$  will of course have to be followed by a decrease in  $c_1$  and the solution will become unsaturated causing more of the carbonate to dissolve. This is an example which falls under a general rule that *the solubility of a salt may be increased by decreasing the concentration of one of its ions.*

**Calcium Chloride.**—Calcium chloride,  $\text{CaCl}_2$ , occurs in nature in sea water and as a constituent of a few minerals for example, tachhydrite,  $\text{CaCl}_2 \cdot \text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ , and apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ .

It may be prepared by dissolving pure calcium carbonate in hydrochloric acid. It is a by-product of several technical processes and is comparatively cheap. It is exceedingly soluble in water and crystallizes with varying amounts of water of crystallization forming a mono, di, two tetrahydrates and a hexahydrate. The hexahydrate crystallizes from highly concentrated solutions at ordinary temperatures. It is very deliquescent and melts at  $30^\circ$ . When mixed with ice in the best proportions, a temperature of  $-55^\circ$  may be obtained. Anhydrous  $\text{CaCl}_2$  and ice do not make a good freezing mixture since the salt evolves so much heat in dissolving, while the hexahydrates absorb heat.

When the hexahydrate is heated to  $200^\circ$ , it loses four moles of water and forms a white porous mass of the dihydrate which is

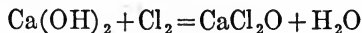
very hygroscopic and is used for drying gases. When heated to a still higher temperature the anhydrous salt is obtained but the reaction represented by the following equation takes place to a certain extent,



and the product contains some calcium oxide.

The use of calcium chloride as a drying agent is subject to the disadvantage that it can reduce the partial pressure of the water vapor only to the vapor pressure, at that temperature of the hydrate which happens to be present. Since each of the hydrates has an easily perceptible vapor pressure even at ordinary temperatures, calcium chloride cannot dry a gas completely, and at slightly elevated temperatures it is very inefficient. Sulfuric acid is a much better drying agent, as has been mentioned before, and phosphorus pentoxide is still better. Calcium chloride forms a compound,  $\text{CaCl}_2 \cdot 8\text{NH}_3$ , with ammonia and cannot be used for drying this substance.

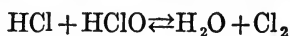
**Calcium Hypochlorite and Bleaching Powder.**—Bleaching powder,  $\text{CaCl}_2\text{O}$ , or chloride of lime, is made by the reaction of chlorine on slacked lime,



The reaction is usually carried out in large chambers lined with sheet lead, which may be 80 to 100 ft. in length, and on the floor of which the slaked lime is spread in a layer 4 in. deep. The chamber is filled with chlorine and allowed to stand until absorption is complete. The lime is then turned over by hand and exposed to chlorine once more until saturated with the gas. The excess of chlorine is then removed and the residual gases absorbed by a cloud of slaked lime dust. The bleaching powder is then packed in casks for shipment. Recently the great amount of hand labor has been reduced by the introduction of mechanical devices which carry the slaked lime on conveyors in a direction contrary to that of the chlorine, and so use the principle of counter currents. The product is automatically delivered into casks ready for the market.

Bleaching powder is a white substance which is partially soluble in water, and yields calcium, chlorine and hydrochlorite

ions. It reacts with all acids, even carbonic, for the formation of hydrochloric and hypochlorous acids which then react forming chlorine and water.



The usefulness of bleaching powder is proportional to the percentage of chlorine which it will produce in this way and it is rated as containing so much "available" chlorine meaning thereby the per cent. of its weight in chlorine which bleaching powder will evolve when treated with an acid. Good bleaching powder contains 35 to 37 per cent. of available chlorine.

When bleaching powder is treated with sodium carbonate in solution, calcium carbonate is precipitated and a mixture of sodium chloride and hypochlorite is left in solution. This finds extensive use as a bleaching solution.

Bleaching powder is used in bleaching cotton, linen, and paper pulps, as a disinfectant, and in the manufacture of chlorates, especially that of potassium. For the latter purpose, the powder is heated with water which transforms the hypochlorite into chloride, and chlorate and potassium chloride is then added and the salts separated by crystallization. It is especially useful for the purification of water since minute quantities will destroy all harmful bacteria.

Pure calcium hypochlorite may be prepared by neutralizing hypochlorous acid with calcium hydroxide. It finds no application.

**Calcium Bromide and Iodide.**—Calcium bromide and iodide are very similar to the chloride, but are even more soluble than the latter. There is nothing noteworthy about them except perhaps that the iodide in solution turns brown rather easier than the iodides of potassium and sodium. This brown color is due to the iodine liberated by the action of oxygen of the air on the hydriodic acid set free by the carbonic acid.

**Calcium Fluoride.**—Calcium fluoride,  $\text{CaF}_2$ , or fluorspar as it is commonly called, occurs in nature fairly abundantly. It crystallizes in cubes and is nearly insoluble in water. It melts at  $1330^\circ$  and has to a marked degree the property of reducing

the melting-point of the slags produced in metallurgical processes and has long been used for this purpose. When heated it becomes luminous at temperatures far below redness, and this gives rise to the term fluorescence.

Calcium fluoride is the source of all other fluorine compounds, and is used in the preparation of hydrofluoric acid for etching glass and for other purposes.

**Calcium Nitrate.**—Calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , is found in all fertile soils. It may be made by the action of nitric acid on the carbonate, and is manufactured on a large scale for use as a fertilizer at the plant for the manufacture of nitrogen compounds from the air at Notodden, Norway. It is very soluble in water and forms a number of hydrates; that stable at ordinary temperatures is  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . The anhydrous salt is used as a drying agent. When heated it gives calcium oxide, nitrogen peroxide, and oxygen.

**Calcium Sulfate.**—Calcium sulfate,  $\text{CaSO}_4$ , occurs in nature in two forms as anhydrite,  $\text{CaSO}_4$ , and as gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; the latter is the more important since from it is made the valuable plaster of Paris and cement plaster.

Calcium and sulfate ions are present in sea water and gypsum is deposited soon after the concentration of such water begins. Without doubt this has been the origin of the great beds of gypsum which are found in various parts of the world. The United States has many such deposits, notably in Michigan, New York, Iowa, Ohio, Virginia, Texas, Oklahoma, and Kansas. The total production of gypsum in the United States in 1910 was about 2,000,000 tons, of which 1,583,669 tons were converted into plaster.

Besides the dihydrate or gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , calcium sulfate forms a hemihydrate,  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ , which is in equilibrium with the dihydrate and water vapor at  $107^\circ$ . When ground gypsum is heated from  $110$  to  $130^\circ$  its aqueous tension is greater than one atmosphere, and it rapidly decomposes, losing water and changing into the hemihydrate. The product obtained in this way is called plaster of Paris. When mixed with water to form a paste, it quickly hardens to a mass of interlaced crystals of the dihydrate. In so doing it increases materially in volume and fills perfectly a mould into which it may be poured; because of this

it is much used in making plaster casts. By far the more extensive use for this product is as a plaster for the interior of buildings, and for such purposes the plaster of Paris sets too quickly. To overcome this, advantage is taken of the fact that many organic substances such as glue, sugar, glycerine, etc., will greatly increase the time of setting; such substances are called retarders and the plaster so treated is known as cement plaster. Cement plaster may also be made without retarder by using gypsum which is mixed with the proper amount of clay or dirt.

These plasters have many advantages over lime plasters for inside work and have very largely replaced them. One important advantage is that they dry quicker and are much harder and stronger than the lime plasters.

The process of manufacture of plaster of Paris and cement plaster is briefly as follows: The gypsum is crushed and ground to a fine powder and run slowly into large iron kettles with bottoms which are curved upward. These kettles are made of boiler steel and hold about 7 to 8 tons of gypsum. They are heated by fires from below and have two to four flues running through them for economy of fuel. The ground gypsum is kept stirred by mechanical stirrers. When the temperature of the contents of the kettle reaches  $110^{\circ}$  the water vapor is given off so vigorously that the whole mass seems to be boiling, the temperature gradually rises to  $132^{\circ}$  at which temperature the evolution of water vapor suddenly decreases and the "boiling" disappears. When this point is reached, the dihydrate has been nearly completely changed into the hemihydrate. If heated still higher, "boiling" begins again at about  $140^{\circ}$  from the decomposition of the hemihydrate. This second boiling is avoided in the manufacture of plaster.

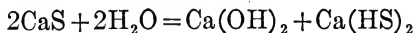
When the dehydration process is nearly finished, the retarder is added if cement plaster is desired, and the charge withdrawn from the kettle and cooled.

Great care must be taken not to overheat the plaster or drive off all the water, since in these cases the plaster either will be too slow in setting or will not set at all. Such plaster is said to be "dead burned." An explanation for this is as follows: 100 gm. of water at  $25^{\circ}$  will dissolve about 0.208 gm. of the

dihydrate and 1.0 grm. of the hemihydrate, so that a saturated solution of this latter is highly supersaturated with respect to the former, and it needs only the presence of a few crystals of the dihydrate to start the crystallization. Properly burned plaster has about the composition of the hemihydrate, but probably contains a large number of undecomposed fragments of gypsum which serve as nuclei for the formation of crystals of this substance and promptly bring about the setting of the plaster. The probable cause of the failure of dead burned plaster to set is that in driving off the water or overheating the plaster the crystals of gypsum are completely decomposed so that none is present to start the crystallization. Another cause is that the anhydrous calcium sulfate formed at high temperatures is very slightly soluble in water.

The solubility of gypsum varies in a rather remarkable way with the temperature; from 0° to 38°, the solubility increases and then decreases as the temperature rises. At the boiling-point of water, in a steam boiler working under the usual pressure, calcium sulfate is nearly insoluble; and under such conditions, it is precipitated from water which contains much of this substance, in the form of a scale which clings closely to the boiler. Hard boiler scale often consists largely of calcium sulfate. Waters containing this substance are said to have permanent hardness in distinction from temporary hardness due to the bicarbonate. The addition of the proper amount of sodium carbonate will precipitate the calcium as carbonate and leave a solution of sodium sulfate. In this way the permanent hardness may be removed.

**Calcium Sulfide.**—Calcium sulfide, CaS, is made by heating the sulfate with charcoal. It is a by-product of the Le Blanc soda process, and is insoluble in water; but is slowly hydrolyzed forming calcium hydroxide and the hydrosulfide,



Many specimens of calcium sulfide especially if slightly impure with compounds of vanadium and bismuth will phosphoresce, *i.e.*, shine in the dark, after being exposed to the light. The pure sulfide does not do this.

**Calcium Phosphate.**—The principal form in which calcium

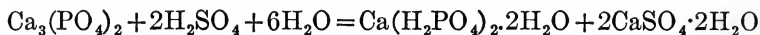
phosphate occurs in nature is apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , or  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ , or isomorphous mixtures of the two. Apatite is found widely distributed being present in small quantities in practically all rocks and all fertile soils. It is sometimes, although rarely, found segregated into large reefs or veins. Commercially important deposits of this character are found in Canada, Norway, and Spain.

Apatite is insoluble but is slowly attacked by the carbonic acid in natural waters, and the calcium and the phosphoric acid pass into solution. Compounds of phosphorus are absolutely indispensable to all forms of life. Animals derive what they need principally from the plants, and the latter take theirs from the soluble phosphates furnished by the weathering of the apatite contained in the soil as described above. Some idea of the importance of calcium phosphate for animals may be obtained from the fact that it constitutes about 83 per cent. of the mineral matter of their teeth and bones. A part of the phosphoric acid which passes into solution during the weathering of apatite finds its way into the sea and there is taken up by the numerous organisms and concentrated in their bones and shells. Great deposits of the remains of these animals have been formed and are found at various places on the earth's surface. These deposits are now among the most available and important sources of phosphorus compounds. The composition of the phosphate in them varies between that of apatite and that of normal calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ ; the whole material is called phosphorite. Similar deposits are found in connection with guano, the decomposed droppings of birds or bats.

As mentioned above plants have an imperative need for soluble phosphates for their growth, and although most soils contain in the aggregate large quantities of apatite, the action of the weather in rendering this soluble is too slow to meet the demands of the crops under intensive cultivation and hence the plants must be fed with ready prepared soluble phosphates. For this purpose 4,616,434 tons of phosphate rock were mined in 1909. Of this quantity, the United States furnished 2,367,434 tons. The production is rapidly increasing so that in 1910 the United States produced 2,654,988 tons, of which nearly 1,100,000 tons were exported.

South Carolina, Florida, and Tennessee are the principal producing states, but very extensive deposits are known in Utah and the neighboring states which will ultimately have to supply a large part of the world's demands. These phosphate beds constitute one of our most important resources, and it is to be regretted that it is necessary to export so large a quantity, since once gone it cannot be regained. The farmers of the prairie regions are accustomed to think that their soils are inexhaustible and that no fertilizers are necessary for them; but it has been demonstrated beyond question by actual results obtained on the farms, that it pays distinctly to use phosphate fertilizers on even the best of the prairie corn lands of Illinois, and there can be little question but that it would pay in other parts of the country also.

The phosphate fertilizers are made by mixing approximately equal quantities of phosphorite and chamber-sulfuric acid. The dihydrates of calcium sulfate and monocalcium phosphate are formed as shown in the following equation:



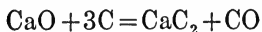
This reaction takes place with the evolution of heat, and the mixture soon solidifies to a mass composed of the two hydrated salts. This is known as superphosphate. The monocalcium phosphate is easily soluble in water, and is the more valuable part of the fertilizer.

Besides the tricalcium phosphate or normal phosphate as it is called,  $\text{Ca}_3(\text{PO}_4)_2$ , there is known the dicalcium salt,  $\text{CaHPO}_4$ , and the monosalt given above. When disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ , is added to a calcium salt in solution, an amorphous precipitate which approximates to the normal salt in composition is thrown down. This gradually changes on standing, or more quickly upon slight acidulation, to crystals of the dicalcium salt. From more strongly acidulated solution, the monocalcium salt may be obtained. All the calcium phosphates are readily soluble in acids, even in those as weak as acetic acid. This is due to the fact that phosphoric acid is weak and that ion,  $\text{H}_2\text{PO}_4^-$ , is formed with especial ease. The calcium salt of this ion is easily soluble as has been mentioned above.

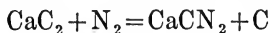


Besides being made into fertilizers, calcium phosphate serves as the source of phosphoric acid and phosphorus.

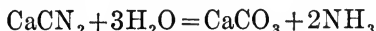
**Calcium Carbide and Calcium Cyanamide.**—Calcium carbide,  $\text{CaC}_2$ , is formed by the reaction of carbon upon lime in an electric furnace. The equation for the reaction is,



The carbide reacts with water producing acetylene, and with nitrogen for the formation of calcium cyanamide,  $\text{CaCN}_2$ ,

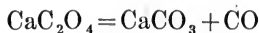


This reaction takes place at  $1000^\circ$  and goes more readily in the presence of calcium chloride. Calcium cyanamide is slowly decomposed by water, forming the carbonate and ammonia,

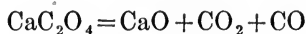


It is therefore useful as a nitrogen fertilizer, and is now being made at Niagara Falls and Mussel Shoals in the United States, and in all about 19 different places in the world. While the nitrogen fertilizers are very important, they are not as absolutely indispensable as the phosphates and potassium fertilizers are since it is practical to introduce the nitrogen compounds into the soil with leguminous plants.

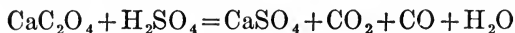
**Calcium Oxalate.**—Calcium oxalate,  $\text{CaC}_2\text{O}_4$ , is a white crystalline salt which is very slightly soluble in water and is formed at once whenever a solution of an oxalate is added to a calcium salt. The precipitate is practically insoluble in water and in acetic acid, but dissolves easily in strong acids like hydrochloric and nitric. The explanation for the difference is to be found in the fact that oxalic acid is a stronger acid than acetic, but weaker than hydrochloric. It will be recalled that the difficultly soluble salts of weak acids are soluble in the stronger acids because of the decrease in the concentration of their anion due to the formation of the undissociated weak acid. The slight solubility of calcium oxalate is made use of in the detection and estimation of calcium as ion. The oxalate reagent used is ammonium oxalate. For the quantitative determination, the calcium oxalate is converted into the carbonate, the oxide, or the sulfate, before it is weighed. The carbonate is obtained by gently heating the oxalate,



To get the oxide, the oxalate is strongly heated, ignited as it is called,

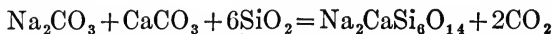


The sulfate is made by heating the oxalate with sulfuric acid,



**Calcium Silicate and Glass.**—Calcium silicate occurs in nature in almost all of the natural silicates. The meta silicate,  $\text{CaSiO}_3$ , forms the mineral wollastonite, but is not of much importance.

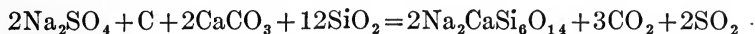
The artificial complex silicates known as glass are, however, of great importance. The most common of these, that known as soft or soda glass, is made from calcium carbonate, sodium carbonate, and glass sand, which is nearly pure silicon dioxide. The equation is,



The substances are mixed in the proper proportions and heated to a temperature below their melting point when the reaction takes place, and most of the carbon dioxide escapes through the porous mass. The temperature is then raised to about  $1200^\circ$  when the glass fuses to a mobile liquid which is fluid enough to allow the bubbles of gas to escape. The temperature is then lowered to  $700$  to  $800^\circ$  when the glass becomes viscous enough to work. Ordinary window glass is made by blowing long cylindrical bulbs of glass. After the bulb is blown to the proper dimensions the bottom is heated and blown out leaving a long cylinder with a bottle-like top and neck. This is allowed to cool and the top cut off by wrapping a string of hot glass around the cylinder near the top and suddenly touching a heated spot on the cylinder with a cold iron. A crack instantly extends round the cylinder following the line heated by the string of hot glass. The result is a long glass cylinder open at each end. This is then split lengthwise by running a red hot iron through the cylinder a time or two and touching the heated glass at the end with a cold iron. The crack instantly runs the whole length of the cylinder. This is then placed upon a flat revolving bed of a furnace upon which

it is smoothed out after being heated to the softening point. Bottles are blown into moulds, but flasks, beakers, etc., are made free hand without any moulds, the glass blower taking advantage of the fact that the surface tension of the glass will cause it to contract when heated, while he can make it expand at will by blowing into the vessel when it is hot. Glass tubing is made by rapidly drawing out a hollow mass of glass. This is done by two men who walk or run in opposite directions. Pressed glass articles are made by pressing the hot glass in moulds having the desired designs cut upon them. The designs in cut glass are worked into the glass with rapidly revolving wheels, armed with wet sand which quickly cuts away the glass. The surface is afterward polished. Plate glass is made by casting the glass into large sheets which are ground until the sides are plane and parallel, and then polished.

The cheaper kinds of soda glass are often made from sodium sulfate, carbon, calcium carbonate, and sand, the equation being,



Soda glasses are rather easily attacked by water, and for many chemical purposes the more difficultly soluble and less fusible potassium glass is made; this is practically the same as the soda glass except the potassium has taken the place of the sodium. Its composition may be represented by  $\text{K}_2\text{CaSi}_6\text{O}_{14}$ . It is commonly called hard or Bohemian glass. Curiously enough a glass composed of a mixture of soda and potash glass is more soluble than one containing either alone.

Many special glasses are made in which the sodium, potassium, and calcium are replaced more or less completely by lead, magnesium, zinc, barium, antimony, arsenic, aluminum, lithium, didymium, thallium, iron, manganese; and the silica by boric or phosphoric oxides. Flint glass, crystal glass, and Strass are potassium lead glasses and have great brilliancy and a high index of refraction. They are easily attacked by water and acids, and are not suitable for chemical purposes, but are used in optical instruments. One kind of Jena glass is especially resistive to chemical action and is a borosilicate glass containing zinc and barium.

Molten glass will dissolve many metallic oxides which often

impart characteristic colors. Cobalt gives blue, chromium and copper oxides green, uranium yellow with a greenish fluorescence, cuprous oxide with a reducing agent, and metallic gold a deep red color due to a colloidal solution of the metals. Milk glass is made by adding bone ash (calcium phosphate) or stannic oxide,  $\text{SnO}_2$ , to the glass. These do not dissolve, but make the glass white and opaque.

Glass is an amorphous substance, and has no definite melting point; it simply gradually softens as the temperature is raised. This has led many to consider glass at ordinary temperatures as a very viscous liquid, but it certainly is highly elastic and has the general properties of a solid. When glass is kept for a long time at temperatures near its softening point, it gradually becomes crystalline or devitrifies as it is called. With certain kinds of glass, this seriously interferes with its working.

All thick glass objects, especially if of irregular shape, must be cooled very slowly, annealed as it is called. If cooled quickly, the outside will harden while the inside is still soft; upon further cooling, the interior tends to contract and this puts great stress upon the glass and makes it extremely likely to crack. A piece in this condition will often fly into minute fragments when scratched at any point on the surface.

**Analytical Properties of Calcium.**—The more important analytical properties of calcium have been given in connection with the oxalate. In addition it may be mentioned that volatile calcium compounds, the chloride for example, color the Bunsen flame brick red and give a red and a green band in the spectro-scope, see frontispiece. The latter test is quite sensitive.

### STRONTIUM

Strontium is the second member of the alkaline Earth metals, if they are arranged in the order of their combining weights.

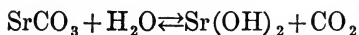
Both the physical and chemical properties of the element and of its compounds closely resemble those of calcium and the calcium salts. It is, however, much less abundant and is relatively unimportant.

The existence of the element was established by Hope in 1792, but the metal was first isolated in 1808 by Davy. It may be prepared by the electrolysis of the fused chloride.

The metal is silvery white and crystalline. It melts at 800° and volatilizes at 950° in vacuum. The density is 2.5. It is more rapidly oxidized in air than calcium and decomposes water and alcohol. It dissolves very rapidly in acids. When heated in oxygen it burns with a bright red flame. It combines with most of the non-metallic elements. The combining weight of strontium is 87.63.

**Occurrence.**—Strontium occurs in nature as strontianite; the carbonate,  $\text{SrCO}_3$ , isomorphous with aragonite and as celestite,  $\text{SrSO}_4$ , isomorphous with anhydrite,  $\text{CaSO}_4$ .

**The Compounds of Strontium.**—The compounds of strontium are made either from the naturally occurring carbonate or sulfate. They are all white unless the anion is colored. The salts may be obtained by simply treating the carbonate with the acid of the desired salt, but the sulfate must first be converted into the sulfide by reduction with carbon at a high temperature, and then treated with the acid. Strontium chloride,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , is a very soluble deliquescent salt, but is not as soluble as the corresponding calcium compounds. The nitrate,  $\text{Sr}(\text{NO}_3)_2$ , crystallizes anhydrous from hot solutions, but has four moles of water of crystallization when it separates at ordinary temperatures. The anhydrous salt was formerly mixed with potassium chlorate and sugar, or charcoal and sulfur to make "red fire," but at present lithium salts have almost completely replaced it. The oxide  $\text{SrO}$  may be obtained by heating the carbonate, but the temperature of decomposition is higher than with calcium carbonate. It is generally made by decomposing the nitrate or hydroxide. Strontium hydroxide,  $\text{Sr}(\text{OH})_2$ , is one of the most important compounds of strontium, and is made by passing superheated steam over the carbonate,



This reaction takes place at a lower temperature than that for the oxide, partly because of the reduction of the partial pressure of the carbon dioxide by the steam, and partly because of the immediate transformation of the oxide into the hydroxide, a change which is accompanied by a decrease in free energy which may assist the decomposition of the carbonate.

Strontium hydroxide is more soluble in water than calcium

hydroxide. It crystallizes from the solution with 8 moles of water forming  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

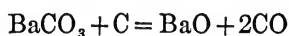
Strontium carbonate is even less soluble than calcium carbonate, and like the latter is more soluble in water containing carbon dioxide owing to the formation of the bicarbonate. The sulfate is much less soluble than the calcium sulfate since 100 grm. of water will dissolve only 0.0114 grm. of  $\text{SrSO}_4$ . The oxalate, however, is more soluble than calcium oxalate. Volatile strontium compounds color the flame carmine red and give a spectrum which consists of a number of strong red lines and a weaker but more characteristic blue line. The spectroscopic test is very sensitive.

## BARIUM

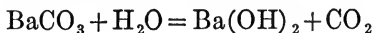
Barium is the third element of the alkaline earth family. It was discovered by Scheele in 1774, but the element was not isolated until 1808 when it was obtained by Berzelius and Pontin and afterward by Davy. The metal is silver white and has a density of 3.78. It melts at about  $850^\circ$  and boils at  $1150^\circ$ . It oxidizes rapidly, sometimes catching fire spontaneously, and decomposes water and alcohol even more vigorously than strontium. It combines readily with hydrogen and nitrogen. The combining weight of barium is 137.37.

**Occurrence.**—Barium occurs in nature principally as barytes or heavy spar which is barium sulfate,  $\text{BaSO}_4$ , and as the carbonate or witherite,  $\text{BaCO}_3$ . From these all the barium compounds are made. They are technically much more important than the corresponding strontium compounds. Barium salts may be obtained by treating witherite with the corresponding acid or by reducing the sulfate to sulfide with carbon at high temperatures, and treating the sulfide with the acid of the desired salt.

**Barium Oxide and Hydroxide.**—Barium oxide,  $\text{BaO}$ , is made by heating the nitrate to a high temperature. It is impractical to prepare the oxide by heating the carbonate alone, since the temperature of decomposition is very high, but a mixture of carbon and barium carbonate reacts easily at a moderate temperature to form barium oxide and carbon monoxide,



The formation of the carbon monoxide aids by reducing the partial pressure of the carbon dioxide. The oxide combines even more readily with water than calcium oxide to form the hydroxide which is often called baryta,  $\text{Ba}(\text{OH})_2$ . Because of this, it is feasible to prepare the hydroxide by heating the carbonate in a stream of superheated steam,

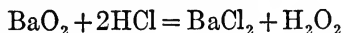


The steam decreases the partial pressure of the carbon dioxide, and the decrease in free energy owing to the formation of the hydroxide aids in the reaction.

The hydroxide is more soluble in water than either the corresponding strontium or calcium compound and is a somewhat stronger base. It crystallizes from its solutions with 8 moles of water,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . These crystals are efflorescent, losing 7 moles of water to the air. Solutions of barium hydroxide are used in quantitative analysis as standard hydroxide solutions, since they have the advantage of always being free from carbonate, owing to the very slight solubility of barium carbonate. The hydroxide has been used in the refining of sugar, but its use is objectionable owing to the highly poisonous nature of the barium compounds.

**Barium Dioxide.**—Barium dioxide,  $\text{BaO}_2$ , is formed when either the oxide or hydroxide is heated in a stream of air. At a higher temperature, or lower pressure of oxygen, it decomposes into oxygen and barium oxide. This was the basis of a process for obtaining oxygen from the air. This process has now been replaced by that founded on the liquefaction of the air.

Barium dioxide is important as the starting point for the preparation of hydrogen dioxide. The method is briefly as follows: The dioxide is dissolved in dilute hydrochloric acid, forming barium chloride and hydrogen peroxide,



Sulfuric acid cannot be used here since the sulfate formed coats the particles of the dioxide, and prevents further action. After the above reaction is complete, a little barium hydroxide solution is added to precipitate the hydroxides of the heavy metals, the solution is filtered, and then an excess of barium hydroxide is

added when a crystalline hydrate of barium dioxide separates,  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ .

These crystals are filtered off and washed and then treated with sulfuric acid. Hydrogen peroxide and barium sulfate are formed. The formation of barium sulfate does not interfere with the reaction between the hydrated dioxide and the sulfuric acid.

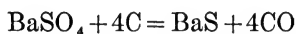
**Barium Carbonate.**—Barium carbonate,  $\text{BaCO}_3$ , as has been mentioned, occurs in nature. It is also formed by bringing together a solution of a carbonate and a barium salt, or by fusing the sulfate with sodium carbonate. It is only slightly soluble, but more so than the carbonates of calcium or strontium. Its solubility in water is increased by the presence of carbon dioxide, owing to the formation of the bicarbonate.

**Barium Sulfate.**—Barium sulfate, barytes,  $\text{BaSO}_4$ , is in some respects the most important salt of barium. It is the chief source of the other compounds, and is itself extensively used as a white pigment, called "permanent white," which is used in paints; for this purpose the native sulfate is ground and treated with sulfuric acid, to dissolve the compounds of iron, etc., which color the sulfate. The product is then washed and dried. The sulfate is very slightly soluble in water, and is precipitated by sulfuric acid and all soluble sulfates when they are added to a solution of a barium salt. The precipitated barium sulfate is more valuable as a pigment than the natural because the particles are smaller and hence it has more "covering" power since it is not so transparent. This precipitated sulfate may be obtained by first dissolving witherite in hydrochloric acid, and then adding sulfuric acid which will precipitate the barium sulfate and regenerate the hydrochloric acid which is then ready to treat another lot of witherite. It may also be obtained by reducing the sulfate to sulfide,  $\text{BaS}$ , by carbon at high temperatures, and treating the extract from this, which will contain the hydroxide and the hydrosulfide, with sulfuric acid. The sulfate has some advantages over white lead as a pigment, in that it is chemically inert and cannot change in color, but it does not "cover" as well.

Barium sulfate is one of the least soluble salts; 100 grm. of water will dissolve 0.00026 grm. of the salt at  $25^\circ$ .



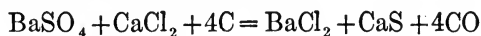
**Barium Sulfide.**—Barium sulfide, BaS, to which frequent reference has been made, is prepared by the interaction of carbon and the sulfate



It is slowly attacked by water, forming the hydroxide and hydrosulfide.

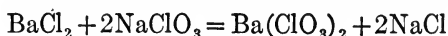
Barium sulfide is phosphorescent when it contains certain impurities, although the pure compound is not.

**Barium Chloride.**—Barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , is made by heating a mixture of the sulfate with carbon, calcium carbonate,  $\text{CaCO}_3$ , and calcium chloride,  $\text{CaCl}_2$ ,



The furnace product is treated with water to dissolve the barium chloride, which is purified by recrystallization. It is not as soluble as calcium chloride and is not deliquescent. It is much used as a reagent for the detection and determination of the sulfate ion. Like all the other soluble barium salts it is highly poisonous.

**Barium Chlorate.**—Barium chlorate,  $\text{Ba}(\text{ClO}_3)_2$ , is made by heating together, in solution, barium chloride and sodium chlorate



It is used in making green fire.

**Barium Nitrate.**—Barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , is made by the action of nitric acid upon the carbonate, sulfide, oxide or hydroxide of barium. It crystallizes as the anhydrous salt and sometimes is used in colored fire. It is used in the preparation of the oxide as noted above.

**Barium Chromate.**—Barium chromate,  $\text{BaCrO}_4$ , is precipitated by bringing together a barium salt in solution and a soluble chromate or dichromate. It has a yellow color and is one of the few colored barium salts. It is but slightly soluble in water and weak acids, but dissolves in strong acids. The chromates of calcium and strontium are very much more soluble than barium chromate, and advantage is taken of this in the analytical separation of the elements.

**Analytical Properties of Barium.**—The properties of barium

which are made use of in analysis are the slight solubility of the carbonate, sulfate, and chromate together with the green color which it will impart to the Bunsen flame, and the spectrum which consists of a number of orange and green lines. These are much less intense than the lines of calcium and strontium so that this test is not very sensitive. In the separation of the group the members are precipitated together as the carbonates. The precipitate is then dissolved in acetic acid and potassium bichromate added which precipitates barium chromate. The solution is filtered and a dilute solution, 5 grm. per liter, of potassium sulfate added. Since strontium sulfate is much less soluble than calcium sulfate, the concentration of the sulfate as ion in this dilute solution will precipitate strontium sulfate, but not that of calcium. The solution is then filtered and ammonium oxalate added to precipitate the calcium.

### RADIUM

The remaining member of the group is the very rare element, radium. This was discovered in 1898 by M. and Mme. Curie. It is widely distributed in nature, but always in very small quantities. All rocks and soils seem to contain a very little. It is most abundant in the minerals which contain uranium and there seems to be a more or less definite ratio between the radium and the uranium content of the ores.

The compounds of radium very closely resemble those of barium, and the corresponding compounds of the two elements are often isomorphous. Radium chloride, bromide, carbonate, and sulfate are less soluble than the corresponding barium salts. This decrease in solubility is in accord with its higher combining weight, 226.4. The volatile compounds color the Bunsen flame carmine red and give two beautiful bands in the red, a line in the blue-green and two weak lines in the violet portion of the spectrum. The spectrum of radium is so distinct and characteristic that there can be no doubt but that it is an element. The radium compounds have the very remarkable property of being highly radio-active and of changing spontaneously into other elements, but the discussion of this phase of the subject will be postponed to a later point when the radio-active elements may be considered in a group.

Metallic radium has recently been obtained by first preparing the amalgam through the electrolysis of a solution of radium chloride using mercury as the cathode, and then carefully driving off the mercury by heating in a vacuum. The radium is left behind as a hard silvery white metal. It blackens in the air, due to the formation of a nitride, acts upon water very vigorously, and is rather more volatile than barium. The radio-activity of the metal is the same as that of an equivalent quantity of one of its salts.

**General Relationships.**—The difference between the combining weights of calcium and strontium is 47.56, which is nearly the same as that between strontium and barium, which is 49.74, so that there is for this triplet of elements about the same relationship which exists for potassium, rubidium, and cesium. The difference between the combining weight of radium and that of barium is 89, which is so much larger than the difference between the other adjacent members of the group that it seems probable that there is still another element closely resembling barium which is yet to be discovered. This element should have a combining weight of about 168.

As with the alkali metals, the properties of the elements vary in a regular way with the combining weight as may be seen from the following table.

As the combining weight increases.

The reactivity of the element increases.

The density of the element and compounds increases.

The basic properties of the hydroxide increases.

The solubility of the hydroxide increases.

The solubility of the halogen compounds and nitrate decreases.

The solubility of the sulfate and chromate decreases.

## CHAPTER XXIII

### THE MAGNESIUM SUB-GROUP

The members of this group, glucinum, magnesium, zinc, cadmium, and mercury do not form as well marked a family as the members of the alkaline earth metals.

Glucinum is perhaps even more like the next group than it is like the other members of this and so makes a good connecting link between the two groups. Magnesium, zinc, and cadmium have many points in common but not as many as calcium, strontium and barium. Mercury differs markedly from the others as will be seen when its compounds are discussed. All the members of the group are more readily reduced to the metallic state than are the members of the alkaline earth group and are less active chemically.

### GLUCINUM OR BERYLLIUM

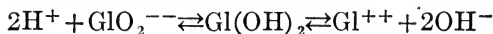
The first member of the magnesium group is glucinum or beryllium as it is called by the Germans. It got the name glucinum from the fact that its salts have a sweet taste and the name beryllium from its occurrence in the gem stone beryl.

The element does not occur free in nature and its compounds are rare. Neither the element nor its compounds have found any application except that some of the latter are used as gems. Beryl, for example, is a double glucinum aluminum silicate,  $\text{Gl}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , which when transparent and green colored is known as emerald and when having a bluish-green tint as aquamarine. The color of emerald is probably due to chromium.

Metallic glucinum may be prepared by the action of reducing agents, such as sodium or magnesium, upon its halogen compounds, or by the electrolysis of the fused double fluorides of sodium or potassium,  $\text{GlF}_2 \cdot \text{NaF}$ . The metal is silver white in color, and has a density of 1.9. It is less active chemically than the metals of the alkaline earth group and decomposes water

only very slowly, even when heated. It dissolves readily in the dilute acids, and in solutions of sodium or potassium hydroxides. Aluminum, the first metal of the next group, shows this same peculiarity and this is but one of several indications that glucinum gives of its position as the connecting element between Groups II and III. It will be recalled that in discussing lithium it was pointed out that the first member of a group often had properties which connected that group with the next higher one.

The salts of glucinum are colorless unless the anion is colored. The chloride,  $\text{GlCl}_2$ , and the sulfate,  $\text{GlSO}_4$ , are the best known. They are both soluble in water and their solutions react acid, owing to hydrolysis. The hydroxide,  $\text{Gl(OH)}_2$ , is a white gelatinous substance which is very slightly soluble in water but dissolves in acids, and also in solutions of sodium or potassium hydroxide. This latter phenomenon seems to be contrary to the rule that the solubility of a salt is decreased by increasing the concentration of one of its ions. The explanation is that glucinum acts both as an acid and as a base and dissociates at the same time into hydrogen as ion and the glucinate ion  $\text{GlO}_2^{--}$ , and also into the glucinum ion and the hydroxyl ion as shown in the following equation:



Of course, a substance which is both an acid and a base cannot be strong in either way. This is in accord with the fact that glucinum hydroxide is a weak base. The solubility of the hydroxide in acids can be easily understood from the above equation as being due to the decrease in the concentration of the  $\text{OH}^-$  while that in bases is due to the decrease in the concentration of the  $\text{H}^+$ . It should be noticed that glucinum is present in this alkaline solution as the glucinate ion,  $\text{GlO}_2^{--}$ , and not as the simple ion  $\text{Gl}^{++}$ . This same behavior is shown by the aluminum hydroxide which is not soluble in water, but is dissolved both by acids and by bases.

When the solution of glucinum hydroxide in sodium hydroxide is allowed to stand for a long time, or when it is boiled, a more stable and less soluble form of the hydroxide is deposited.

Glucinum carbonate is very unstable and decomposes in the air at temperatures below the boiling-point of water into the

oxide and carbon dioxide; in water it goes even more readily into the hydroxide and carbon dioxide. Conditions are especially favorable for hydrolysis, since the carbonate is a salt of a weak acid and weak base. Aluminum carbonate acts in much the same way as also does that of magnesium. Another point of resemblance between glucinum and a member of the magnesium group is found in the fact that zinc hydroxide is soluble in an excess of sodium or potassium hydroxide.

The combining weight of glucinum is 9.1.

### MAGNESIUM

Compounds of magnesium have been known since 1695, when the sulfate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , was discovered by Grew in the water from a mineral spring at Epsom, England. From its place of discovery this substance is called Epsom salts. The compounds of magnesium and calcium were confused for a long time and the distinction was first drawn by Black in 1755. The metal was first obtained, though in an impure state, by Davy.

It occurs very abundantly in nature as a component of a large number of silicates of which mention may be made of olivene,  $\text{Mg}_2\text{SiO}_4$ , serpentine,  $(\text{MgFe})_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , asbestos,  $\text{CaMg}_3(\text{SiO}_3)_4$ , meerschaum,  $\text{H}_2\text{Mg}_2(\text{SiO}_3)_3 \cdot \text{H}_2\text{O}$ , as the carbonate, magnesite,  $\text{MgCO}_3$ , and as a double salt with calcium carbonate,  $\text{MgCO}_3 \cdot \text{CaCO}_3$ , known as dolomite. The sulfates and chloride and mixtures of the double salts are found in Stassfurt. This by no means exhausts the list of its occurrence which might be greatly extended.

**Preparation of the Metal.**—Metallic magnesium is now prepared by the electrolysis of fused dehydrated carnallite,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ . This when heated loses its water and melts at  $700^\circ$  to a good conducting liquid. The electrolysis is carried out in closed electrical furnaces through which a current of hydrogen or coal gas is passed to protect the metal from the air.

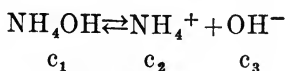
Magnesium is a silver white metal having a density of 1.75. It melts at  $633^\circ$  and boils at  $1000^\circ$ . When heated nearly to its melting-point it softens and may be pressed into wire which can then be rolled into ribbons. It preserves its luster in dry air but tarnishes in moist. When heated in the air it burns with

a very intense light, forming a mixture of the oxide,  $MgO$ , and the nitride,  $Mg_3N_2$ . At a moderately high temperature, the metal decomposes steam, forming hydrogen and the oxide. It will burn in carbon dioxide with the deposition of carbon and the formation of the oxide. As may be judged from these examples, magnesium is an excellent reducing agent.

The light produced when magnesium burns is especially rich in the violet rays which most affect the photographic plates and hence the metal finds application as the active component of "flash powder," which may be prepared from powdered magnesium and potassium chlorate or similar oxidizing agents. With aluminum, it forms useful alloys, that containing 10 per cent. of magnesium known as Magnalium, is like zinc, and that having 15 per cent. like brass, while the alloy having 25 per cent. resembles aluminum bronze. These alloys can easily be cast and worked and are lighter than aluminum.

The combining weight of magnesium is 24.32.

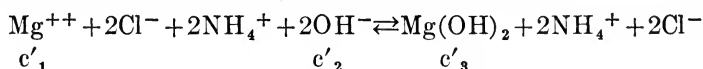
**Magnesium Oxide and Hydroxide.**—Magnesium oxide,  $MgO$ , may be made by heating the hydroxide, but is more frequently prepared from the carbonate, which breaks down into the oxide and carbon dioxide at a much lower temperature than calcium carbonate. The oxide so obtained is known as "calcined magnesia." It is a white, highly infusible substance, which is used as a lining for electric furnaces. It slowly reacts with water to form the hydroxide,  $Mg(OH)_2$ , which is only slightly soluble. The solution has a very faint alkaline reaction, due to the fact that the hydroxide is a weaker base than calcium, as well as being less soluble. One hundred grams of water at  $18^\circ$  dissolve only 0.0008 gm. of the compound. Because of its slight solubility the hydroxide is precipitated when a soluble hydroxide is added to a magnesium salt. An exception to this is found in the fact that if ammonium salts are present in sufficient concentration, magnesium hydroxide is not precipitated by ammonium hydroxide. The explanation is as follows: Ammonium hydroxide is a weak base and the reaction represented by the equation,



takes place only to a slight extent for the formation of ammonium

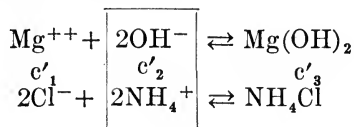
and hydroxyl ions. From the law of mass action,  $c_2c_3/c_1 =$  constant. Ammonium salts are largely dissociated and give a high concentration of the ammonium ion. So, if some salt, say ammonium chloride, be added to an ammonium hydroxide solution, the concentration of the ammonium ion,  $c_2$ , will be increased and this will cause a decrease in the concentration of the hydroxyl ion,  $c_3$ , and an increase in that of the undissociated hydroxide  $c_1$ . Ammonium hydroxide is then a weaker base in the presence of ammonium salts than when alone; and when the concentration of the salt is high, that of the hydroxyl ion becomes very small indeed.

When ammonium hydroxide is added to a magnesium salt, the reaction is represented by the following equation,



The conditions for equilibrium are represented by the equation  $c'_1c'_2{}^2/c'_3 = K$ . Now, before magnesium hydroxide can be precipitated, the solution must be saturated with the substance; which means the  $c'_3$  must have reached a certain definite value; and hence  $c'_1c'_2{}^2$  must have attained a fixed and definite magnitude known as the solubility product or "precipitation value." When ammonium hydroxide is added to a magnesium salt in the *absence* of an ammonium salt,  $c'_2$  is large enough so that  $c'_1 \times c'_2{}^2$  exceeds the solubility product of magnesium hydroxide and this compound is precipitated; but if an ammonium salt is present,  $c'_2$  will be so reduced as shown above that  $c'_1 \times c'_2{}^2$  will be smaller than the solubility product, and  $\text{Mg}(\text{OH})_2$  will not be precipitated. Correspondingly, magnesium hydroxide is dissolved by ammonium salts, such as the chloride or nitrate.

This may be shown as follows:



$$\frac{c'_1c'_2{}^2}{c'_3} = K'$$

The ammonium ion from the salt unites with the hydroxyl ions from the magnesium hydroxide, and thereby decreases  $c'_2$ ; this

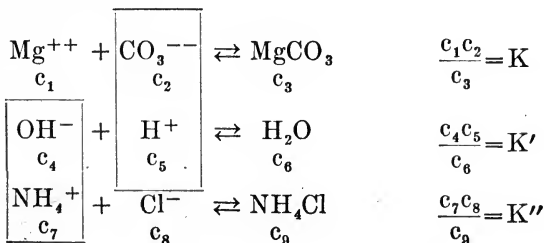


will, of course, decrease  $c'_3$ , and hence increase the solubility of the hydroxide.

Acids would of course act in much the same way and decrease the concentration of the hydroxyl ion through the formation of water. Their action, however, is more vigorous than that of ammonium salts. Many other hydroxides are affected in the same way, so that the general rule may be formulated, that moderately soluble hydroxides will be dissolved by ammonium salts and even very difficultly soluble ones by acids, in each case, because of the decrease in the concentration of the hydroxyl ion.

**Magnesium Carbonate.**—The normal carbonate occurs in nature as magnesite,  $MgCO_3$ . It is but slightly soluble in water, although more soluble than the hydroxide. It forms isomorphous mixtures with calcite. In addition it forms with calcium carbonate a compound called dolomite. This compound is formed by the union of one mole of each carbonate and is a true chemical compound of the type called double salts, while the isomorphous mixtures are solid solutions. Dolomite occurs in enormous quantities in nature.

When a soluble carbonate, such as sodium carbonate, is added to a magnesium salt, a mixture of magnesium carbonate and hydroxide is precipitated. The cause of the precipitation of the hydroxide is found in the fact that the sodium carbonate is hydrolyzed, giving a certain amount of the hydrocarbonate ion, and of the hydroxyl ion, in addition to the carbonate. Then, since magnesium hydroxide is even less soluble than the carbonate, the two salts are precipitated together. This mixed precipitate is soluble in ammonium salts. The reason for the solubility of the hydroxide is given above. The explanation for that of the carbonate may be worked out with the aid of the following interrelated equilibria.



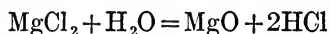
Because of the weakness of ammonium hydroxide, the ammonium ion will combine with the hydroxyl of the water to form undissociated  $\text{NH}_4\text{OH}$ . The decrease in  $c_4$  which this causes is followed by an increase in  $c_5$ , but the hydrogen ion tends to combine with the carbonate ion to produce the hydrocarbonate ion with a consequent decrease in  $c_2$ , and therefore in  $c_3$ . But a decrease in  $c_3$ , the concentration of the undissociated  $\text{MgCO}_3$  in the solution, will make the solution unsaturated and of course more of the precipitate will dissolve.

From this, the general rule that carbonates are more soluble in ammonium salts solutions than in water, and that the moderate soluble ones are dissolved in large quantities by such salts may be readily understood.

Magnesium carbonate is more soluble in water containing carbon dioxide than in pure water, because of the formation of the bicarbonate.

The basic salt prepared by precipitation is washed and dried and put on the market under the name of *magnesia alba*. It is used in medicine as a mild alkali.

**Magnesium Chloride.**—Magnesium chloride,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , is found in the Stassfurt salts and is called *bischofite*; it is very soluble and is highly deliquescent. When it is attempted to dehydrate the salt by heating, decomposition takes place and magnesium oxide and hydrochloric acid are formed as shown in the following equation:



It will be recalled that a tendency toward this same sort of action is shown by calcium chloride. This reaction may become technically important for the preparation of hydrochloric acid, if the Le Blanc soda process is replaced by the Solvay.

Magnesium chloride forms a double salt with potassium chloride,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ , which is known as *carnallite*. It is found in large quantities at Stassfurt. It is important because a large proportion of the potassium chloride of commerce is obtained from it. The magnesium chloride formed at the same time is nearly all thrown away.

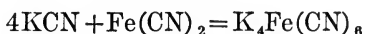
When *carnallite* is heated it loses its water of crystallization readily and the magnesium chloride is not decomposed. An

ammonium magnesium double chloride,  $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ , isomorphous with carnallite is known. This may be dehydrated without decomposition of the magnesium chloride, and when heated to a still higher temperature the ammonium chloride is driven off and anhydrous magnesium chloride is formed.

The term **double salt** has been used a number of times without definition. By it is meant a salt formed by the chemical union of two salts and characterized by the fact that its solution shows the properties of all the ions of the component salts.

A **complex salt** is similar to double salts in that it is formed by the chemical union of two or more salts, but differs in that its solutions do not exhibit the properties of the ions of the salts from which it was formed but instead some of these properties are found to have disappeared and to have been replaced by entirely new properties.

A typical complex salt is potassium ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ . This may be formed by bringing together potassium cyanide, KCN, and ferrous cyanide,  $\text{Fe}(\text{CN})_2$ ,



It might be expected to show the properties of potassium, ferrous, and cyanogen ions, but it shows the properties of potassium as ion and of a new very stable complex ion called ferrocyanogen,  $\text{Fe}(\text{CN})_6^{4-}$ , and not the properties of either ferrous or cyanogen ions. A salt of such a complex ion is called a complex salt. Complex salts and double salts gradually merge into one another, so that the difference is one of degree rather than kind.

Isomorphous mixtures are solid solutions, as has been said before.

**Magnesium Sulfate.**—Magnesium sulfate,  $\text{MgSO}_4$ , occurs in nature as kieserite,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , epsomite,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , schoenite,  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , kainite,  $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ , and in a number of other double salts in the Stassfurt deposits and in other places.

The hepta-hydrate or Epsom salts is an important compound, being used in the manufacture of potassium sulfate from the chloride, as described under potassium, as a dressing for cotton goods, and in medicine is a purgative. It is freely soluble in water,

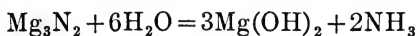
and in this way differs strikingly from the sulfates of the alkaline earths and is like the sulfate of glucinum. The monohydrate is remarkable because of its apparently slight solubility which does not appear to be greater than that of gypsum; but since a paste made of it and water soon sets to a mass of crystals of the hepta-hydrate, it would seem that the slight solubility is more apparent than real and that the monohydrate is actually more soluble than the hepta-hydrate, but simply dissolves slowly.

Schoenite,  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , belongs to a rather large group of isomorphous salts which have the general formula,  $\text{MAO}_4 \cdot m_2\text{AO}_4 \cdot 6\text{H}_2\text{O}$ , in which M stands for Mg, Zn, Cd, Ni, Fe, Mn, and m for K, Rb, Cs,  $\text{NH}_4$ , and A for S, Se, or Cr. These salts are characterized by the fact that they readily lose their water of crystallization, in general without the decomposition of the salt in other ways.

**Magnesium Sulfide.**—Magnesium sulfide,  $\text{MgS}$ , is made by the direct union of the elements. It is even more readily hydrolyzed than calcium sulfide, owing to the smaller solubility and weakness of the hydroxide. By boiling the solution, all the sulfur may be obtained as hydrogen sulfide.

**Phosphates of Magnesium.**—Magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , is the most important phosphate of magnesium. It occurs in nature as struvite, and because of its slight solubility is formed whenever magnesium, ammonium, and phosphate ions are brought together. The solution must be alkaline in order to have a sufficient amount of the phosphate ion  $\text{PO}_4^{---}$  present (see sodium phosphate, p. 357), and hence the solution must contain ammonium salts to prevent the precipitation of  $\text{Mg}(\text{OH})_2$ . The precipitate is of course soluble in acids, since phosphoric acid is weak. This compound is analytically the most important of the magnesium salts, since magnesium is always detected and determined through its formation.

**Magnesium Nitride.**—Magnesium nitride,  $\text{Mg}_3\text{N}_2$ , is formed by the interaction of magnesium and nitrogen at a fairly high temperature. It reacts with water to form ammonia and magnesium hydroxide,



**Analytical Reactions of Magnesium.**—Compounds of magnesium do not color the Bunsen flame, and consequently no spectrum is to be obtained in this way; but by passing electric sparks between pieces of the metal, a characteristic spectrum may be secured. The analytical importance of the magnesium ammonium phosphate has been discussed. The ion and all of its compounds which do not contain colored anions are colorless.

**Water Softening.**—Natural waters almost invariably contain bicarbonates, chlorides, sulfates, and occasionally nitrates of calcium, magnesium, sodium, potassium, iron, and aluminum and also some free carbonic acid and silica. Of course, they sometimes contain other salts and acids in addition. For example, free sulfuric acid is often found in mine waters and in river water in the vicinity of factories using this acid.

Waters which contain calcium and magnesium salts are called hard waters and are a source of considerable annoyance and expense in the household, owing to the fact that calcium and magnesium soaps are practically insoluble, and that before a lather can be produced, soap must be added equivalent to all such salts which are present. The calcium and magnesium soaps so produced form a dirty disagreeable scum and are objectionable from every point of view. Many of the calcium and magnesium salts also cause a great deal of trouble and expense through the formation of "scale" in steam boilers, which not only increases the cost of repairs, but also causes a great waste of fuel. Magnesium salts are somewhat hydrolyzed, owing to the weakness of magnesium hydroxide and hence are acid in reaction. This is often the cause of serious pitting of boilers.

It is very desirable, therefore, that the salts of calcium and magnesium be removed from the waters before they are used for domestic or boiler purposes. This may be readily done at a cost far less than that of the soap, repairs and extra fuel, which would be otherwise required. For the removal of the objectionable salts, advantage is taken of the fact that calcium carbonate and magnesium hydroxide are nearly insoluble in water, and the treatment is so managed that these salts shall be precipitated. This is done by adding the proper amount of slaked lime and of crude sodium carbonate, or soda ash as it is called,

to the water. The quantities to be added are calculated from the analysis of the mineral content of the water. Before treatment, the average water will contain free carbonic acid, bicarbonates, sulfates, and chlorides of magnesium, calcium, and sodium or more correctly, it will contain the corresponding ions. After treatment it will contain sulfate and chloride of sodium and the slight amount of calcium carbonate and magnesium hydroxide corresponding to the solubilities of these compounds, which is so small that it may be neglected.

Now, of course, the treated water will contain all the sulfate and chloride as ion which was in the original water and since there must always be present in every solution equivalent quantities of cations and of anions the number of equivalents of sodium as ion (see p. 189) present in the treated water must be equal to the sum of the equivalents of sulfate and chlorine in the water.

To secure this, there must be added to the original water such a quantity of sodium carbonate as will contain the sodium necessary to make up the difference in the sodium content of the original and of the treated water. This determines the quantity of soda ash,  $\text{Na}_2\text{CO}_3$ , used. For illustration, let us suppose that a certain volume of water contained in addition to calcium and magnesium and hydrocarbonate ions, 3 grm. equivalents of sulfate, 4 grm. equivalents of chlorine and 1 grm. equivalent of sodium as ion before treatment. After treatment, it must contain 3 grm. equivalents of sulfate, 4 grm. equivalents of chlorine and 7 grm. equivalents of sodium. This shows a gain of 6 grm. equivalents of sodium ion which must be furnished by the soda ash. The molar weight of  $\text{Na}_2\text{CO}_3$  is 106 and a gram mole or 106 grm. will yield 46 grm. of sodium as ion or two gram ions or gram equivalents of sodium, so the equivalent weight of sodium carbonate is one-half the molar weight and, therefore,  $6 \times 106/2 = 318$  grm. of sodium carbonate must be added.

The calculation of the weight of slaked lime that must be used is equally simple and all that is necessary for an understanding of it is to consider the purpose for which it is added. Such a quantity of the calcium hydroxide is used that it shall furnish enough hydroxyl; first, to neutralize any free acid, including carbonic acid, which may be present; second, to change the hydrocarbonate ion to the carbonate; and third, to

precipitate the magnesium as the hydroxide. No attention need be paid to the calcium, because there will be left automatically in the solution just enough carbonate to precipitate this substance.

So there should be added to the water, along with the sodium carbonate calculated as above, that weight of slaked lime which is equivalent to the sum of the equivalents of  $H^+$ ,  $HCO_3^-$ , and  $Mg^{++}$  which the water contains. For example, if a given quantity of water contains one equivalent of  $H^+$ , three of  $HCO_3^-$ , and two of  $Mg^{++}$ , there should be added to it  $1 + 3 + 2 = 6$  equivalents of slaked lime. But, since calcium is divalent, a mole of calcium hydroxide,  $Ca(OH)_2$ , or 74 parts by weight of  $Ca(OH)_2$ , contains two equivalents and, therefore, the weight of slaked lime necessary is  $6 \times 74 / 2 = 222$  parts by weight.

Water analyses made for scientific purposes are usually expressed in grams of the various ions per liter. But water softening is now carried out by all the leading railroads and many of the manufacturing concerns, and the analyses made by them are usually expressed in terms of grains per gallon of the various salts which it is imagined the water contains. Since in this case, the calculation of the chemicals needed for softening is more complicated than for the other, an example of it will be given.

The following is a specimen analysis of a water which is softened by lime, soda ash treatment.

Hypothetical salts	Grains per gallon	Grain equivalents per gallon
$H_2CO_3$ .....	1.24	.020 <sup>1</sup>
$Ca(HCO_3)_2$ .....	25.90	.320
$CaSO_4$ .....	16.09	.237
$MgSO_4$ .....	19.65	.328
$MgCl_2$ .....	1.61	.0339
$Na_2SO_4$ .....	3.76	.0530

Grain equivalents per gallon may be obtained by dividing the grains per gallon by equivalent weight, *i.e.*, by the molar weight divided by the valence of the highest valent ion.

<sup>1</sup> Assuming that  $H_2CO_3$  dissociates into  $H^+ + HCO_3^-$ .

Now the number of equivalents of any given ion is equal to the sum of the equivalents of the salts containing that ion; for example, the number of equivalents of calcium is the sum of that for  $\text{Ca}(\text{HCO}_3)_2$  (.320) and that for  $\text{CaSO}_4$  (.237) or .557.

Expressing this data in equivalents of each ion present, we have:

Cations	Grain equivalents per gallon	Anion	Grain equivalents per gallon
$\text{H}^+$ .....	.020	$\text{HCO}_3^-$ .....	.340
$\text{Ca}^{++}$ .....	.5570	$\text{SO}_4^{--}$ .....	.618
$\text{Mg}^{++}$ .....	.3619	$\text{Cl}^-$ .....	.0339
$\text{Na}^+$ .....	.0530		
Total.....	.9919	Total.....	.9919

The weight of sodium carbonate which must be added per gallon may now be calculated by adding together the equivalents of  $\text{SO}_4^{--}$  and  $\text{Cl}^-$  and subtracting that of  $\text{Na}^+$ ,  $.618 + .0339 - .053 = .5989$  gr. equivalents of sodium carbonate to be added or  $.5989 \times 106/2 = 31.74$  gr. of sodium carbonate per gallon.

But the result is usually expressed in pounds per 1000 gallons, and since there are 7000 gr. per avoirdupois pounds this becomes,

$$\frac{31.74 \times 1000}{7000} = 4.55 \text{ lb. Na}_2\text{CO}_3 \text{ per 1000 gallons of water.}$$

The weight of the lime is calculated by adding together the equivalents of the hydrogen, hydrocarbonate, and magnesium and multiplying by the equivalent weight of slaked lime which is 37. In this case it is  $(.020 + .340 + .3619)37 = 26.71$  gr. of  $\text{Ca}(\text{OH})_2$  per gallon, or

$$\frac{26.71 \times 1000}{7000} = 3.82 \text{ lb. of Ca(OH)}_2 \text{ per 1000 gallons of water.}$$

Since soda ash is worth approximately 1 cent per pound and slaked lime about one-quarter of a cent, the chemicals for the treatment of 1000 gallons of water will cost 5.50 cents. This water was a rather bad one, so that the cost of treatment is fairly high. Ten softening plants on the Union Pacific Railroad



treated 1,441,000 gallons a day at an average cost of 1 1/8 cents per 1000 gallons, removing 2790 lb. of solids per day, the greater part of which would otherwise have gone into boiler scale. In carrying out the operation, the slaked lime is mixed with the sodium carbonate and the mixture pumped into the treating tanks in proper proportions along with the untreated water. Precipitation takes place slowly, especially in the winter, because it is done in the cold, so time is allowed for completion and settling.

What promises to become an important method for softening water is based upon the fact that when a hard water is filtered slowly through a bed of artificial zeolite,  $\text{NaAlSiO}_4 \cdot 3\text{H}_2\text{O}$ , called "permutite" the calcium, magnesium, manganese, and iron are automatically removed and replaced by sodium from the zeolite. The filtering medium becomes exhausted, but may be rejuvenated by treatment with a strong solution of sodium chloride which reverses the action and dissolves the calcium magnesium, etc., replacing them by sodium.

## ZINC

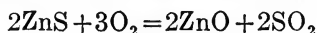
**General and History.**—Starting with glucinum, zinc is the third member of the magnesium sub-group. It does not occur as abundantly in nature as magnesium, but is of far more importance technically. The world's annual production of metallic zinc is about 880,000 tons, of which the United States furnishes about 30 per cent.

Compounds of zinc were known to the ancients, and were heated with copper in order to prepare the alloy of zinc and copper known as brass which has been in use from prehistoric times. The metal itself has been prepared since the sixth century in China, and was first brought into Europe from the far East. Its European manufacture began in England in 1730. Its early discovery in China need not surprise us, because their civilization is much older than ours and many chemical processes were known there long before they were rediscovered in Europe.

**Occurrence.**—It has been reported that zinc occurs free in nature, but the evidence is by no means conclusive. The principal ores of zinc are the sulfide,  $\text{ZnS}$ , known as sphalerite,

blende, rosin-jack, or black-jack; the carbonate,  $\text{ZnCO}_3$ , called smithsonite, zinc spar and sometimes calamine; the silicates, calamine,  $\text{Zn}_2\text{H}_2\text{SiO}_5$  and willimite,  $\text{Zn}_2\text{SiO}_4$ ; and franklinite,  $(\text{FeZnMn})(\text{FeO}_2)_2$ , a compound analogous to the spinels. Many other compounds of zinc have been found in nature.

**Metallurgy.**—The ores which contain the silicates or oxides of zinc merely require drying to remove the water before they are ready for reduction, but the carbonate should and the sulfide must be converted into the oxide before further treatment. The carbonate changes to the oxide when heated to a very moderate temperature, being like magnesium carbonate in this respect. The sulfide must be roasted in the presence of air when the oxide and sulfur dioxide are formed:



A part of the sulfur dioxide so produced is used to make sulfuric acid, and now furnishes about 250,000 tons of this substance per year.

After getting the zinc in the form of anhydrous silicate or oxide, the next step is to reduce with carbon. The temperature of reduction is about  $1200^\circ$ , while the boiling-point of zinc is  $930^\circ$ ; hence, the zinc will be vaporized as rapidly as formed, and provision must be made to catch and condense the vapors. Zinc vapors will burn in the air to zinc oxide and will react vigorously with water vapor or carbon dioxide to form zinc oxide and hydrogen or carbon monoxide; therefore, the conditions of working must be such as to avoid the presence of water and carbon dioxide.

These conditions are met by carrying out the reduction in cylindrical fire clay retorts about 11 in. in diameter and 50 in. long, which are charged with 47 lb. of ore and 28 lb. of carbon in the form of coal or coke. In some plants there are 640 retorts to a furnace. The carbon is largely in excess, enough to reduce any carbon dioxide that may be found before it acts on the zinc. The equations are:

- (1)  $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$
- (2)  $2\text{ZnO} + \text{C} = \text{Zn} + \text{CO}_2$
- (3)  $\text{CO}_2 + \text{C} = 2\text{CO}$
- (4)  $\text{Zn} + \text{CO}_2 = \text{ZnO} + \text{CO}$

The last is the one that it is desired to suppress by adding the excess of carbon.

When the condenser is cold, that is below  $419^{\circ}$ , the zinc collects in the form of a fine powder which contains a few per cent. of the oxide, and is known as zinc dust; when it is above  $419^{\circ}$  and below  $550^{\circ}$ , the zinc collects in the liquid state and is tapped off and cast into moulds forming what is known as spelter. Above  $550^{\circ}$ , the vapor pressure of the zinc becomes so great that the condensation is too incomplete for economical working.

Under the best working conditions, the loss is great, as indicated by the bluish-green color of the flames burning at the mouths of the condensers, and the great amount of zinc oxide fumes which are given off and lost. In fact, zinc smelting is the most wasteful of metallurgical operations, a yield of 90 per cent. is the best which has ever been obtained and 80 per cent. or lower is not uncommon. It may be that the refuse from the present zinc smelters will be worked over with profit at some future date. The cost of fuel for the process is comparatively great, and consequently the zinc smelters are located where it is cheapest. Electrolytic processes are possible, but so far have not proved practicable.

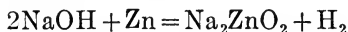
**Physical Properties.**—A fresh surface of pure zinc is brilliantly white, but quickly tarnishes and then has the familiar bluish-gray tinge. It melts at  $419^{\circ}$  and boils at  $930^{\circ}$ . Cast zinc is crystalline and very brittle, but when heated to between  $100^{\circ}$  and  $150^{\circ}$ , it becomes malleable and may be rolled into thin sheets or drawn into wire. At about  $200^{\circ}$  it again becomes brittle and may be powdered in a mortar. The density of the cast zinc is about 6.93 and of the rolled 7.18.

**Chemical Properties.**—Zinc belongs to the more active of the elements, but is far less so than the alkali or alkaline earth metals. It is not affected by dry air at ordinary temperatures, but burns brilliantly above  $500^{\circ}$ . In ordinary air which contains water vapor and carbon dioxide, it quickly becomes covered with a basic carbonate which acts as a protective coating and keeps the rest of the metal from further corrosion. Pure zinc is neither affected by water nor by dilute sulfuric acid.

If a piece of pure zinc lying quietly in dilute sulfuric acid without any perceptible evolution of hydrogen be touched with a piece

of copper, platinum, carbon, etc., the evolution of hydrogen will instantly begin at a rapid rate; but the hydrogen will be given off from the copper, etc., and not from the zinc, and yet the latter will waste away, while the copper is unchanged. The explanation usually offered is this: The hydrogen ion tends to oxidize the zinc to zinc ion, but the hydrogen thereby liberated has great trouble to get away in the form of bubbles from the surface of the zinc, and therefore collects on the metal until it forms a complete protective coating and prevents further action. If now the zinc be touched with a piece of copper, the following may take place: The hydrogen ion may give up its charges to the copper and go over into the gas which has little difficulty in escaping from the copper. The positive charges given to the copper by the hydrogen may flow from the copper to the zinc and change the latter into zinc as ion, thus doing indirectly what could not be done directly. Commercial zinc dissolves readily in acids because there are always enough impurities on the surface to furnish points for the easy escape of hydrogen.

Pure zinc is soluble in nitric acid, because the latter is a strong oxidizing agent and acts directly without first liberating hydrogen. Of course, in this case, water and oxides of nitrogen or even ammonia are formed instead of hydrogen. Concentrated sulfuric acid acts on zinc with the production of sulfur dioxide and zinc sulfate. Sodium or potassium hydroxide will slowly dissolve zinc forming hydrogen and zincate:



Zinc is used in making brass, which is 63 to 70 per cent. copper and 37 to 30 per cent. zinc; in many other alloys; in electric batteries; and especially in galvanizing iron.

**Galvanized Iron.**—Two-thirds of the 880,000 tons of zinc produced per year goes into galvanized iron, that is, iron coated with a layer of zinc. This resists the action of the weather better than plain iron, because the zinc oxidizes first and so protects the iron. The iron is coated with zinc in three ways: first, by dipping very clean sheets of iron into molten zinc; second, by electrically depositing zinc upon cathodes of iron from properly prepared solutions of zinc salts; third, by the process known as sherardizing, which consists in exposing the cleaned

iron object to the vapors of metallic zinc. In some ways this last method has the advantage, because the zinc and iron adhere better than they do by the other methods.

**Zinc Oxide and Hydroxide.**—Zinc oxide,  $ZnO$ , or zinc white, occurs in nature in impure form in the mineral known as zincite. It is by far the most important manufactured compound of zinc, and is prepared on a very large scale, 59,000 tons per year, either directly from the ores or from the metal. In this country the ores are used exclusively and the process is briefly as follows: the ore, either franklinite or roasted sulfide, is mixed with anthracite coal and charged into a furnace upon a brisk fire of hard coal with a good draft of air; the zinc oxide is reduced, the metal volatilizes, and then is reoxidized, forming a very fine white powder which is carried along with the flue gases until well cooled, and is then collected in cloth bags which act as filters. The product is used as a pigment in paints, in rubber goods, as a starting point for the manufacture of other zinc compounds, and as a base for ointment in medicine. Its largest single use is in paints. It is not as poisonous as white lead, and does not blacken with hydrogen sulfide. A paint containing zinc oxide as the only pigment gets very hard and brittle, so it is unsuited for exterior work; but a mixture of white lead (basic lead carbonate) and zinc white is a great favorite and lasts better than either alone. Rubber goods consume a great deal of zinc oxide, automobile tires alone are said to require 40,000,000 pounds a year.

Zinc oxide is yellow when hot and white when cold. The change is due to a shift in the region of the absorption of light from the invisible to the visible part of the spectrum.

The hydroxide is not formed by the combination of the oxide and water, but may be obtained by adding a soluble base to a zinc salt. It is a white difficultly soluble substance which dissolves either in acids or in an excess of sodium or potassium hydroxide. This is due to the fact that zinc hydroxide not only yields zinc and hydroxyl as ion, but also dissociates to give hydrogen and zincate,  $ZnO_2^{--}$ , ion:



Acids decrease the concentration of the hydroxyl ion, and

bases that of the hydrogen; so either, if strong enough, will dissolve the hydroxide. As will be seen from the above, zinc hydroxide is a weak base, and hence the zinc salts will be acid in reaction when in solution.

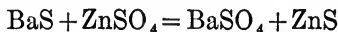
Zinc hydroxide is also soluble in excess of ammonia, due to the formation of a complex zinc ammonia ion,



**Zinc Chloride.**—Zinc chloride,  $\text{ZnCl}_2$ , may be made by the combination of the elements; by the action of hydrochloric acid on zinc, or on the oxide or the carbonate. It is a white, very deliquescent substance, which has a caustic action on the tissues. It melts at  $262^\circ$  and boils at  $719^\circ$ . When a concentrated solution of the salt is mixed with zinc oxide, the whole sets to a hard mass of the oxychloride,  $\text{Zn}(\text{OH})\text{Cl}$ , hence the mixture is used as a cement. Solutions of the chloride have been successfully employed in the treatment of wood to prevent decay.

Zinc chloride either in solution or in the fused state has the power of dissolving the oxides of the metals; so it is used as a flux in soft soldering to clean the surfaces to be joined by the solder.

**Zinc Sulfate.**—Zinc sulfate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , occurs in a hydrated form in nature to a small extent. It is known commercially as zinc vitriol or white vitriol. It may be prepared by the action of sulfuric acid on zinc oxide or metallic zinc or by very careful roasting of  $\text{ZnS}$ . It is a colorless salt, very soluble in water. It finds considerable use in medicine, in dyeing, in the manufacture of glue, and in the preparation of a zinc sulfide and barium sulfate mixture known as lithophone which has been used as a white pigment, but is not durable.



**Zinc Carbonate.**—Zinc carbonate,  $\text{ZnCO}_3$ , occurs in nature as smithsonite or calamine and is of considerable importance as an ore of zinc. A basic carbonate is precipitated upon the addition of a soluble carbonate to a solution of a zinc salt. The precipitate is readily soluble in ammonium hydroxide or an excess of ammonium carbonate, owing to the formation of the zinc ammonia ion, but is not dissolved by an excess of either sodium or potassium carbonates.

**Zinc Sulfide.**—The occurrence of zinc sulfide,  $ZnS$ , in nature has already been discussed. It is commonly known as blende and in its pure state is nearly white, but it shades to brown and even black depending upon the impurities it contains. It may be prepared artificially by heating zinc oxide with sulfur, or in a stream of hydrogen sulfide, by heating zinc filings with cinnabar,  $HgS$ , and by the reduction of zinc sulfate with carbon. It may also be precipitated by the addition of ammonium sulfide or sulfuretted hydrogen to solutions of zinc salts. In this form, it is a fine white amorphous powder and is used as a pigment. Of the ordinary heavy metals, zinc is the only one that forms a white sulfide. It is soluble in dilute acids, and hence must be precipitated from neutral solutions. If the precipitation is to be complete, the concentration of the hydrogen ion must be kept low. This may be done by adding an acetate to the solution. Most of the hydrogen is withdrawn in this way from the solution to form undissociated acetic acid. Zinc sulfide is infusible and very difficultly volatile. Its most important use is in the extraction of the metal.

**Analytical Properties of Zinc.**—Analytically, zinc is in a group with manganese, nickel and cobalt. These all have the common property of being precipitated as their sulfides by ammonium sulfide, but not by hydrogen sulfide in acid solution. Zinc and manganese sulfides are soluble in dilute sulfuric acid, while cobalt and nickel sulfide are practically unaffected. Zinc is distinguished from manganese by the fact that its hydroxide is soluble in an excess of potassium hydroxide, while that of manganese is not. From this alkaline solution, hydrogen sulfide will reprecipitate white zinc sulfide. The color of the sulfide is very characteristic, for it is the only common sulfide of a heavy metal which is white. The facts that the oxide is yellow when hot and white when cold, and that a green mass is formed when the oxide is wet with cobalt nitrate solution and then strongly heated are used in analytical work.

#### CADMIUM

Cadmium is an element which is very closely allied to zinc in its properties and is found in nature in comparatively small

amounts associated with this metal. The boiling-point of cadmium is much lower than that of zinc, consequently it is present quite largely in the first portions of the distillate obtained in the preparation of the latter metal. It may be freed from the zinc by repeated distillations at as low a temperature as possible, in an atmosphere of hydrogen to prevent its oxidation. This product may be further purified by electrolysis, a solution of  $\text{CdSO}_4$  being used as the electrolyte.

The element thus obtained is a bluish-white soft metal of a crystalline structure, density 8.64, melting at  $321^\circ$  and boiling at  $778^\circ$ . The molar weight as determined from the vapor density is very nearly 112.4, the number which represents the combining weight, consequently the formula is Cd.

Cadmium forms but the one simple ion,  $\text{Cd}^{++}$ , which is colorless and very poisonous to all organisms. This ion unites with hydroxyl to form the difficultly soluble hydroxide, a white compound, which is not redissolved on the addition of an excess of sodium hydroxide, but which does dissolve in ammonium hydroxide, due to the formation of the complex ion,  $\text{Cd}(\text{NH}_3)_4^{++}$ .

The **oxide** is a brown powder which may be formed by simply heating the hydroxide or by heating the metal somewhat strongly in the presence of oxygen. This substance dissolves readily in acids and may be used in the preparation of the various salts. Because of its color, the presence of cadmium oxide in zinc oxide is detrimental to the use of the latter in white paints.

The **salts** of cadmium show marked resemblance to those of the other members of the magnesium group; the sulfate, however, crystallizes as shown by the formula  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  and is not analogous to  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  or  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . This salt is used in medicine, but finds more extensive application in the manufacture of "standard cells" for electrical measurements.

Although cadmium sulfate, nitrate, etc., are as highly dissociated as the corresponding salts of other divalent cations, the halogen compounds are but slightly ionized. Zinc shows a tendency in this same direction, and the effect is most pronounced with mercury.

**Cadmium Sulfide.**—Cadmium sulfide,  $\text{CdS}$ , occurs in nature as greenockite and is formed when hydrogen sulfide is passed into a solution of a cadmium salt. This produces as a bright yellow



precipitate which is slightly soluble in strong acids, but is thrown down quantitatively from alkaline solutions. Because of its fine yellow color it is used as a pigment under the name of cadmium yellow. It is not soluble in yellow ammonium sulfide, but does dissolve in the presence of a high concentration of the halogen ions due to the formation of the undissociated cadmium halide. The precipitate is more soluble in solutions of iodides than in chlorides, because cadmium iodide is even less dissociated than cadmium chloride.

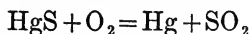
Cadmium hydroxide, also, is soluble in solutions of the alkaline halides for the same reason as the sulfide.

**Analytical Properties.**—Analytically, cadmium is in a group with mercury, lead, bismuth, and copper; in the separation, a solution is finally obtained which contains both copper and cadmium. These are separated by taking advantage of the fact that cadmium sulfide is soluble in strong solutions of common salt while copper sulfide is not or else that copper sulfide is not precipitated from solutions containing potassium cyanide while cadmium sulfide is.

### MERCURY

Mercury or quicksilver as it is often called has been known for so long that the name of its discoverer is lost in antiquity.

**Occurrence.**—It occurs free in nature to a limited extent, but the greatest part of the world's supply is obtained from the native sulfide, cinnabar,  $\text{HgS}$ , which is a red crystalline substance. The most important mines are in Spain, Italy, Austria, and the United States. In the United States, California and Texas are the principal producing states. The world's production amounts to about 3399 tons per year, of which the United States produces about 700 tons. The metal is obtained from the sulfide by roasting in air, when sulfur dioxide and vapors of mercury are formed; the latter are then condensed in air or water-cooled chambers. The equation for the reaction is:



The great simplicity of the chemistry of this process is due to the instability of mercuric oxide at the high temperature of roasting.

The crude mercury is put on the market in wrought-iron flasks holding 75 lb. of metal. It is purified by treatment with 5 per cent. nitric acid, or with sulfuric acid and potassium dichromate, or if it must be very pure by distillation in a vacuum.

**Physical Properties.**—Mercury is a silver-white liquid metal which freezes at  $-39.4^{\circ}$  and boils at  $357^{\circ}$ . Its vapor is transparent and colorless and does not conduct electricity at temperatures near its boiling-point, although it becomes a good conductor at higher temperatures. This property is made use of in the mercury vapor lamps and rectifiers.

The density of the vapor shows that the molar weight of mercury is 200, the same as its combining weight. Mercury has a perceptible vapor pressure even at ordinary temperatures, at  $0^{\circ}$  this is 0.00002 cm. of Hg., at  $100^{\circ}$  it is 0.026 cm., at  $240^{\circ}$  it is 5.69 cm., and at  $300^{\circ}$  it is 24.68 cm. Hg. The density of the liquid is 13.596 at  $0^{\circ}$ .

The metal is much used in physical and chemical apparatus and in the extraction of gold and silver from their ores, since it readily forms amalgams with these metals. Amalgams as the alloys of mercury are called, are formed by nearly all of the metals. Iron and platinum are generally exceptions, but even these may be amalgamated under special conditions.

Pure mercury does not wet glass but runs around on it in clean round drops. When it contains even a small quantity of foreign metal it becomes covered with a film of oxide and then when it runs on glass it strings out or forms a tail. This is a fairly sensitive test for impurities in the mercury.

It is interesting to note that mercury is the only metal which is liquid at ordinary temperatures, although cesium melts at temperatures which are often reached during the summer.

**Chemical Properties.**—Mercury does not oxidize upon exposure to the air at ordinary temperatures, but does so very slowly at about  $300^{\circ}$ , forming mercuric oxide. This fact was of great importance in the development of the present conception of combustion. (See p. 18.)

Mercury combines readily with sulfur and the halogens. It is not attacked by dilute hydrochloric or sulfuric acids, since the hydrogen as ion from these is not a strong enough oxidizing agent to oxidize the mercury to ion. It is dissolved by nitric

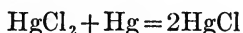
acid or by hot sulfuric acid with the reduction of a part of the acids, and the evolution of nitric oxide or sulfur dioxide instead of hydrogen. Hydrogen sulfide and hydrogen iodide will attack the mercury with the formation of the corresponding salts and hydrogen. In each case, however, the mercury compound formed is especially stable, and its formation is accompanied by a great decrease in the free energy which goes to assist in the evolution of the hydrogen.

The compounds of mercury which are soluble enough to be absorbed by the human system are decidedly poisonous, but mercury in its compact form is not. If, however, the mercury is very finely divided as it is in "blue mass" or in the form of vapor it exhibits its poisonous action whenever taken into the body. Mercury compounds are extremely poisonous toward bacteria and enough of the metal dissolves in pure water to kill these organisms in a short time. As has been mentioned, mercury forms two series of compounds. In the one, it is divalent; and in the other it is at least apparently monovalent. The monovalent compounds are called mercurous and the divalent mercuric salts, and it is through the latter that the element establishes its connection with the magnesium group. The mercurous compounds will be discussed first.

#### MERCUROUS COMPOUNDS

**Mercurous Oxide.**—Mercurous oxide,  $\text{Hg}_2\text{O}$ , is a blackish-brown substance which is formed by the action of an excess of sodium or potassium hydroxide upon a mercurous salt. It is not soluble in water and is very unstable, breaking down under the action of light or moderately high temperature into mercury and mercuric oxide. Mercurous hydroxide is unknown.

**Mercurous Chloride.**—Mercurous chloride or calomel,  $\text{HgCl}$  or  $\text{Hg}_2\text{Cl}_2$ , is the most important mercurous salt. It is very difficultly soluble in water and may be precipitated by adding hydrochloric acid or sodium chloride to a solution of mercurous nitrate. It is usually prepared by subliming a mixture of mercuric chloride,  $\text{HgCl}_2$ , and mercury,



The vapor of the chloride is run into a condensing chamber

together with steam and there condenses to a yellowish-white powder. The water produced by the condensation of the steam washes away the mercuric chloride which may come over. This is very important, since the mercurous chloride is largely used in medicine and the mercuric chloride is intensely poisonous. The usefulness of calomel as a medicine apparently depends upon the fact that it stimulates the liver and other organs producing the secretions.

When ordinary mercurous chloride volatilizes, the vapor density corresponds to  $\text{HgCl}$ ; but it is at least partially decomposed into  $\text{Hg}$  and  $\text{HgCl}_2$ . How far the decomposition goes it is impossible to say. The carefully dried salt has a molar weight which corresponds to the formula  $\text{Hg}_2\text{Cl}_2$ , and perhaps this should be used to represent the compound.

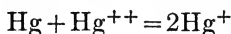
The vapor pressure of mercurous chloride reaches one atmosphere below the melting-point, and therefore the substance sublimes.

Unless very pure, it should be protected from light which decomposes the ordinary salt, forming mercury and mercuric chloride.

**Mercurous Bromide.**—Mercurous bromide,  $\text{HgBr}$ , is precipitated, as a white powder, by adding a bromide to mercurous nitrate.

**Mercurous Iodide.**—Mercurous iodide,  $\text{HgI}$ , may be formed directly from the elements or by precipitation from mercurous nitrate by an iodide. It is unstable and changes into mercury and mercuric iodide. The change takes place easily in the presence of an excess of  $\text{KI}$ , since the latter dissolves the mercuric iodide formed.

**Mercurous Nitrate.**—Mercurous nitrate,  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ , is the most important soluble mercurous salt. It is made by acting upon an excess of mercury with cold dilute nitric acid. It hydrolyzes, forming a basic nitrate,  $\text{Hg}_2(\text{OH})\text{NO}_3$ , which is but slightly soluble. Hence, a clear solution of the salt must contain nitric acid; some metallic mercury should be kept in the solution to reduce any mercuric ion which might form,



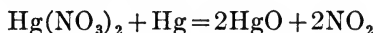
**Mercurous Sulfate.**—Mercurous sulfate,  $\text{Hg}_2\text{SO}_4$ , may be pre-

pared by the action of sulfuric acid upon an excess of mercury, or upon a mercurous nitrate solution. It may also be obtained by the electrolysis of dilute sulfuric acid using mercury as anode. It is white and but slightly soluble in water, but more so than the chloride. It is used in the construction of standard cells for the comparison of electromotive forces.

**Mercurous Sulfide.**—Mercurous sulfide,  $\text{Hg}_2\text{S}$ , is very unstable and can exist only at temperatures below  $-10^\circ$ ; at ordinary temperatures it decomposes into mercuric sulfide and mercury.

### MERCURIC COMPOUNDS

**Mercuric Oxide.**—Mercuric oxide or red precipitate,  $\text{HgO}$ , may be prepared as a red crystalline substance by heating mercury in the air to from  $300^\circ$  to  $350^\circ$ . The process is very slow and the oxide is usually prepared by heating an intimate mixture of mercuric nitrate and mercury until no more red fumes of nitrogen peroxide are given off.



When a solution of potassium or sodium hydroxide is added to a mercuric salt, a yellow precipitate of mercuric oxide is formed. This precipitate is composed of very small crystals, much smaller than the crystals of the red oxide; it is also more active chemically and therapeutically, but whether this is due to its being more finely divided or to its being a different modification of the oxide has not yet been decided.

When mercuric oxide is heated it darkens, becoming almost black, and at a red heat it is decomposed into the elements. It will be recalled that it was through this reaction Priestly discovered oxygen.

Mercuric oxide is very poisonous, but is used in medicine.

Mercuric hydroxide is so unstable that it has not yet been prepared. The mercuric salts of the oxy-acids are highly hydrolyzed, so it must be a very weak base.

**Mercuric Chloride.**—Mercuric chloride or corrosive sublimate,  $\text{HgCl}_2$ , may be made by the direct combination of the elements at a slightly elevated temperature. The combination takes place with a peculiar green flame.

The salt is usually obtained as a crystalline sublimate by heating a mixture of mercuric sulfate, common salt, and a little manganese dioxide, the latter being added to oxidize any mercurous sulfate which may be present.

It melts at  $288^{\circ}$  and boils at  $303^{\circ}$ . Its molar weight corresponds to the formula  $\text{HgCl}_2$ . It is not very soluble in cold water, 7.4 parts per 100 gm. at  $20^{\circ}$ , but is much more soluble in hot. It is soluble in alcohol and ether and a number of other organic solvents. Its aqueous solution is slightly acid, indicating some hydrolysis, but no basic salt is deposited as is the case with mercuric nitrate and sulfate. The explanation for this is furnished in the fact that as indicated by the electrical conductivity, the halogen compounds of mercury are but slightly ionized, while the sulfate and nitrate and the salts of other oxyacids are strongly dissociated. The inevitable results of this would be that the mercuric salts of the oxyacids would hydrolyze further than the halides. In this connection it will be recalled that the halogen compounds of cadmium were less dissociated than the salts of the oxyacids.

When sodium or potassium chloride is added to a solution of mercuric chloride the latter becomes neutral and by evaporation salts of the types  $\text{KHgCl}_3 \cdot \text{H}_2\text{O}$  and  $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$  may be obtained. These salts dissociate in such a way as to leave the complex ion  $\text{HgCl}_3^-$  which is slightly broken down, but gives a smaller concentration of  $\text{Hg}^{++}$  than  $\text{HgCl}_2$ ; and this decrease in the concentration of the mercuric ion, upon the addition of sodium chloride, accounts for the decrease in hydrolysis of the solution, and its consequent neutrality. These complex salts are more soluble than mercuric chloride, so that the solubility of the latter may be increased by the addition of an alkali chloride which is not according to the general rule that an increase in the concentration of one of the ions of a salt will decrease its solubility; but the cause of the exceptional behavior is found in the formation of the complex ion.

Mercuric chloride is stable toward sulfuric acid, and does not evolve hydrochloric acid, even when heated with it; nor does it yield chlorine, with nitric acid as other chlorides do. Both of these facts find an explanation in the slight ionization of  $\text{HgCl}_2$ .

Mercury compounds are highly poisonous to all forms of life,

and mercuric chloride is much used as an antiseptic. For this purpose it is often put up in tablets with sodium chloride which makes it dissolve more rapidly, but weakens its antiseptic powers, since the latter seems to depend upon the concentration of the mercuric ion. The solutions are, however, sufficiently active for all practical purposes. It is used in medicine both internally and externally, but because of its highly poisonous nature must be used very cautiously. Its antidote is white of egg, with which it forms a difficultly soluble compound.

**Mercuric Bromide and Iodide.**—Mercuric bromide,  $\text{HgBr}_2$ , is much like the chloride, but is less soluble in water; it is also less dissociated than the chloride. Mercuric iodide,  $\text{HgI}_2$ , is but slightly soluble in water and is formed as a yellow precipitate which rapidly becomes scarlet when a solution of an iodide is added to a solution of a mercuric salt. One hundred parts of water dissolve .005 part of the salt at  $22^\circ$ . It is more soluble in alcohol and ether. It dissolves freely in solution of potassium iodide forming a colorless very soluble complex salt,  $\text{K}_2\text{HgI}_4$ , which fails to give most of the reactions of mercury; for example, potassium hydroxide does not precipitate mercuric oxide. After the addition of potassium hydroxide, the solution is called Nessler reagent, and is very sensitive toward ammonia which gives a yellow precipitate having the formula  $\text{Hg}_2\text{NI}\cdot\text{H}_2\text{O}$ .

Mercuric iodide exists in the two forms; the scarlet, stable from ordinary temperatures to  $126^\circ$ , and the yellow, stable above this temperature up to the melting-point,  $253^\circ$ . On cooling, the yellow modification persists down to ordinary temperatures, but changes quickly when touched with some of the scarlet or rubbed with a hard object. The yellow always appears first when the iodide is precipitated, furnishing another example of the law of successive reactions.

Mercuric iodide and its complex potassium salt are used in medicine.

**Mercuric Nitrate.**—Mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2$ , is prepared by dissolving the metal in hot nitric acid, and boiling until a portion of the solution does not yield a precipitate of mercurous chloride upon the addition of a chloride. It forms colorless very deliquescent crystals having the composition  $\text{Hg}(\text{NO}_3)_2\cdot\text{H}_2\text{O}$ , easily soluble in water

Its solution is highly acid owing to hydrolysis, and unless an excess of nitric acid is present, a yellow basic salt,  $\text{Hg}_3(\text{NO}_3)_2\text{O}_2$ , is deposited.

**Mercuric Sulfate.**—When mercury is heated with concentrated sulfuric acid, mercuric sulfate,  $\text{HgSO}_4$ , water, and sulfur dioxide are formed. The mercuric sulfate so obtained is a white crystalline salt which is easily soluble in water containing sulfuric acid, but hydrolyzes in pure water forming a yellow basic salt,  $\text{Hg}_3(\text{SO}_4)_2\text{O}_2$ .

It has already been pointed out that mercuric nitrate and sulfate are more hydrolyzed than the halogen compounds, the explanation being that they are more dissociated than the latter. Silver chloride is far more soluble in solutions of mercuric nitrate and sulfate than in pure water, and the explanation is to be found in the decrease of the concentration of the chlorine ion through the formation of undissociated mercuric chloride.

**Mercuric Sulfide.**—The most stable compound of mercury is the sulfide,  $\text{HgS}$ . This exists in the two forms, black amorphous and red crystalline. The latter occurs in nature as cinnabar and is the most important ore of mercury. As is the general rule, the amorphous form is the less stable and the more soluble of the two, but both are exceedingly slightly soluble substances. The black form is precipitated whenever hydrogen sulfide or a soluble sulfide acts upon a mercuric salt. It is somewhat soluble in sodium and potassium sulfide forming in the case of the sodium sulfide a white crystalline compound,  $\text{Na}_2\text{HgS}_2 \cdot 8\text{H}_2\text{O}$ . From this solution the less soluble red crystalline form is gradually deposited. The red crystalline modification may also be obtained by subliming the black.

The artificial red sulfide is called vermilion and is used as a pigment.

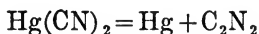
Both forms of mercuric sulfide are very stable and are not attacked by hydrochloric acid or by dilute nitric acid hot or cold. Concentrated nitric acid attacks the black sulfide forming the yellowish-white compound,  $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$ , which is but little more soluble than the sulfide. Corresponding compounds which are also light colored are often thrown down when hydrogen sulfide is first passed into mercuric salt solutions. Mercuric sulfide is dissolved by aqua regia, the sulfur as ion being



liberated as free sulfur or oxidized to the sulfate. Mercuric sulfide is the most stable sulfide of the metals and this is utilized in the analytical separation and identification of the metal.

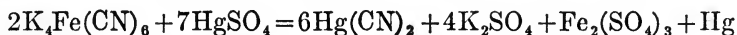
**Mercuric Cyanide.**—Mercuric cyanide,  $\text{Hg}(\text{CN})_2$ , resembles the halogen compounds of mercury in many ways. It is more soluble than the halides, but is even less dissociated than these, and its solution is a very poor conductor of electricity. The molar weight as determined by the lowering of the freezing-point indicates no dissociation. In accordance with this, the solution fails to show most of the reactions of either mercury or cyanogen. Hydrogen sulfide, however, precipitates  $\text{HgS}$  from its solutions. Mercuric cyanide forms a complex salt with potassium cyanide,  $\text{K}_2\text{Hg}(\text{CN})_4$ , analogous to the complex chlorides.

When heated, mercuric cyanide decomposes into mercury and cyanogen,  $\text{C}_2\text{N}_2$ ,



and this furnishes a very convenient way for the preparation of cyanogen.

Because of the slight dissociation of mercuric cyanogen, it is formed whenever a mercury salt and a salt containing even a very small concentration of cyanogen, such as potassium ferrocyanide, are brought together, as shown in the equation for the reaction which is commonly used in the preparation of mercuric cyanide,



**Mercuric Thiocyanate.**—Mercuric thiocyanate,  $\text{Hg}(\text{SCN})_2$ , is a white crystalline substance precipitated by ammonium thiocyanate from mercuric solutions. When dry it burns and leaves behind an exceedingly voluminous ash. This is made use of in the firework called "Pharaoh's serpents."

**Mercury Fulminate.**—When mercury is dissolved in hot nitric acid and alcohol added to the still hot solution, a white precipitate of mercury fulminate,  $\text{Hg}(\text{ONC})_2$ , is soon formed. This, when dry, explodes upon being struck, and is used in percussion caps and in the caps for exploding guncotton and dynamite.

**Complex Compounds of Mercury.**—Mercury forms a very large

number of complex compounds far too large for them all to be considered in detail or even mentioned in a book of this kind. The nitrogen compounds, however, demand a little attention.

**Mercuric Ammonia.**—The mercuric salts react with ammonia to form compounds which may be grouped into three classes: first, those with ammonia of crystallization similar to salts with water of crystallization; second, ammonio basic salts analogous to ordinary basic salts with  $\text{NH}_2$  in place of OH or either NH or N in place of O; third, mixed aquo ammonio basic salts containing both OH or O and  $\text{NH}_2$  or N.

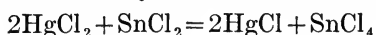
The first class with ammonia of crystallization may be prepared by the action of ammonia in the gaseous or liquid state upon mercuric salts, or by the action of aqueous ammonia upon these salts in the presence of ammonium salts. As examples of these compounds the following may be given:  $\text{HgCl}_2 \cdot 2\text{NH}_3$  [fusible white precipitate],  $\text{HgCl}_2 \cdot 12\text{NH}_3$ ,  $\text{HgI}_2 \cdot 2\text{NH}_3$ ,  $3\text{HgI}_2 \cdot 4\text{NH}_3$ ,  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{NH}_3$ .

The second class, ammonio basic mercuric salts, may be formed by the action of aqueous ammonia upon mercuric salts in the absence of ammonium salts. Examples of these salts are  $\text{HgNH}_2\text{Cl}$  [infusible precipitate],  $\text{Hg}(\text{NH}_2)\text{NO}_3$ ,  $\text{Hg}_2(\text{NH})\text{Br}_2$  and  $\text{Hg}_2\text{NI}$ .

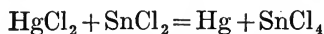
The third class, the mixed aquo ammonio basic salts, are formed under conditions which are more favorable to hydrolysis than those for the preceding classes. The compound  $\text{Hg}_2(\text{OH})(\text{NH})\text{Cl}$  may be cited as an example.

**Analytical Reactions of Mercury.**—Both the mercurous and mercuric ions are colorless, and the former is distinguished from all others by the fact that it will form a slightly soluble white precipitate of mercurous chloride with chlorine as ion which precipitate turns black when treated with ammonium hydroxide.

Both the mercuric and mercurous ions give mercuric sulfide with hydrogen sulfide in acid solution. This precipitate is insoluble in hot dilute nitric acid, but is dissolved by aqua regia. Mercuric salts are reduced by stannous chloride to mercurous salts or even metallic mercury as shown in the following equations,



and



When metallic copper is introduced into a solution of a mercury salt the copper is oxidized to copper as ion and the mercuric ion is reduced to metallic mercury which forms a bright mirror-like coat on the remaining copper.

The mercury salts are all volatile, and when heated with lime or sodium carbonate, give metallic mercury.

**General Relations of the Group.**—As is evident from the discussion given above, the members of the magnesium group do not form as close a family as do the members of the alkali and alkaline earth metals, but still there are some general relationships throughout the group. The increasing stability of the sulfides with increasing combining weight is noticeable. Glucinum and magnesium sulfides are not formed in the presence of water even, while zinc sulfide is stable in the presence of weak acids, but is not in contact with any but very dilute solutions of the strong acids. Cadmium sulfide is stable in the presence of dilute solutions of the strong acids, but is dissolved by concentrated solutions of them and by hot dilute solutions, while mercuric sulfide is stable even against boiling dilute nitric acid and is scarcely attacked by this acid in the concentrated state.

Beginning with zinc, the halogen compounds show a regular decrease in their degree of dissociation with increasing combining weight both of the halogen and of the metal. The melting- and boiling-points of the members of the sub-group become lower as the combining weights decrease.

## CHAPTER XXIV

### COPPER, SILVER AND GOLD

**General.**—Copper, silver, and gold occupy the lower part of the right-hand column of Group I of the periodic system. From their position, they should bear some resemblance to the alkali metals, but from what has been learned concerning the relations between the members of the alkaline earth metals and magnesium sub-group it is evident that the resemblance need not be close. As a matter of fact the divergence is so great that it is necessary to search for points of resemblance. Perhaps the most striking point of similarity is that copper, silver and gold each form a series of compounds in which it is monovalent. In addition copper forms another series in which it is divalent and gold one in which it is trivalent. The following table will give at a glance a comparison of the more prominent properties of the two sub-groups:

The Alkali Metals	The Copper Family
Low density .59–2.4.	High density 8.94–19.4.
Very active chemically.	Decidedly inactive.
Never occur free.	Often found free.
Halogen compounds are soluble.	Nearly all of the halogen compounds of the monovalent series are but slightly soluble.
Strong bases.	Weak bases, except silver.
Do not form complex ions.	Form many complex ions.

#### COPPER

**History.**—Copper has been known from prehistoric times and since it is found free in nature in abundance, it was probably the first metal to be used by man. Before the extensive use of iron, tools were made of bronze, an alloy of copper and tin.

**Occurrence.**—Copper occurs in nature both free and in combination. The native copper is sufficiently abundant so that it constitutes a very important ore as may be judged from the facts

that the region in Michigan near Lake Superior produces about 220,000,000 lb. of copper per year from this source. The compounds which are used as ores may be divided into two classes: the oxidized ores and the sulfide ores. The oxidized ores include cuprous oxide,  $\text{Cu}_2\text{O}$ , which is called cuprite or red oxide; cupric oxide,  $\text{CuO}$ , called melaconite or black oxide; and the basic cupric carbonates, malachite,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , and azurite,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . The sulfide ores include cuprous sulfide,  $\text{Cu}_2\text{S}$ , or chalcocite and the double sulfides of copper and iron known as chalcopyrite,  $\text{CuFeS}_2$ , and bornite,  $\text{Cu}_3 \cdot \text{FeS}_3$ . The sulfide ores are the most important because from them this country produces about 800,000,000 lb. per year out of a total production of nearly 1,100,000,000 lb.

**Metallurgy.**<sup>1</sup>—The method of extracting the copper is different in each of the three classes of ores. If the copper is native the rock containing it is crushed and the copper extracted by mechanical concentration. The product of nearly pure copper is freed from the remaining rock materials by melting in large reverberatory furnaces, and is refined and toughened by a further fusion in which impurities are oxidized and skimmed off, followed by a final stirring with long wooden poles. This process known as “poling” removes traces of copper oxide formed during the refining process, which would greatly injure the ductility and malleability of the metal. The product “Lake Copper,” is very pure and always commands the highest price in the market.

By far the most important deposits of copper ores are the sulfide deposits. The great mines of Montana, Arizona, Mexico, Tennessee, etc., are chiefly producers of sulfide ores, and the metallurgical treatment of such ores is of the greatest importance.

The ores carrying sulfides of copper and iron are found associated with greater or less quantities of barren rock materials or “gangue,” consisting usually of quartz (silica,  $\text{SiO}_2$ ) or of various other silicate minerals. A proper understanding of the smelting process about to be described may be most readily obtained by keeping in mind the following points: First, that

<sup>1</sup> The sections on the Metallurgy of Copper, Silver, Gold and Lead were written for this book by Assistant Professor David F. McFarland, formerly of Kansas, now of the University of Illinois.

copper sulfide is more resistant to oxidation than iron sulfide, so that when a mixture of the two is acted upon by the oxygen of the air, the copper sulfide is not attacked until all the iron sulfide has been changed into the oxide and sulfur dioxide. Second, that copper oxide is more easily reduced than iron oxide. Third, that when some copper oxide has finally been produced by the air's acting on copper sulfide, it will at once react with the latter to form sulfur dioxide and copper.

The smelting process involves a concentration of the sulfides and complete separation of these from the "gangue" by converting the latter into easily fusible silicates (slags) through fusion with calcium and iron oxides. The calcium oxide comes from limestone charged with the ore and the iron oxide from the partial oxidation of the sulfide in the ore.

If the proportions of iron oxide and calcium oxide are properly adjusted to the amount of silica in the ore, the entire mass will melt at a moderately high temperature and the fluid slag will separate from the heavier molten mixture of concentrated iron and copper sulfides which is known as *copper matte*. The matte usually produced carries about 50 per cent. of copper.

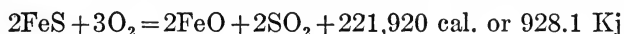
Of the two types of furnaces, blast and reverberatory, used in this concentrating or "matte smelting" only the former will be described. The copper blast furnace is rectangular in cross-section 4 to 5 ft. wide, 10 to 87 ft. long and from 12 to 25 ft. high. The walls of the furnace are built almost entirely of hollow steel jackets which are cooled by water's circulating through them. Air under a pressure of from 3 to 4 lb. is blown in through numerous blast pipes in the walls near the bottom. The ore and flux with the proper quantity of coke for fuel are charged in at the top of the furnace. A very high temperature is attained in the lower part of the furnace, sufficient to liquefy completely the entire contents of this portion. A part of the sulfur in the ore burns and helps to furnish this heat, while the coke gives the rest.

The molten slag and matte are drawn off together from the bottom of the furnace into large fore-hearths or settling basins. The heavy matte settles out from the lighter slag and both are tapped off from here separately. The slag is a waste product, while the matte is further treated to recover its copper.

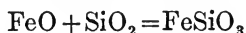
Further treatment of the matte involves the elimination of iron and sulfur and the purification of the impure copper thus produced.

Iron and sulfur are usually removed in the copper converter, which is a large, approximately barrel-shaped vessel resting on a rotating mechanism. The converter has a thick lining of magnesia, MgO. Air at a high pressure is blown into the converter from several blast pipes near the bottom.

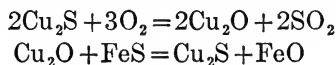
The operation is carried out as follows: Molten copper matte from the blast furnace or the reverberatory furnace is poured into the converter, the necessary amount of silica, SiO<sub>2</sub>, added and the blast started. The large supply of air, oxidizes both iron and sulfur in the matte to iron oxide and sulfur dioxide, thus liberating heat which serves to keep the mass fluid.



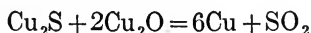
The sulfur dioxide escapes as such, while the ferrous oxide combines with the silica to form ferrous silicate slag,



Some cuprous sulfide is oxidized, but the cuprous oxide formed reacts at once with iron sulfide reforming cuprous sulfide,



After some time, by these reactions, practically all of the iron and part of the sulfur have been eliminated and the copper remains as cuprous sulfide; which by its greater density sinks down below the lighter ferrous silicate slag. This point can be distinctly recognized by the appearance of the flame issuing from the mouth of the converter. The slag is now poured off and the second period of blowing begins. The cuprous sulfide (about 70 per cent. Cu) is now oxidized to some extent, forming cuprous oxide. This reacts with the remaining cuprous sulfide forming sulfur dioxide and metallic copper.



At the completion of this operation only metallic copper remains and this is poured into moulds. It is known as blister

copper and carries practically all of the nickel, gold, silver, and platinum that were in the original ore. It also contains some other impurities and is not fit to be used for most commercial purposes. Further purification is best obtained by means of electrolysis.

**Electrolytic Refining.**—For this process, the crude blister copper is cast into large plates which are used as anodes in electrolytic cells where the cathodes are thin plates of pure copper, and the electrolyte is an acidified solution of copper sulfate. On passing a suitable current through the cells, copper is dissolved from the impure anodes and deposited in nearly pure condition on the cathodes. The impurities in the anode are either dissolved and held in solution in the electrolyte or remain undissolved and fall to the bottom of the cell. Gold, silver and platinum are thus precipitated and are recovered by subsequently melting up the slimes or mud from the bottom of the cells.

The electrolytic copper so obtained is nearly pure. It is melted again and "poled" to remove oxide and then cast into bars for the market.

**Physical Properties of Copper.**—Copper is one of the very few colored metals. In the pure state it has a beautiful yellowish-red color which upon exposure to the air gradually changes to the darker red known as copper color. This change is due to the formation of a film of cuprous oxide,  $\text{Cu}_2\text{O}$ . Very thin layers are translucent and bluish-green in color. The density of the metal is 8.94 and it melts at  $1080^\circ$  and boils at  $2240^\circ$ . The metal is a very good conductor of heat and only silver exceeds it in conductivity for electricity. A large proportion of the copper which is put upon the market is used for electrical conductors. For this purpose it must be extremely pure. It is highly malleable, ductile and tenacious, so it may be rolled or hammered into thin sheets or drawn into fine wire.

**Chemical Properties.**—Copper is not oxidized in perfectly dry air but in ordinary air it soon becomes coated with an adherent film of cuprous oxide and finally, especially if exposed to the weather, with a basic carbonate. The underlying metal is thoroughly protected by these films and is very durable. On this account, it is used for the roofs of important buildings and as a sheathing for ships. Thin copper foil burns in chlorine



forming cupric and cuprous chlorides. It also combines easily with sulfur. Copper does not act on water at any temperature and is not dissolved by acids with evolution of hydrogen. This is connected with the fact that the cupric ion is a stronger oxidizing agent than the hydrogen ion. (See potential series p. 465.) In fact, hydrogen gas dissolved in platinum which gives it better contact with the solution, will precipitate metallic copper from a solution of one of its salts and be itself oxidized to hydrogen ion. Such acids as are stronger oxidizing agents than hydrogen as ion, nitric or hot concentrated sulfuric acid for example, will dissolve copper but with the reduction of the acid and not the evolution of hydrogen. On the other hand, when in contact with the air, acids like hydrochloric and even acetic dissolve the metal. The oxygen of the air is the oxidizing agent in this case.

The combining weight of copper is 63.57.

**Alloys.**—Copper forms many varied and useful alloys with the other elements. With zinc it forms brass, 30 to 37 per cent. zinc, and tombac 2 to 15 per cent. zinc, and with zinc and iron, an alloy which is malleable when hot. Bronze contains essentially copper and tin, although other metals are often added, especially zinc. Gun metal contains 10 per cent. tin and bell metal from 17 to 20 per cent. tin. Speculum metal is one-third tin and contains a little arsenic. It takes a very high polish. Phosphor bronze contains tin and a little phosphorus. Aluminum bronze has from 3 to 10 per cent. of aluminum. That with the higher percentage of aluminum has about the color of gold, is easily cast, takes a high polish and is nearly as strong as cast steel. Manganese bronze has a content of about 30 per cent. manganese. Silicon bronze contains up to 5 per cent. silicon. It is sometimes used for exposed electric wires since its tenacity is greater than that of copper although its conductivity is smaller. German silver is an alloy of copper, nickel and zinc and usually contains about 22 per cent. each of zinc and nickel.

**Cuprous Compounds.**—The cuprous or monovalent compounds are formed as the first step in the oxidation of the element or in the reduction of the cupric, or divalent compounds. In some ways many of them are more stable than the cupric

compounds, and are formed from the latter by spontaneous decomposition; but in general they are relatively unstable and are transformed by oxidizing agents into the cupric compounds. The principal cuprous compounds are  $\text{Cu}_2\text{O}$ ,  $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ,  $\text{CuCN}$ , and  $\text{Cu}_2\text{S}$ . Some of the cuprous oxyacid salts can be obtained in solution, but they soon decompose in such a manner that half the cuprous is reduced to metallic copper while the other half is oxidized to cupric. The cuprous ion  $\text{Cu}^+$  seems to be incapable of existing in any appreciable concentration for all the soluble stable salts are those of complex ions.

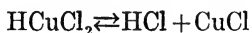
When a given quantity of electricity is passed through a cuprous salt, just twice as much copper is deposited as when the same quantity is passed through a cupric solution. This of course, would follow from the relation between their valencies.

**Cuprous Oxide.**—Cuprous oxide occurs in nature and is known as cuprite or red oxide of copper. It may be prepared by the direct union of the elements, or by the reduction of an alkaline solution of a cupric salt with glucose. It has a red color and is not soluble in water. It dissolves in hydrochloric acid forming the compound,  $\text{HCuCl}_2$  which gives the complex ion  $\text{CuCl}_2^-$ ; and in ammonium hydroxide owing to the formation of the complex ion  $\text{Cu}(\text{NH}_3)_2^+$ . Both of these ions are colorless. Cuprous hydroxide is not known.

**Cuprous Chloride.**—Cuprous chloride,  $\text{CuCl}$ , is one of the most important of the cuprous salts. It is most readily prepared by adding hydrochloric acid to a solution of cupric chloride,  $\text{CuCl}_2$ , and boiling for some time with finely divided copper out of contact with air. The solution which at first was dark brown finally becomes nearly colorless, and when poured into a large volume of water, deposits the cuprous chloride as a white crystalline precipitate. The equations for the reactions are as follows:



When the solution is poured into water, the compound  $\text{HCuCl}_2$  breaks up,



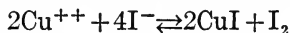
Cuprous chloride is but slightly soluble in water and is slowly hydrolyzed with the formation of cuprous oxide. It is dissolved

by concentrated hydrochloric acid and soluble chlorides in general through the formation of the complex ions  $\text{CuCl}_2^-$  or  $\text{CuCl}_3^{--}$ . These solutions are colorless when pure, but quickly become colored when exposed to the air, owing to the oxidation to cupric compounds. Cuprous chloride is also soluble in ammonium hydroxide solutions owing to the formation of the colorless ion  $\text{Cu}(\text{NH}_3)_2^+$ . The solution, however, quickly turns blue upon exposure to the air owing to oxidation to the highly colored cupric ammonia ion.

Both the ammoniacal and hydrochloric acid solutions of cuprous chloride have the property of absorbing carbon monoxide through the formation of an unstable compound. Advantage is taken of this in gas analysis.

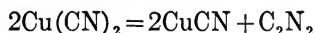
**Cuprous Bromide.**—Cuprous bromide,  $\text{CuBr}$ , is very similar to the chloride. It may be prepared by simply heating the anhydrous cupric bromide out of contact with the air when it decomposes into bromine and the cuprous salt. The chloride shows a tendency in the same direction but the decomposition is incomplete.

**Cuprous Iodide.**—Cupric iodide is so unstable that it decomposes at ordinary temperatures even when in solution; so when a soluble iodide is added to a solution of a cupric salt, cuprous iodide is at once precipitated and iodine liberated,



The cuprous iodide is colorless but appears brown from the color of the liberated iodine. The reaction is reversible and is far from complete unless the iodine is reduced by the addition of a sulfite or other suitable reducing agent.

**Cuprous Cyanide.**—When potassium cyanide is added to a cupric salt, cupric cyanide is precipitated; but this is unstable and soon decomposes into the cuprous cyanide,  $\text{CuCN}$ , and cyanogen,



The cuprous cyanide is practically insoluble in water, but dissolves readily in an excess of potassium cyanide owing to the formation of the colorless very stable complex anion  $\text{Cu}(\text{CN})_3^-$ . The solution so obtained is colorless and deposits colorless

crystals of potassium cuprocyanide,  $\text{KCu}(\text{CN})_2$ . The ion  $\text{Cu}(\text{CN})_2^-$  is very stable and gives an exceedingly low concentration of copper as ion, so low in fact, that it does not show the properties of copper as ion and will not give a precipitate of copper sulfide (which see) with hydrogen sulfide. Because of the very small concentration of the copper ion from this cuprocyanogen ion, all the slightly soluble salts of copper will dissolve in an excess of potassium cyanide.

**Cuprous Sulfide.**—Cuprous sulfide,  $\text{Cu}_2\text{S}$ , is formed by heating the cupric compound in a stream of hydrogen. It is found in nature and is then known as copper glance. It is dark colored and is not soluble in water or cold dilute acids, but is dissolved by hot dilute nitric acid and by potassium cyanide. It dissolves in the latter for the reason given above, and in the former because of the oxidation of the sulfur ion by the nitric acid. This causes a more radical reduction in the concentration of sulfur ion than does the formation of hydrogen sulfide.

**The Cupric Compounds.**—The cupric compounds are divalent and are in general more common and more important than the cuprous. The halogen compounds, as noted in the discussion of the cuprous salts, show a marked tendency to pass over into the cuprous salt and the free halogen. On the other hand, the only stable oxy salts of copper belong to the cupric series. When in dilute solution in water, the cupric salts all show a blue color which consequently is said to be the color of the cupric ion,  $\text{Cu}^{++}$ . When an excess of ammonium hydroxide is added to a cupric salt, the precipitate of cupric hydroxide or basic salt which is first formed is redissolved and the solution becomes intensely blue. Such a solution acts as though it contained a complex cupric ammonia ion,  $\text{Cu}(\text{NH}_3)_4^{++}$ , having a very blue color.

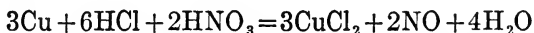
**Cupric Oxide and Hydroxide.**—Cupric oxide,  $\text{CuO}$ , occurs in nature in the ore melaconite. It may be prepared by heating the metal in a stream of oxygen or air; cuprous oxide is first formed. It may also be obtained by gently heating the carbonate, nitrate, or hydroxide. It is a black substance which although insoluble in water is very hygroscopic. When heated to redness, it acts as a good oxidizing agent toward hydrogen and organic substances, oxidizing them to water and carbon

dioxide and being itself reduced to metallic copper. This property is made use of in the quantitative synthesis of water and in the analysis of organic compounds. It is also used in the refining of petroleum to remove sulfur compounds.

Cupric hydroxide,  $\text{Cu}(\text{OH})_2$ , is a weak base which is but slightly soluble in water. It is precipitated as a light blue gelatinous substance when a soluble hydroxide is added to a cupric salt. Upon standing or more quickly when the solution is boiled, it becomes black and is transformed into a hydrated form of the oxide. The dry hydroxide is more stable, but is changed into the oxide by gentle heating.

Cupric hydroxide is of course soluble in acids. It is not dissolved by sodium hydroxide in ordinary concentrations, but is soluble in ammonium hydroxide owing to the formation of the deep blue complex cupric ammonia ion  $\text{Cu}(\text{NH}_3)_4^{++}$ . It is also soluble in solutions of sodium and potassium tartrate, especially in the presence of sodium hydroxide, a complex copper tartrate ion  $\text{CuC}_4\text{H}_2\text{O}_6^{--}$  is formed. This solution is deep blue like the ammoniacal solution, and is used in the determination of glucose since the latter reacts in a definite manner with it for the formation of cuprous oxide which is precipitated. It is called Fehling's solution.

**Cupric Chloride.**—Cupric chloride,  $\text{CuCl}_2$ , may be prepared by the direct union of its elements or by the interaction of hydrochloric acid with the oxide, hydroxide, or carbonate. It cannot be made by the action of hydrochloric acid upon the metal, because the hydrogen ion is not a strong enough oxidizing agent to oxidize the metal to the ion. In the presence of a little nitric acid which is a stronger oxidizing agent than the hydrogen ion, the metal will dissolve, and if hydrochloric acid is present, a solution of the chloride will be formed as shown in the following equation:



Anhydrous cupric chloride is yellow, a dilute solution of the salt is blue and a concentrated solution is green, perhaps because of the simultaneous presence of the ion and of the undissociated salt. From the concentrated solution, the hydrate,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , crystallizes out. This hydrate really is blue but gener-

ally appears green from the adhering mother liquor. When this hydrate is heated, it loses water and hydrogen chloride, and is converted into an oxychloride,  $\text{Cu}_2\text{OCl}_2$ , a reaction which is much like that when magnesium chloride is heated. This same oxychloride is formed together with free chlorine when the anhydrous salt is heated in oxygen. This perhaps is involved in the reactions which take place in the Deacon process for the preparation of chlorine (which see). Solutions of the chloride are acid in reaction as would be expected from the fact that the hydroxide is a weak base.

The deep blue solution formed by the addition of an excess of ammonia to a solution of cupric chloride deposits upon concentration crystals having the formula  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ . The anhydrous chloride will combine directly with ammonia for the formation of the compounds,  $\text{CuCl}_2 \cdot 6\text{NH}_3$  and  $\text{CuCl}_2 \cdot 2\text{NH}_3$ , these are analogous to salts with water of crystallization.

**Cupric Sulfate.**—Copper sulfate or blue vitriol,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is the most important copper salt. It may be made on a small scale by heating copper with concentrated sulfuric acid. The sulfuric acid here acts as the oxidizing agent, and is itself reduced to sulfur dioxide,



On a large scale, it is made by carefully oxidizing naturally occurring sulfides by roasting them in the air and dissolving out the sulfate with water, or by roasting the ores or matte and dissolving in dilute sulfuric acid. The salt is easily soluble in water, 20.7 gm. of the anhydrous salt to 100 gm. of water, and crystallizes from solution as the blue pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . This easily loses  $4\text{H}_2\text{O}$  forming the monohydrate which at  $200^\circ$  changes into the colorless anhydrous salt. The latter takes up water very vigorously and is used both as a drying agent and as a reagent for water, since in contact with the latter it turns blue. With ammonia, it forms the compounds  $\text{CuSO}_4 \cdot \text{NH}_3$ ,  $\text{CuSO}_4 \cdot 2\text{NH}_3$ ,  $\text{CuSO}_4 \cdot 4\text{NH}_3$ , and  $\text{CuSO}_4 \cdot 5\text{NH}_3$  and the mixed salt  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ . Other copper sulfates are known in which the five moles of water of crystallization are successively replaced by a corresponding number of moles of ammonia. A similar thing is true for other salts and serves to strengthen the

resemblance between ammonia and water. With potassium sulfate, copper sulfate forms the double salt,  $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , isomorphous with the corresponding magnesium compound. Copper sulfate forms isomorphous mixtures with ferrous sulfate. If the copper is in excess, the salts in the mixed crystals both have five moles of water of crystallization and take the form of copper sulfate crystals. On the other hand, if the ferrous sulfate predominates, the salts crystallize together with the form of the heptahydrate of ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

Copper sulfate is used in the preparation of other copper compounds, in calico printing, in the purification of copper by electrolysis, in electroplating and electrotyping, as a germicide and fungicide (mixed with slaked lime it forms Bordeaux mixture). Since it is very poisonous to the lower orders of plants, it is used extensively to destroy such organisms as often give to public water supplies a disagreeable taste and odor. It is used in making the electric cell known as the Daniel's battery and also in the gravity battery.

**Cupric Nitrate.**—Copper nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is a blue salt which may be made by dissolving the metal, the oxide or carbonate in nitric acid. It is very easily soluble in water. When heated it gives the oxide.

**Cupric Carbonate.**—Cupric hydroxide is such a weak base that the normal carbonate does not seem to be able to exist since it has neither been found in nature nor prepared in the laboratory. Two basic carbonates, malachite,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  and azurite,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  occur fairly abundantly in nature and are valuable copper ores. The green coating which gradually forms on copper exposed to the weather has the composition of malachite. When a soluble carbonate is added to a cold solution of copper sulfate, an amorphous blue basic copper carbonate is formed whose composition depends upon the dilution and the temperature.

Copper carbonate is of course soluble in acids, in potassium cyanide, and in ammonium hydroxide; it is also somewhat soluble in concentrated solutions of sodium carbonate, probably because of the formation of a complex ion similar to the cupri-tartrate.

**Cupric Acetate.**—A basic copper acetate, known as verdigris

having a fine bluish-green color and used as a pigment, is formed by the action of the air and of the crudest kind of vinegar (acetic acid) upon plates of copper. The oxygen of the air is the oxidizing agent in this case. The normal salt,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  may be obtained by crystallization from dilute acetic acid. It forms dark green crystals and is used as a pigment.

**Cupric Sulfide.**—When hydrogen sulfide is passed through a neutral or acid solution of a cupric salt, a brownish-black precipitate is thrown down; this consists principally of the cupric sulfide,  $\text{CuS}$ , but always contains some cuprous sulfide,  $\text{Cu}_2\text{S}$ . By drying this precipitate and heating it in a current of hydrogen, it is completely transformed into the cuprous compound. The hydrogen assists by sweeping away the sulfur.

Cupric sulfide is practically insoluble in cold dilute acids, but dissolves in hot dilute nitric acid. In the latter case, hydrogen sulfide is not evolved; but the sulfur as ion is oxidized to free sulfur and the nitric acid reduced to nitric oxide.

Cupric sulfide occurs in nature in indigo blue crystals known as covellite or indigo copper.

**Copper Ferrocyanide, Osmotic Pressure.**—Copper ferrocyanide,  $\text{Cu}_2\text{Fe}(\text{CN})_6$  has a very intense brownish-red color and is exceedingly slightly soluble. Because of these properties, it is of some importance to analytical chemistry. It is, however, of far greater importance to biology and to theoretical chemistry, because of the part which it plays in the study of the phenomena of osmotic pressure.

Copper ferrocyanide is a colloidal substance, and may be obtained as a membrane filling the pores of a porous cell (Fig. 41) by putting a solution of copper sulfate on the inside of the cell and a solution of potassium ferrocyanide on the outside and allowing the whole to stand for some time. The ferrocyanide is precipitated in the pores of the cell where the two solutions meet. After this cell has been thoroughly washed to free it from soluble

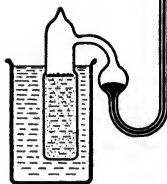


FIG. 41.



salts, it behaves in a very peculiar manner. Pure water will pass through it in either direction very much as through an ordinary porous cell only more slowly; but if a solution of sugar or of many other substances is placed in the cell, and the latter then set into a dish of pure water, the water will pass through into the solution. If the cell be closed with a cork, the water will continue to enter until it has produced a certain pressure which can be measured upon an attached manometer. When this pressure is reached, the water ceases to enter, and if by any means the pressure within the cell is increased *pure water and not solution* is forced out of the cell until the pressure is reduced to its former value. This pressure at which there is equilibrium between pure water and a solution separated by a membrane such as copper ferrocyanide is called the osmotic pressure of the solution.

When the conditions which affect the osmotic pressure are investigated, it is found that for fairly dilute solutions, the osmotic pressure is directly proportional to the concentration of the solution and to the absolute temperature at which it is measured. In these ways it corresponds exactly to the pressure of a gaseous substance. *In fact, the osmotic pressure of a solution is the same as the pressure which the solute would have if it were in the state of a gas and occupied the volume of the solvent in which it is dissolved at the temperature at which the osmotic pressure is measured.* The general gas law equation,  $PV=RT$  applies to osmotic pressure also, P is the osmotic pressure, V the volume of the solvent (not the volume of the solution), R a constant which is the same as that for gases, and T the absolute temperature. The osmotic pressure of a solution containing one gram mole in a liter of solvent is approximately 22.4 atmospheres at 0° C.

Other membranes than copper ferrocyanide may be used without altering the value of the osmotic pressure of a solution provided always that they will permit the solvent to pass through; but not the solute. Such membranes are called semipermeable membranes. They seem to act as selective solvents and to dissolve the solvent but not the solute of the main solution.

The osmotic pressure of salt solutions is abnormally high

having about twice the calculated value, in the case of sodium chloride, for example. The significance in connection with the dissociation hypothesis is obvious, but really it adds nothing to the evidence already given in favor of this theory, because the science of thermodynamics has shown that the osmotic pressure of a solution is directly proportional to the relative lowering of the vapor pressure of the solution and hence to the lowering of the freezing-point and to the rise in the boiling-point. If these are abnormal, as they are, for salts, the osmotic pressure must be abnormal also.

The osmotic pressures of concentrated solutions are by no means small and pressures up to 36 atmospheres have been measured. Such a pressure is equal to that exerted by a column of water 1200 ft. in height. And this enormous pressure it must be remembered is produced simply by the water's passing spontaneously through a semipermeable membrane into a solution.

Many of the processes which take place in the living organisms are at least partially osmotic in their nature, the movement of sap in plants and of the bodily fluids in animals, for example. The membranes lining the intestinal tract are at least partially semipermeable to sodium and magnesium sulfates and sodium phosphates. The use of these salts as purgatives depends largely upon this property; they attract and retain considerable water, because of their high osmotic pressure, and so increase the fluidity of the contents of the bowels. Calomel works in an entirely different way, and depends for its activity upon the fact that it increases the secretions. It is also useful in certain cases because of its germicidal tendencies.

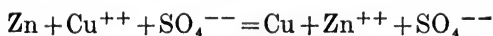
**Analytical Properties of Copper.**—In analysis, use is most frequently made of the following properties: namely, the sulfide is but very slightly soluble in water and cold dilute acids, but soluble in hot dilute nitric acid (separation from mercury); the sulfate is soluble in water (separation from lead); the hydroxide is soluble in an excess of ammonia (separation from bismuth); and the sulfide is soluble in potassium cyanide (separation from cadmium). The intense blue color of the cupric ammonia ion which is formed by the addition of an excess of ammonium hydroxide to the cupric salt is fairly characteristic, since nickel is the only other metal which has similar properties.

The brownish-red color of copper ferrocyanide is visible in more dilute solutions than the blue of the ammonia ion. A very characteristic test for copper is based on the fact that metallic iron will precipitate bright metallic copper upon its surface when it is introduced into a solution of a copper salt.

In quantitative analysis, the copper is usually weighed as the metal, into which condition it is brought by electrolysis of its sulfate or nitrate with platinum electrodes.

**Voltaic Cells.**—*Voltaic cells are devices for the conversion of free chemical energy into electrical. They all have the following characteristic in common. They are made up of spontaneously occurring oxidation and reduction reactions which are capable of taking place at two different points.* The reactions in the cell must be spontaneous because these cells can transfer work from one system to another, and therefore must lose free energy; and only such changes as take place of themselves are accompanied by a decrease in free energy. These changes must be oxidation and reduction, because such processes take place with the transfer of positive electricity from the oxidizing agent to the reducing agent, and the transfer of electricity is an essential part of the voltaic phenomena. They must be able to take place at two different points, so that positive charges may be given up by the oxidizing agent to an electrode, and then flow through a wire or other conductor to another electrode where they are given to the reducing agent and so oxidize it. During this passage of electricity from one electrode to the other, it may be made to do the various kinds of work which a voltaic cell is called upon to perform.

The Daniell cell furnishes a good illustration of all that has been said above. This cell may be made by filling a porous cup with a solution of zinc sulfate and putting in a zinc electrode, the cup is then placed in a solution of copper sulfate in which there is a copper electrode. When the two electrodes are connected by a wire, positive electricity flows through the wire from the copper to the zinc electrode. At the same time, metallic copper is deposited upon the copper electrode and metallic zinc passes from the zinc electrode into the solution and becomes zinc as ion. The changes may be represented by the following equation:



From this it may be seen that the cupric ion has oxidized the zinc to zinc as ion, and has been itself reduced to metallic copper. This change will quickly take place if a piece of zinc is placed in solution of copper sulfate; soon there will be a solution of zinc sulfate and a precipitate of metallic copper. It is then a spontaneous change. But this arrangement does not yield electrical energy, and the energy of the reaction simply goes to heat the solution. This is because the oxidation and the reduction take place at the same point. In the cell which is described above, the oxidizing agent is kept from direct contact with the reducing agent by the porous cup, and the only way in which the copper ion can oxidize the zinc is by becoming metallic copper, thereby giving its positive charges to the copper electrode from which they may flow through the wire to the zinc electrode, and oxidize it to the zinc ion. While this electricity is flowing through the wire, it may be made to do work.

The electrical energy which a voltaic cell is able to produce is equal to the decrease in the free energy that accompanies the chemical change which takes place. Now electrical energy is the product of two factors; the coulombs and the volts, the coulombs being the quantity factor and the volts the intensity. There is then the following relation between the free energy and the electrical energy:

$$\text{Free energy} = \text{volts} \times \text{coulombs}$$

The unit of electrical potential, the volt, has such a magnitude that a volt  $\times$  a coulomb is equal to a joule or 10,000,000 ergs.

Now when a gram equivalent of any oxidizing agent is reduced, 96,500 coulombs (see Faraday's Laws p. 135) of positive electricity are transferred to the reducing agent.

From the relation given above that the free energy is equal to the product of the volts times the coulombs, it follows that the potential or electromotive force of a cell is equal to the free energy produced during 1 gm. equivalent of change divided by 96,500. Expressed in the form of an equation,

$$\text{E.M.F.} = F/96,500$$

in which E.M.F. stands for electromotive force, and F for the

free energy of 1 gram equivalent of chemical change. From this, it follows that the potential of a cell is directly proportional to the decrease in the free energy accompanying the transformation of a gram equivalent of the oxidizing and reducing agents in the cell. Since this free energy is different for different combinations, the potentials of various cells are quite dissimilar. Oxidizing agents can be arranged in the order of their activity, *i.e.*, the decrease in the free energy involved in the transformation of a gram equivalent, and a number can be assigned to each which represents the potential of an electrode in the normal ionic solution<sup>1</sup> of the oxidizing agent. This number may be represented by E and then,  $E = F'/96,500$ ; where F' is the free energy produced when 1 gram equivalent of the oxidizing agent is reduced. The following table gives a short list of oxidizing agents arranged in the order of their oxidizing power, and also gives the value of E. This table is a part of what is called the potential series.

Agent	E in volts	Agent	E in volts
NO <sub>3</sub> <sup>-</sup> .....	+1.75	H <sup>+</sup> .....	+0.277
Cl <sub>2</sub> .....	+1.694	Pb <sup>++</sup> .....	+0.129
O <sub>2</sub> .....	+1.396	Ni <sup>++</sup> .....	+0.049
Br <sub>2</sub> .....	+1.270	Co <sup>++</sup> .....	+0.045
Ag <sup>+</sup> .....	+1.048	Tl <sup>+</sup> .....	-0.045
Hg <sup>+</sup> .....	+1.027	Fe <sup>++</sup> .....	-0.063
Cu <sup>++</sup> .....	+0.606	Cd <sup>++</sup> .....	-0.143
		Zn <sup>++</sup> .....	-0.493

A + sign before the value of E indicates that the electrode is positive against the solution of that oxidizing agent, and a - sign means that the electrode is negative toward the solution, and the significance of a negative sign is that free energy is taken up instead of being given out when the ion is changed to the

<sup>1</sup> A normal ionic solution is one which contains in a liter such a quantity of the salt that there will be 1 gram equivalent of the ion present in the actually dissociated state. Because of the incomplete dissociation, such a solution will contain per liter more than one equivalent of the salt.

metal. This is the case with all the metals which are hard to reduce from their compounds.

Any oxidizing agent in this list is able to oxidize anything lying below it and is oxidized by all that stand above. For example, the cupric ion will oxidize anything from hydrogen to zinc and change it from the element to the ion, while copper is itself oxidized by mercury and all that stand above to the cupric ion. A voltaic cell then may be made up of a combination of any two of these agents, and its electromotive force will be the algebraical difference between the value of  $E$  for the two electrodes. For example, a cell might be made up of a silver electrode in a silver solution and a copper electrode in a copper solution, and it would have an E.M.F. of  $1.048 - 0.606 = 0.442$  volts. The silver electrode would be positive toward the copper and the latter would dissolve, while metallic silver would be deposited. The electromotive force of the Daniell cell may be calculated from this table by subtracting the value of zinc,  $-0.493$  from that of copper,  $+0.606$ ;  $0.606 - (-0.493) = 0.606 + 0.493 = 1.099$  volts. Here in contrast to the above, the copper is positive toward the zinc and is deposited while the zinc dissolves.

The activity of an oxidizing agent depends upon the concentration. The figures given above apply to normal ionic solutions containing 1 grm. equivalent of "actual ion" per liter; in more dilute solutions, the electrodes are less positive if the oxidizing agent is a cation. Anything which tends to reduce the concentration, of the copper ion for instance, will tend to bring the potential of the copper electrode nearer the zinc and reduce the potential of the copper zinc cell. The concentration of copper in a solution containing an excess of ammonia is very small, and the potential of a cell made up of a copper electrode in such a solution and a zinc electrode in zinc sulfate solution is much smaller than that of the Daniell cell. If potassium cyanide is used instead of the ammonia, the concentration of the copper is still further reduced, so that the potential of the copper electrode is actually made smaller than that of the zinc; and in a cell made up of the two, the processes which take place in the Daniell cell are reversed, copper going into solution and the zinc being deposited.

## SILVER

**General.**—Because of its occurrence free in nature, silver has been known and used from prehistoric times. Its relationship to the other elements is rather complex as will be seen by a study of its compounds. Physically it is much like copper aside from the difference in color; chemically it is like mercury in the mercurous, and copper in the cuprous states in that it is monovalent and also in the solubilities of its halogen compounds. It differs radically though from both mercury and copper in that its hydroxide is a strong base, and that its soluble salts of strong acids are neutral. In this it resembles the alkali metals, and some of its salts are isomorphous with the corresponding salts of potassium. The silver ion  $\text{Ag}^+$  is a good oxidizing agent, and the metal is obtained very easily from many of its compounds. The oxide for example, when heated, acts like mercuric oxide in that it is changed into the metal and oxygen. Scheele took advantage of this in one of his methods for the preparation of oxygen.

**Occurrence.**—Like copper, silver is found in nature both free and in combination. The native silver is a fairly important ore, but is practically never found pure, being alloyed with gold, copper or mercury. Another ore of some importance is the chloride,  $\text{AgCl}$ , which is known as cerargyrite or hornsilver; but by far the most important ore is the sulfide  $\text{Ag}_2\text{S}$  called argentite or silver-glance. In addition there are compounds of silver sulfide and antimony or arsenic sulfides known as pyrargyrite  $\text{Ag}_3\text{SbS}_3$ , stephanite,  $\text{Ag}_5\text{SbS}_4$ , and proustite,  $\text{Ag}_3\text{AsS}_3$ .

Silver compounds are very commonly found associated with those of gold, copper, lead, and zinc, and the metallurgy of silver is therefore often closely bound up with that of these other metals. The mineral galena, lead sulfide, is especially liable to contain silver sulfide in isomorphous mixture, and the lead obtained from it contains the silver.

**Metallurgy.**—The metallurgy of silver is complicated by the fact that it is generally associated with other metals such as copper, lead, zinc and gold which it is necessary and desirable to extract at the same time. To meet the needs of individual cases, a considerable variety of methods for extracting the silver have been devised. These may be grouped into smelting

or dry processes, amalgamating and leaching or wet processes. The smelting methods are usually applied to ore which contains relatively more copper or lead than silver. If they are mainly copper ores, they are worked as described under that metal, and the blister copper obtained will carry practically all the silver in the ore. This crude copper is then purified by electrolysis, and the silver is obtained in the anode mud. The lead ores are smelted as will be described under that metal, and the lead will contain the silver. This is called work lead or base bullion. The silver is removed from this by what is known as the Parke's process which is as follows: Work lead is melted in large kettles and kept molten for some time to allow other impurities to be oxidized and skimmed off as "dross." Then a quantity of zinc equal to from 0.5 to 2.0 per cent. of the weight of the lead is stirred into the molten mass. Zinc and lead are only slightly soluble in each other, while zinc is a much better solvent for silver than lead is. The zinc, therefore, acts as an extractive solvent, and dissolves the greater part of the silver (see the Law of Distribution) from the lead. The silver zinc alloy being much the lighter, rises to the surface, and on being allowed to cool, forms a solid crust while the lead is still molten. This is skimmed off and freed from most of the lead which adheres to it, and the zinc is then distilled from the alloy in large graphite retorts. The silver is heated in a cupellation furnace where any lead which it retains is oxidized to litharge,  $PbO$ , and absorbed in the bone ash which forms the bottom of the furnace. The silver remains unoxidized, accompanied by any gold that was in the original bullion. These are separated by dissolving the silver in hot concentrated sulfuric acid; the gold is left unchanged. The silver is precipitated from the silver sulfate solution by means of metallic copper.

There are also electrolytic processes for getting silver and gold from work lead. The silver and gold are found in the residues in the bottom of the cell.

**Amalgamation Processes.**—These depend upon the solution of silver from an ore in metallic mercury, forming silver amalgam. After separating this from the ore gangue, it is freed from excess mercury by straining through canvas and buckskin. The solid



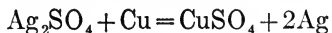
amalgam is then distilled in an iron retort, the mercury passing over and the silver remaining in the retort.

Silver chloride is decomposed by mercury, forming silver amalgam and mercurous chloride. Silver sulfide is not affected by mercury alone, but in the presence of metallic iron, cupric chloride, or other reagents, it is decomposed and the silver amalgamated.

**Leaching Processes.**—In these processes, silver contained in the ores or metallurgical products is first converted into compounds soluble in water or in solutions of certain reagents in water; these compounds are then dissolved or leached out, and the silver precipitated from the solution by suitable means.

The silver compound may be silver chloride, which is soluble in salt, or sodium thiosulphate solutions; silver sulfate, soluble in hot water; or potassium silver cyanide,  $KAg(CN)_2$ , which is soluble in cold water.

From solutions of silver chloride in brine or from silver sulfate solution, the metal is precipitated by metallic copper,



From thiosulfate solutions, silver is precipitated as silver sulfide by sodium or calcium sulfides, while from cyanide solutions it may be thrown down as metal by metallic zinc.

Roasting processes are frequently utilized to produce a soluble silver compound in the ore to be treated. Silver chloride is formed from silver sulfide by roasting with salt, (chloridizing roasting). Careful roasting of the sulfide in air causes silver sulfate to be produced.

No specific description of the processes based on these principles can be given for want of space.

The annual production of silver in the United States is about 57,000,000 oz. worth about \$30,000,000.

**Physical Properties.**—Pure silver has a very high luster and a beautiful white color. It melts at  $955^\circ$  in the presence of air or at  $962^\circ$  in its absence. The difference being due to the fact that oxygen is soluble in molten silver, 22 volumes of oxygen to 1 of silver, and this of course lowers the melting-point of the metal. When a molten mass of silver cools, the outside hardens before the liquid interior has lost its oxygen, and the latter forcing its

way out as the cooling continues breaks the crust of solid silver and ejects portions of the metal from the interior producing very strange shapes. The phenomenon is known as "sprouting."

Silver boils rapidly at temperatures easily reached by an oxygen-hydrogen blowpipe. The density of the vapor at 2000° corresponds to a molar weight of 107–111 and since the combining weight is 107.88 there is one combining weight per mole. Silver is very malleable and ductile so that it may be beaten out into leaves having a thickness of 0.00025 mm. or drawn into wire so fine that 1800 meters weigh only a gram.

When an electric arc is formed between silver wires under water, a colloidal solution of silver is produced. Similar colloidal solutions may be made by the action of certain reducing agents upon silver salt solutions. These solutions vary in their color, brown, white, blue, red, and yellow being well known. When examined with an ultra microscope in a beam of very strong light, these colloidal solutions are seen to contain very small particles which in one case were estimated to be  $3.4 \times 10^{-5}$  mm. in diameter.

Because of its high luster, beautiful color, and chemical resistivity, silver is much used for ornaments and for coinage. For such purposes, the pure metal is too soft so it is alloyed with copper. Silver coins usually contain 10 per cent. of copper. The coinage of England, however, contains 7.5 per cent. of copper and this is also the composition of "sterling silver."

Silver is the best conductor of heat and of electricity that is known.

**Chemical Properties of Silver.**—Under ordinary conditions, silver does not combine oxygen at any temperature, but it is oxidized at ordinary temperatures by moist ozone forming silver per oxide,  $\text{Ag}_2\text{O}_2$ . It will combine slowly with sulfur and the halogens. Because of its resistance towards oxygen at high temperatures, silver was formerly called one of the "noble metals."

It is even harder to oxidize silver to the ionic state than it is copper, and consequently it does not dissolve in the ordinary acids with the evolution of hydrogen. It is, however, oxidized and dissolved by nitric acid and by hot concentrated sulfuric acid with the evolution of oxides of nitrogen or of sulfur, the

reduction products of these acids. Silver sulfide is an exceptionally stable substance, and its formation takes place with a great decrease in free energy; because of this, hydrogen sulfide is able to react with silver with the evolution of hydrogen.

Silver is not attacked by the alkalis either in solution or in the fused state, so silver dishes are often used in working with these substances. Platinum and other metals whose oxides have a tendency to form acids are attacked by strong bases especially in the fused state.

The combining weight of silver is unusually important since the combining weights of a number of other elements are determined with its aid, it is 107.88.

**The Oxides of Silver.**—Silver oxide is deposited as a brown precipitate which darkens on drying, when a solution of sodium or potassium hydroxide is added to a solution of a silver salt or is boiled with silver chloride. The oxide is slightly soluble in water and the solution has an alkaline reaction showing that it contains silver hydroxide,  $\text{AgOH}$ , but this evidently breaks down into silver oxide and water. In spite of this, silver hydroxide is a strong base and its solutions take up carbon dioxide and precipitate the carbonate. It dissolves in ammonium hydroxide because of the formation of the silver ammonia ion; and the resulting solution contains silver ammonium hydroxide,  $\text{Ag}(\text{NH}_3)_2\text{-OH}$ , which is a strong base. The oxide is dissolved by acids giving solutions of the corresponding salts.

Silver oxide is reduced by hydrogen at temperatures as low as  $100^\circ$ , and when heated alone it decomposes at  $250$  to  $270^\circ$ .

Silver peroxide,  $\text{Ag}_2\text{O}_2$ , is formed by the action of moist ozone upon the metal; it is unstable. A suboxide  $\text{Ag}_4\text{O}$ , is known.

**The Halogen Compounds of Silver.**—Silver fluoride may be made by the action of hydrofluoric acid upon the oxide or carbonate. It is highly soluble in water and is deliquescent.

The chloride, bromide, and iodide of silver are very slightly soluble in water and in dilute acids, and are thrown down as curdy precipitates upon the addition of the corresponding halogen salts to a solution of a silver salt. The chloride is white and soluble to the extent of 0.002 gm. per liter of water. The bromide has a pale yellow color and is less soluble than the

chloride since a liter of water dissolves only 0.000137 gm. of the salt. The iodide is distinctly yellow, and is the least soluble of the three, 0.000028 gm. being dissolved in a liter of water. Because of the difference in solubility, the chloride may be converted into the bromide or the bromide into the iodide by treatment with a solution of the corresponding potassium salt. When exposed to the light, silver chloride and bromide darken and some free halogen is formed together with a subchloride or bromide,  $\text{Ag}_2\text{Cl}$  or  $\text{Ag}_2\text{Br}$ . Silver iodide is unchanged in the light unless an excess of  $\text{AgNO}_3$  is present. These facts are important in connection with photography (p. 475).

The silver halides at ordinary or lower temperatures will combine directly with ammonia for the formation of the following compounds,  $2\text{AgCl}\cdot 3\text{NH}_3$ ,  $\text{AgCl}\cdot 3\text{NH}_3$ ,  $\text{AgBr}\cdot \text{NH}_3$ ,  $2\text{AgBr}\cdot 3\text{NH}_3$ ,  $\text{AgBr}\cdot 3\text{NH}_3$ ,  $2\text{AgI}\cdot \text{NH}_3$ ,  $\text{AgI}\cdot \text{NH}_3$ . The compounds containing the larger amounts of ammonia are usually not stable at ordinary temperatures under atmospheric pressure.

Silver chloride is fairly soluble in concentrated solutions of hydrochloric acid and of the easily soluble chlorides, apparently because of the formation of the ion  $\text{AgCl}_3^{--}$ . This property is sometimes taken advantage of in the extraction of silver from its ores. Silver chloride is precipitated from these solutions upon dilution. The chloride is easily soluble in solutions of ammonium hydroxide owing to the formation of the stable complex ion,  $\text{Ag}(\text{NH}_3)_2^+$  called the silver ammonia ion. Silver bromide is somewhat soluble in ammonium hydroxide, but the iodide is scarcely affected. The explanation is that silver bromide because of its slight solubility gives a concentration of silver as ion in the solution which is but little higher than that of the silver ion, which together with the ammonia is in equilibrium with the complex silver ammonia ion, so its concentration cannot be much reduced through the formation of this ion. Silver iodide is still less soluble, and the concentration of the silver ion in its solution is smaller than that from the silver ammonia ion. So silver iodide is not dissolved in ammonium hydroxide, in fact, silver iodide is precipitated from ammoniacal solutions of silver chloride upon the addition of potassium iodide. Either silver bromide or chloride is precipitated from its ammoniacal solutions when the latter is acidulated with nitric acid;

since the hydrogen ion combines with the ammonia to form the ammonium ion, and thus breaks up the silver ammonia ion.

Sodium thiosulfate interacts with silver salts for the formation of the complex crystalline salt,  $2\text{NaAgS}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3$ . When in solution, this seems to give the complex ion,  $\text{AgS}_2\text{O}_3^-$ . The concentration of the silver as ion from this seems to be about the same as that from silver iodide for it does not have much effect upon the latter although it dissolves silver bromide with ease.

**Silver Cyanide.**—Soluble cyanides give with the soluble silver salts a precipitate of silver cyanide which is somewhat less soluble than the chloride. The cyanide is soluble in ammonium hydroxide and very easily in an excess of potassium cyanide owing to the formation of the very stable complex silver cyanogen ion,  $\text{Ag}(\text{CN})_2^-$ , similar to the complex cuprocyanogen ion,  $\text{Cu}(\text{CN})_2^-$ . The concentration of the silver ion from this ion is so very small that silver iodide and all of the other difficultly soluble salts of silver except the sulfide are dissolved by potassium cyanide in excess.

Solutions of this potassium silver cyanide are used in silver electroplating. The object to be plated is made the cathode and a plate of pure silver the anode.

**Silver nitrate.**—Silver nitrate,  $\text{AgNO}_3$ , is the most important salt of silver. It is made by the action of nitric acid upon the metal;



If the silver contained any copper, the silver nitrate may be purified by evaporating the solution to dryness and heating to fusion. Under these conditions, the copper nitrate decomposes, giving the oxide and oxides of nitrogen, while the silver nitrate is stable and may be separated from the copper oxide by solution in water.

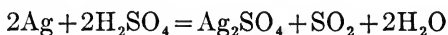
Silver nitrate is a white crystalline salt, isomorphous with potassium nitrate. It is soluble in water, 100 grm. of the latter dissolve 257 grm. of the nitrate at  $25^\circ$  and 1900 grm. at  $130^\circ$ . It melts at temperature a little over  $200^\circ$ . Sticks of silver nitrate are sometimes used in medicine as a caustic under the name of lunar caustic. These sticks are made by melting the

salt either with or without the addition of potassium nitrate and casting into moulds. Its use as a caustic depends upon the property of rendering insoluble certain nitrogenous substances, called the albuminoids.

In the pure state, it is not altered by light; but in the presence of reducing agents, it is changed to finely divided metallic silver having a black color. This is the cause of the stains which it produces on the skin. The nitrate is much used in the laboratory for the detection and estimation of the halogens and is also the starting point for the preparation of most of the other silver salts.

**Silver Sulfate.**—Silver sulfate,  $\text{Ag}_2\text{SO}_4$ , is a white crystalline salt which is isomorphous with anhydrous sodium sulfate. It is moderately soluble in water and will combine with aluminum sulfate for the formation of the alum  $\text{AgAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , which is isomorphous with the corresponding potassium salt and with the whole series of alums.

Silver sulfate may be made by the action of hot concentrated sulfuric acid upon the metal;



Advantage is taken of this reaction in the "parting" of the alloys of gold and silver which are obtained in the smelting and refining of these metals. The silver is dissolved while the gold is not. The silver is reprecipitated from its sulfate solution by metallic copper an equivalent quantity of copper sulfate being formed. This is one of the minor sources of the latter salt. Silver sulfate is more soluble in solutions of sulfuric acid than in pure water because of the formation of an acid salt.

**Silver Sulfide.**—Silver sulfide,  $\text{Ag}_2\text{S}$ , is so very slightly soluble that it is formed by the action of hydrogen sulfide upon all silver compounds except the complex potassium silver cyanide in the presence of a very large excess of potassium cyanide. It is even formed, as noted above, by the action of hydrogen sulfide or of other sulfides upon metallic silver.

**Silver Carbonate.**—Silver carbonate,  $\text{Ag}_2\text{CO}_3$ , is a pale yellow salt slightly soluble in water to which it imparts a faint alkaline reaction. It resembles lithium carbonate in that it is more soluble in the presence of carbon dioxide. The fact that the

normal salt exists indicates that silver hydroxide is a strong base.

**Other Salts.**—Silver thiocyanate,  $\text{AgSCN}$  (white), silver chromate,  $\text{Ag}_2\text{CrO}_4$  (red), silver arsenite,  $\text{Ag}_3\text{AsO}_3$  (yellow) and silver arsenate,  $\text{Ag}_3\text{AsO}_4$  (reddish-brown) are a few of the salts which are useful in analysis.

**Photography.**—The most important of the modern photographic processes depend upon the sensitiveness of the silver halides toward light. The "dry plate" upon which the picture is originally taken consists of a plate of glass or a film of celluloid covered with a dried emulsion of silver bromide in gelatine. This emulsion is prepared by adding an ammoniacal solution of silver nitrate to an excess of a solution of potassium or ammonium bromide and gelatine. The gelatine causes the silver bromide to be precipitated in very small particles. If plates were coated with the emulsion in this state they would be too "slow" and would require relatively long exposure to the light. To overcome this the emulsion is kept warm for some time when the smaller particles gradually dissolve and are reprecipitated on the larger ones so that the precipitate grows coarser, finally, reaching 0.003 to 0.004 mm. in diameter. This process is called "ripening." Very small particles of any substance are more soluble than larger ones, apparently because of the greater pressure produced by the action of surface tension upon a particle as its dimensions decrease. When the emulsion has ripened sufficiently, it is cooled until the gelatine hardens, cut into cubes and washed with cold water until the potassium or ammonium nitrate and the excess of bromide are removed. It is then melted and poured upon the plates. Of course, these operations must be carried out in the absence of light, or in very weak red light.

When such a plate is exposed for a fraction of a second to light, no visible action takes place; but if it is then placed in a suitable reducing agent called the "developer," the portions of the silver bromide which were exposed to the light are reduced to metallic silver at a rate which is proportional to the intensity of the light and the time of exposure. The reduced silver is deposited as a black substance in the very position of the bromide from which it was obtained. If the exposure was made in a camera, there will be developed upon the plate an image which in its light and shade effects is the reverse of the object, that is it will be

dark where the object is light. This is called the negative. After the plate is "developed," it has then to be "fixed"; that is to say, the unchanged silver bromide must be removed so that the plate may not be further acted upon by the light. This is done by taking advantage of the solubility of the bromide in sodium thiosulfate or "hypo" as it is often called.

Just why the bromide which has been exposed to light is more easily reduced than the unexposed is not known with certainty, but it may be connected with the fact that light will transform it into a subbromide as noted above.

From the negative, "positives" or "prints" are made by allowing light to pass through the negative and strike sensitized paper which is placed in direct contact with the gelatine film of the negative. The dark portions of the negative which correspond to the light portions of the object protect the paper from the action of light, and when the print is finished it will be light just where the object was. Some printing-out papers are sensitized with silver bromide and these require only very brief exposure, but must be developed like plates. Others contain silver chloride and the printing is continued until the image is plainly visible upon the paper. Such prints are then "toned" by treating them with a solution of sodium chloraurate,  $\text{NaAuCl}_4$ , sodium gold chloride as it is called. The silver which has been reduced by the light, in turn reduces the gold to metallic gold which in the finely divided state has a pleasing reddish tint. By replacing the gold solution by potassium chlorplatinate,  $\text{K}_2\text{PtCl}_4$ , platinum will be precipitated instead of gold, giving a very dark tone. By whatever process made, the prints after development or toning must be fixed by dissolving out the unchanged silver salts with sodium thiosulfate.

The dry plate contains gelatine and the printing paper similar substances which make the silver compounds much more sensitive to the light, perhaps because they combine with the halogen set free in the formation of the sub-salts.

Light of different colors affects the bromide plate at very different rates. The time required to produce a given effect upon a plate stand in the following ratios, violet 1; blue 2; green 2.5; yellow 22; and red 40. So it will take forty times the exposure to red light to produce a given effect that would be



required for violet light of equal intensity. The result is that the bromide plate greatly distorts color intensity effects. When light produces a given change, it is only that part and that kind of light which is absorbed that is active. The silver bromide absorbs the violet, blue, and green rays much more strongly than the yellow and red, and hence the great difference in the result. By dyeing the plates with certain coloring matters which are able to absorb the yellow and red rays, they are made much more sensitive toward these kinds of light and the negatives give more nearly the true color intensity effects. Such plates are called orthochromatic plates.

Other photographic processes are in use which do not involve silver salts. They will be considered in their proper places.

**Mirrors.**—Mirrors are now usually made by coating glass with silver. This is done by the action of reducing agents such as the tartrates, glycerine, formaldehyde, or a reducing sugar upon ammoniacal solutions of silver nitrate. These mirrors are far superior to the old-fashioned ones which were backed with an amalgam of tin.

**Analytical Properties of Silver.**—The silver ion is colorless, and forms but slightly soluble compounds with chlorine as ion, a property which is also possessed by the mercurous, cuprous, and lead ions. Analytically, the cuprous compounds are unimportant. Silver chloride is not soluble in hot water, a distinction from lead chloride; but is soluble in ammonium hydroxide, a distinction from mercurous chloride. In quantitative analysis, it is usually weighed as the chloride, but often as the metal, which is obtained either by electrolysis or by oxidizing all the other metals, except gold and platinum, in the air at a high temperature and weighing the metallic bead which is so obtained, then dissolving out the silver with nitric acid or sulfuric acid and weighing the residue of gold. The difference in weight is the weight of the silver.

## GOLD

Gold has been known from prehistoric times. From its striking appearance and its occurrence free in nature it must have been among the earliest of the metals to attract the attention of men.

Gold forms a comparatively small number of compounds since all of its simple salts with the oxy acids are very unstable. In fact, gold seems to be practically incapable of existing as a simple ion although several complex ions are known. The compounds of gold belong to two series, the aurous in which the gold is monovalent and the auric in it is trivalent. These compounds are characterized by the great ease with which they decompose to give metallic gold. This, in general, may be brought about by comparatively feeble reducing agents or by a moderate rise in temperature. The simple aurous halogen compounds are not soluble in water and this establishes a sort of relationship with copper and silver.

**Occurrence.**—Gold generally occurs free in nature, its only native compounds being those with tellurium. Native gold is rarely found pure, being almost always alloyed with silver. It is carried in finely divided conditions in quartz and other rock materials and in pyrites, galena and other sulfides. It may be found in its original deposits in veins running through the main rock masses or in alluvial beds of sand or gravel formed by the breaking down of the original deposits through weathering action. Gold in deposits of the former kind is called reef gold while that in the latter kind is called placer gold.

Among the minerals containing gold and tellurium, sylvanite,  $(\text{AuAg})\text{Te}_2$  and calaverite,  $\text{AuTe}_2$ , may be mentioned. These minerals are much less frequently found than native gold, but are of importance in some gold districts.

**Metallurgy.**—The processes for extraction of gold may be classified like those for silver as smelting, amalgamation, and leaching processes; but for gold there is an additional class, simple washing processes.

In the latter, gold in placer deposits of sand or gravel is concentrated by shaking up the material with water and allowing the gold to separate by its greater density from the lighter sands. These methods do not save all of the gold even when carried out under good conditions, and hence are used chiefly by prospectors, and in the opening up of new gold fields. They are greatly increased in efficiency if mercury is used to collect the concentrated gold as an amalgam and in this form they are rather widely used.

**Amalgamation Processes.**—Amalgamation processes for gold are very similar to those used for silver, and gold and silver are frequently recovered in the same operation. Amalgamation is used in connection with gold washing as described above, and in addition to this, gold disseminated in quartz or other massive rock or mineral is recovered by crushing the ore in stamp mills and leading the crushed material over amalgamated plates, *i.e.*, copper plates coated with mercury. The gold is amalgamated and held by this mercury, and from time to time the gold amalgam is scraped from the plate; excess mercury is removed by filtering the amalgam through canvas or buckskin and the resulting solid amalgam is distilled to free the gold from mercury.

**Smelting Processes.**—Gold in copper or lead ores is concentrated during the smelting of these ores into the blister copper or the work lead which is obtained. It is removed from these products, along with silver by the refining processes already described under silver and copper.

When both gold and silver are thus obtained, a separation or “parting” is necessary. A common method of doing this is to treat the gold-silver alloy with boiling concentrated sulfuric acid. Silver dissolves almost completely while gold is unaffected. The gold, after removal of silver sulfate solution, is melted, refined and cast into bars.

**Leaching Processes.**—The most important wet methods for gold extraction are the *chlorination* and the *cyanide* processes.

In the former, finely crushed gold ore containing the free metal is treated with a solution of chlorine in water. This dissolves gold, forming gold chloride,  $\text{AuCl}_3$ . From the solution, gold is precipitated as the sulfide by means of hydrogen sulfide. The process is now usually carried out in very large lead lined barrels or cylinders, the chlorine being generated from a mixture of bleaching powder, and sulfuric acid added with the ore and a considerable quantity of water. In some cases, chlorine generated electrolytically in outside cells, is dissolved in water, and the solution used in the chlorinating barrels.

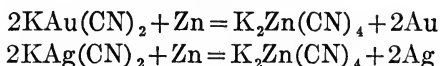
The *cyanide* process, patented in 1890 by McArthur and Forrest, is very widely used for the treatment of low grade ores that cannot be profitably worked by smelting. It is carried out by allowing the crushed ore to remain in contact for a considerable

time with a very dilute solution of potassium cyanide, KCN. This solution dissolves both gold and silver from the ore forming potassium aurocyanide,  $\text{KAu}(\text{CN})_2$ , and potassium argenticyanide,  $\text{KAg}(\text{CN})_2$ . The equations representing the reactions are discussed in detail under the complex cyanides of gold (p. 482).

Oxygen is essential, for the reaction and solution of the gold ceases when the oxygen supply is exhausted. Admission of fresh air causes it to begin again.

The gold dissolves very slowly, the time required for complete solution and the strength of potassium cyanide solution, varying greatly with different ores.

To recover the precious metals the cyanide solution is passed through boxes containing zinc dust or turnings. Zinc dissolves while the gold and silver are precipitated;



The precipitation of gold from cyanide solutions is also accomplished by an electrolytic process, where lead cathodes and iron anodes are used in an electrolyte composed of the dilute cyanide solution of gold. Gold is deposited on the lead and is recovered by melting up the cathodes and cupelling off the lead.

Enormous quantities of gold have been extracted by the cyanide process from the low grade ores of South Africa and this has been an important factor in cheapening gold and hence, raising the price of other things and thus has contributed to the "high cost of living."

The gold production for the United States in 1910 was 4,657,018 oz. worth \$96,269,100.

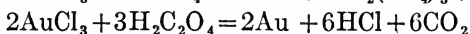
**Physical Properties.**—Gold has a high luster and a beautiful yellow color. It melts at  $1062^\circ$  and begins to volatilize at an appreciable rate at temperatures  $100^\circ$  above its melting-point. The density of gold is 19.4. It is exceedingly malleable and ductile and may be beaten out into leaves so thin that 280,000 will make a pile only an inch in thickness. Such leaves are somewhat translucent and appear green by transmitted light although by reflected light they have the color and luster of gold. Gold wire can be drawn so fine that 3240 meters of it will weigh only a gram. Very finely divided gold usually has

a purple color although red, blue and green colloidal solutions of the metal have been obtained. Ruby glass owes its color to finely divided gold as does "purple of Cassius" which appears to be minute particles of gold intimately mixed with stannic oxide.

Gold is a very good conductor of heat and electricity being exceeded by only silver and copper.

**Chemical Properties.**—Gold is even more resistant to chemical action than silver. It is not altered by oxygen at ordinary temperatures nor by hydrogen sulfide. It is not dissolved by any dilute acid nor by concentrated nitric or sulfuric acids, indicating that it requires a very strong oxidizing agent to cause the gold to pass into the ionic state. This is confirmed by the fact that it is dissolved by selenic acid which is a most active oxidizing agent. The metal is also dissolved by "aqua regia" a mixture of nitric and hydrochloric acids.

This mixture evolves chlorine and the gold is transformed by it into chlorauric acid,  $\text{HAuCl}_4$ , which gives the complex ion,  $\text{AuCl}_4^-$ . The chlorine, of course, cannot be a stronger oxidizing agent than the nitric acid which set it free, but it has the advantage in this case that the product of the reaction is very stable. Gold is also attacked by the fused hydroxides and nitrates of the alkali metals. The soluble chlorine compounds of gold are easily reduced by even such feeble reducing agents as the ferrous salts or oxalic acid.



Because of its chemical resistivity, its beauty and its comparative rarity, gold has long been used for ornaments and for coinage. For such purposes, the pure metal is too soft and it is alloyed with copper or silver, usually the former. The gold coins of most countries contain 90 per cent. of gold or are 900 "fine"; those of England, however, contain 91.367 per cent. or are 916.67 fine. The composition of gold alloys is often expressed in carats, pure gold being 24 carat and 18 carat gold being 18/24 gold.

**The Oxides and Hydroxides.**—Auric hydroxide  $\text{Au}(\text{OH})_3$ , is formed when sodium hydroxide is added to an auric solution. It is slightly soluble in concentrated sulfuric and more easily in concentrated nitric acids, but is precipitated from these solu-

tions upon dilution. This indicates that it is a very weak base which is also in accord with the fact that it acts as an acid and dissolves in an excess of sodium or potassium hydroxides, forming aurates, potassium aurate,  $\text{KH}_2\text{AuO}_3 \cdot 2\text{H}_2\text{O}$  for example. When the hydroxide is carefully heated, it goes over into auric oxide,  $\text{Au}_2\text{O}_3$ , which at higher temperatures decomposes into the elements. Both the hydroxide and the oxide are soluble in hydrochloric acid forming chlorauric acid.

Aurous hydroxide,  $\text{AuOH}$ , is formed by the action of dilute potassium hydroxide upon aurous chloride. Sulfuric and nitric acids do not act upon it. When heated to  $200^\circ$  it is changed into the oxide,  $\text{Au}_2\text{O}$ , and this decomposes at  $250^\circ$ . Both the oxide and the hydroxide give gold and chlorauric acid when treated with hydrochloric acid.

**The Halogen Compounds of Gold.**—Gold will combine directly with chlorine or bromine for the formation of auric chloride or bromide,  $\text{AuCl}_3$ ,  $\text{AuBr}_3$ . These compounds dissolve easily in water with the formation of complex acids of the type  $\text{H}_2\text{AuCl}_3\text{O}$ . They will also combine with hydrochloric or hydrobromic acid or with the corresponding halide salts for the formation of chlorauric or bromauric acids or their salts. The sodium chloraurate,  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  is a common commercial salt and is used in photography as noted above in the toning of silver prints. Chlorauric acid is formed by dissolving gold in aqua regia.

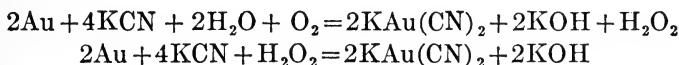
When either the simple chloride or bromide or the complex acids are cautiously heated, aurous chloride or bromide is formed. At still higher temperatures, these decompose into the free halogen and the metal. They are not soluble in water, but slowly decompose in contact with it forming the auric compound and free gold. This is much like the behavior of some of the cuprous compounds. Auric iodide is decidedly unstable and passes easily into the aurous compound even at ordinary temperatures.

**Sulfides.**—Hydrogen sulfide precipitates a mixture of aurous sulfide,  $\text{Au}_2\text{S}$ , and auric sulfide,  $\text{Au}_2\text{S}_3$  from auric solutions. These sulfides are soluble in the alkaline sulfides owing to the formation of the thio aurites,  $\text{K}_3\text{AuS}_2$ , and thio aurates,  $\text{KAuS}_2$ . In this respect gold is like antimony, arsenic, and tin.

**The Complex Cyanides.**—One of the most important chemical

properties of gold is its ability to form complex ions with cyanogen; aurocyanogen,  $\text{Au}(\text{CN})_2^-$ , and auricyanogen,  $\text{Au}(\text{CN})_4^-$ , are well known examples of such ions. They are formed by the action of an excess of sodium or potassium cyanide upon the compounds of gold. They are very stable and the solutions are utilized in gold electroplating, an anode of gold being used and the object to be plated being made the cathode. Although the gold is in the anion it is deposited upon the cathode by secondary electrolysis.

The aurocyanides are of especial importance, because it is through their formation that a large part of the gold is extracted from its ores. This depends upon the fact that finely divided gold is dissolved by solutions of potassium or sodium cyanides when in contact with the air. The equations for the reactions are as follows:



These reactions are really ionic so that they succeed as well with the cheaper sodium cyanide as with the more expensive potassium salt. It is very common to find hydrogen peroxide as one of the products of oxidation brought about by oxygen of the air in the presence of water. Usually half of the oxygen goes to the peroxide.

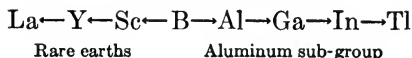
**Analytical Properties of Gold.**—Gold may be detected by its reduction to the metallic state by ferrous salts, oxalic acid, or stannous chloride. It is almost invariably determined by the fire assaying processes. This is often done as follows: a weighed quantity of the material containing gold is mixed with a relatively large quantity of lead and a little borax and heated in a shallow clay dish called a scorifier to a fairly high temperature in contact with the air. A part of the lead and practically all of the copper and other impurities in the gold save the silver are oxidized, and these together with the "gangue" form a sort of a glass with the borax and the lead oxide which is formed. At the close of this operation the molten mass is poured into a mold and allowed to cool. A lead button containing the gold and silver is obtained. This is then heated to a high temperature in contact with the air in a "cupel" or little cup made of bone ash, the lead oxidizes and

the oxide is absorbed in the cupel. There is finally left a button of gold and silver. The silver is then removed by treating the alloy with nitric acid which does not dissolve the gold. In order that the operation, which is called parting, shall succeed easily this button should not be much more than 25 per cent. gold although it is possible to part alloys containing 33 per cent. Concentrated sulfuric acid may be used instead of nitric. The fire assay is a smelting process carried out on a small scale.



## CHAPTER XXV

### GROUP III



The elements of this group fall naturally into two sub-groups, the rare earth metals and the aluminum sub-group. The members of the first are scandium, yttrium, and lanthanum, those of the aluminum sub-group are boron, aluminum, gallium, indium, and thallium. The elements are all trivalent although some have other valencies in addition. As was the case in groups I and II the members which stand in the left hand column of the group as it appears in the periodic system, scandium, yttrium, and lanthanum are stronger bases than those of the aluminum group which are on the right. Aluminum is the third element in the order of abundance in the earth's crust, boron is fairly abundant and all the other members of the group are decidedly rare.

**The Rare Earth Metals.**—The metals of the rare earths are found in a large number of rare minerals each of which contains a great many elements. The names of a few of these minerals are euxenite, gadolinite, orthite, and monazite. Monazite is found in considerable quantities in North and South Carolina, but comes chiefly from Brazil. The hydroxides of the members of this sub-group are fairly strong bases and are not soluble in excess of sodium or potassium hydroxides.

#### SCANDIUM

Scandium whose combining weight is 44.1 is interesting because it is one of the elements whose existence and properties were predicted by Mendelejeff. Its hydroxide  $\text{Sc}(\text{OH})_3$  is a colorless gelatinous precipitate soluble in acids but not in bases.

The salts are colorless and are not especially hydrolyzed. The salts of the oxy-acids as well as of the halogen acids are known.

### YTTRIUM

Yttrium has a combining weight of 89. The metal decomposes water slowly, its hydroxide is colorless and gives colorless salts. It is a stronger base than scandium hydroxide.

### LANTHANUM

Lanthanum, La, combining weight 139, is an iron gray colored metal, which is very slowly acted upon by water. It dissolves in dilute acids. The hydroxide is white and somewhat soluble in water, the solution is alkaline, absorbs carbon dioxide and decomposes ammonium salts. It is the strongest base of the group.

There are several elements, some of them of rather doubtful individuality, whose combining weights are near to that of lanthanum and which so far as that is concerned have a claim on the same position in the periodic system. They have so nearly the same properties that it is difficult to separate them. Ostwald has likened this group of closely related elements with about the same combining weight which appear in the periodic system where one element might be expected, to the planetoids which are found in the solar system where one large planet might be looked for.

**The Aluminum Sub-group.**—The first member of Group III and of this sub-group is boron (comb. wt. 11). This is almost exclusively an acid-forming element; that is to say, it does not form cations, and for that reason has already been treated among the non-metals.

### ALUMINUM

**General.**—Aluminum is the most abundant of the metals. It is never found free in nature. The compounds of aluminum have been known for centuries but the element was first obtained by Wöhler through the reduction of the chloride by potassium.

It is now prepared on a very large scale. In 1910, 47,734,000 lb. were produced in the United States. The process is electrolytic and will be described later. The metal is trivalent, and the element is like zinc in that its hydroxide is soluble both in acids and in bases. In addition to its fairly close relationship to the other members of this sub-group, it is very much like ferric iron and trivalent chromium as will be seen when these metals are studied.

**Occurrence.**—The compounds of aluminum are of course exceedingly abundant, since it is an essential constituent of nearly all rocks except the sand-stones and lime-stones and is almost invariably present in these. It is found chiefly as the double silicates, the feldspars and the micas; as the simple silicate clay; as the double fluoride with sodium in cryolite; as the oxide corundum; as the hydroxide and the partially dehydrated hydroxide in bauxite; and in many other compounds. The ruby is aluminum oxide colored by a little chromium, the garnet is calcium aluminum silicate, and turquoise is a basic phosphate.

**Preparation of the Metal.**—Metallic aluminum is prepared by the electrolysis of highly purified aluminum oxide dissolved in a molten bath the exact composition of which is kept secret. In the early days of the industry it consisted of cryolite,  $\text{Na}_3\text{AlF}_6$ , later a mixture of cryolite, aluminum fluoride  $\text{AlF}_3$ , and a small quantity of calcium chloride was patented. It is perhaps significant as showing the changes which have taken place in the nature of this bath, that while the production of aluminum has steadily increased, the importation of cryolite fell off to 1/12 what it was in 1907, while the consumption of fluorspar increased; but recently the importation of cryolite has again become very heavy. The electrolysis is carried out in iron cells lined with carbon which is made the cathode, the anodes being large carbon rods. The current is high, about 10,000 amperes per cell, while the drop of potential around the cell is about 5 volts. The bath is kept melted by the heat produced by the current in overcoming the resistance. Upon electrolysis after the addition of the oxide, the metal collects at the cathode and runs down to the bottom of the cell while oxygen is evolved, and combines largely with the carbon anodes. As the process goes on more aluminum oxide is

added from time to time, and the metal is tapped off so that the operation is continuous. This process differs materially from most metallurgical operations in that it is impracticable to purify the product, and so it is necessary to start with the very purest raw material. The aluminum oxide is made from bauxite, and the simplest process for its purification is to melt the bauxite in an electric furnace with the proper amount of carbon. This reduces the oxides of iron, silicon, and titanium which are present and leaves the aluminum oxide untouched. The metallic aluminum is very pure, often running 99.9 per cent.

**Physical Properties.**—Aluminum is a white metal with a bluish cast. It melts at  $655^{\circ}$  and has a density of 2.7 becoming 2.72 if it is hammered or rolled. The cast aluminum is about as hard as pure silver while the hammered is as hard as soft iron. Its tensile strength is high although much lower than that of steel. It is malleable and ductile and may be rolled or hammered into very thin sheets or drawn into fine wire. It is best worked at 100 to  $150^{\circ}$ . At temperatures near its melting-point it becomes so brittle that it may be easily powdered in a mortar. It is not readily worked in a lathe, but many of its alloys are.

Alloys with magnesium known as magnalium are very light, easily machined and fairly strong. Aluminum bronze has already been discussed under copper.

Pure aluminum has a high conductivity for electricity, about two-thirds that of copper for conductors of equal cross-section, but since the density of aluminum is so much smaller than that of copper, an aluminum conductor will weigh less than a copper conductor of equal carrying capacity. The difference in weight is so great that although the price of aluminum is higher than that of copper the cost of an aluminum conductor is less than that of a corresponding copper wire. There are, however, difficulties attending its use which partially make up for the difference in price.

**Chemical Properties.**—Metallic aluminum is really a very active element and passes into its compounds with a great decrease in free energy, and yet it acts in the main like a rather inert metal. It seems not to be acted upon by air or water or many other chemical agencies. But this indifference is apparent rather than real and is due to the formation of a very thin,

closely adhering film of the oxide which acts as a sort of varnish, and in a great measure protects the metal from further attack. Aluminum may be amalgamated by contact with solutions of mercuric chloride. The aluminum oxide seems to be unable to cling to the surface of the fluid or semi-fluid aluminum amalgam, and the latter shows the real activity of the metal. It is rapidly acted upon by air and water giving hydrogen and aluminum hydroxide. In warm moist air the aluminum hydroxide grows out from the metal in a moss-like formation which in a short time may extend a centimeter or more from the amalgamated surface. Amalgamation of the aluminum cannot increase its activity but simply allows it full play. For this reason amalgamated aluminum is used as a reducing agent.

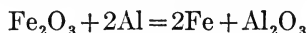
Aluminum dissolves in solutions of sodium hydroxide with the evolution of hydrogen. The explanation for this action is found in the fact that sodium hydroxide will dissolve aluminum oxide, and therefore it is supposed that it removes the protecting film from the surface of the metal and allows the latter to display its activity. Because of this protecting film, massive aluminum is but superficially attacked even at high temperatures by the air. The powdered metal, however, will burn with a very bright light when blown into a flame especially if carried by a stream of oxygen. It is sometimes used in flashlight powders. Aluminum dissolves readily in hydrochloric acid, not so easily in dilute sulfuric, and very slowly in dilute nitric. In the two former cases, hydrogen is evolved while in the latter, ammonium salts are produced. The difference in the rate of attack is probably connected with the film mentioned above. Another phenomenon which is probably due to this is, that if a piece of aluminum is made anode in certain salt solutions, sodium sulfate, carbonate, phosphate, etc., it will not allow a current to pass until a certain potential is reached, which in the case of the phosphate is 300-400 volts; while if it is made the cathode, the current passes easily at a low voltage. The aluminum electrode changes its properties very rapidly with the change in the direction of the current, and this property may be made the basis of a method for changing an alternating into a direct current. It is also of use in certain kinds of lightning arrestors.

Aluminum is trivalent in all of its compounds. Its hydroxide

acts both as an acid and as a base and therefore cannot be strong in either way, consequently both classes of salts are hydrolyzed to a certain degree.

The combining weight of aluminum is 27.1.

**Goldschmidt Process.**—The most striking chemical property of aluminum is its great tendency to combine with oxygen. As mentioned above this is generally concealed by the film of oxide, but under the proper conditions, aluminum will reduce all other oxides except magnesium. To bring this about, the oxide to be reduced is mixed in the proper proportions with powdered aluminum and the mixture heated at one point to a high temperature by burning magnesium or a mixture of magnesium and potassium chlorate, when a very vigorous reaction takes place which spreads through the entire mixture. The temperature attained is usually high enough to melt the other metal and the aluminum oxide. Naturally it varies with the oxide reduced. The process was invented by Goldschmidt and called by him "Aluminothermy" and the mixtures "thermite." They are used both to get high temperatures and pure metals. The equation for the reaction with ferric oxide is,



This reaction produces a temperature of 3000° and is often used for welding operations and in the repair of breaks in large castings or forgings. It can be used almost anywhere and has proved to be of very great benefit for making repairs at a distance from a machine shop. With sulfides, a very similar reaction takes place, aluminum sulfide,  $\text{Al}_2\text{S}_3$ , and the metal being formed.

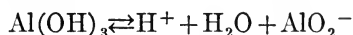
**Aluminum Oxide and Hydroxide.**—Aluminum oxide,  $\text{Al}_2\text{O}_3$ , or alumina as it is often called, is found in nature in the mineral corundum. When colored red by chromium it is called ruby, when blue, sapphire. Corundum mixed with magnetite is called emery. Corundum is next to diamond and carborundum (silicon carbide) in hardness, and is used for making wheels for grinding. Aluminum oxide which has been fused in an electric furnace is identical with corundum and is now being used instead of the mineral under the name "alundum". Artificial

rubies which are identical with the natural stones, are made by fusing a mixture of aluminum oxide and a chromium compound.

Aluminum oxide may be made by the Goldschmidt process mentioned above or by heating the hydroxide. In the latter event, if the temperature has not been raised too high, the oxide dissolves readily in acids; but the crystalline varieties or that which has been ignited will dissolve only in fused potassium acid sulfate.

Aluminum oxide prepared by gently heating the hydroxide is a very efficient drying agent and is suitable for many gases which cannot be dried by  $P_2O_5$ .

Aluminum hydroxide is found in nature in the mineral hydrargillite,  $Al(OH)_3$ , and may be made in the laboratory by the addition of a solution of a base or of a carbonate to a solution of an aluminum salt. It is not soluble in water, but is dissolved by acids and by strong bases, resembling the hydroxides of glucinum and zinc in this respect. It differs from zinc hydroxide in that it is very slightly soluble in ammonium hydroxide. The hydroxide dissolves in acids because of the usual dissociation of the bases into the cation and hydroxyl the concentration of the latter being decreased by the hydrogen. The bases dissolve it, because it splits off hydrogen as ion and forms the aluminate ion  $AlO_2^-$ ,



The hydroxyl ion of the base unites with the hydrogen ion and decreases its concentration. The salts formed are aluminates. Sodium aluminate and the corresponding potassium salt,  $NaAlO_2$  and  $KAlO_2$ , are soluble in water, but are highly hydrolyzed because aluminum hydroxide is a very weak acid. The ammonium aluminate, being the salt both of a weak acid and of a weak base, is practically completely hydrolyzed and for this reason the hydroxide is not dissolved to any great extent by ammonia. Most of the aluminates are insoluble and many are found in nature; those of the bivalent metals are called spinels from the magnesium aluminate, spinel,  $Mg(AlO_2)_2$ , which is the typical mineral of the class.

Because of the great weakness of aluminum hydroxide as a base, aluminum carbonate does not exist; and aluminum hydroxide is precipitated upon the addition of carbonates to solution of

aluminum salts. Obviously salts of other weak acids will work in the same way and  $\text{Al}(\text{OH})_3$  is precipitated by solutions of alkali sulfides and cyanides.

Aluminum hydroxide is made on a large scale by dissolving bauxite,  $\text{Al}_2\text{O}(\text{OH})_4$ , in hot sodium hydroxide under a steam pressure of about 5.5 atmospheres, and then allowing the filtered solution to stand in contact with some of the  $\text{Al}(\text{OH})_3$  from the previous operation. Under these conditions the hydroxide separates in a more stable and hence less soluble form than the ordinary hydroxide. The sodium hydroxide solution is then ready for use to dissolve more bauxite.

**Halogen Compounds.**—The mineral cryolite was formerly the most important halogen compound because of its connection with the preparation of the metal. Its formula is  $\text{AlF}_3 \cdot 3\text{NaF}$ . Aluminum chloride,  $\text{AlCl}_3$ , is the most important of the artificially prepared halogen compounds of aluminum. It may be obtained in the form of a crystalline hydrate,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , from solutions prepared by dissolving the hydroxide or metal in hydrochloric acid. When heated to drive off the water, the chloride is completely decomposed, aluminum oxide and hydrochloric acid being formed. The anhydrous chloride may be obtained by heating the metal in chlorine or in hydrogen chloride.

Aluminum chloride is a white crystalline solid which melts under pressure at  $193^\circ$ . The vapor pressure of the solid reaches that of one atmosphere at about  $183^\circ$  so the substance usually sublimes without melting. It fumes when exposed to moist air. The anhydrous salt is used in organic chemistry as a catalytic agent.

Because aluminum hydroxide is a weak base the solutions of aluminum salts, including the chloride, are acid in reaction from hydrolysis, and generally can be kept clear only in the presence of an excess of acid.

**Aluminum Sulfate.**—Aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , is made on a large scale from sulfuric acid and either aluminum hydroxide or aluminum silicate,  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$  or kaolin as it is often called. At the present time, the hydroxide is more commonly used. It is very soluble in water and the solution is acid because of hydrolysis. Its trade name is "concentrated alum." It is used as a mordant in dyeing and in sizing paper



to prevent the spreading of ink and in clarifying water. When a solution of potassium sulfate is added to a strong solution of aluminum sulfate, octahedral crystals of a double salt named alum,  $KAl(SO_4)_2 \cdot 12H_2O$ , are formed. This is the type of a rather large number of double salts which are isomorphous and are called alums. To distinguish it from the others, it is usually called potassium alum. The alums have the general formula  $M^+M^{+++}(AO_4)_2 \cdot 12H_2O$  in which  $M^+$  represents any member of the alkali metals except lithium and in addition ammonium, silver, and monovalent thallium;  $M^{+++}$  stands for aluminum, gallium, indium, trivalent iron, chromium, and manganese; and finally A may be either sulfur or selenium. The aluminum alums are distinguished by prefixing the name of the monovalent metal while in the case of the other alums both the mono- and trivalent metals are named, for example, potassium chrome alum,  $KCr(SO_4)_2 \cdot 12H_2O$ . The  $12H_2O$  is an essential part of an alum. Double sulfates are known which differ from alums only in this respect and yet they are not alums. Since the alums are isomorphous they can all form mixed crystals and a single crystal may contain a large number of elements.

Potassium alum is the most important alum; it was formerly the most important aluminum salt but has now been largely replaced by the sulfate. It may be prepared by roasting alunite, a basic alum found in Italy and in Hungary, and extracting with hot water. It is soluble in water to the extent of 5.9 parts of the anhydrous salt at  $20^\circ$  and 109 parts at  $90^\circ$  per 100 parts of water. The crystals melt in their own water at  $92^\circ$ .

Solutions of alum are acid and will react with carbonates and bicarbonates with the evolution of carbon dioxide, the precipitation of aluminum hydroxide and the formation of a solution of the sulfates of potassium and the metal of the carbonate. It is upon this property that its use in cheap baking powders depends. The soluble sulfates formed impart a strong bitter taste to the food and the use of such powders is objectionable on this account if for no other. A solution of alum will dissolve a considerable quantity of aluminum hydroxide forming the so-called "neutral alum,"  $KAl_2(OH)_3(SO_4)_2$ . It is used as a mordant in dyeing and as a clarifying agent in the purification of water. The

aluminum hydroxide which it readily forms is the active agent in each case.

Alum loses all of its water at 100°. It is then known as burnt alum, and is used in medicine.

**Mordants.**—Some dyes will combine directly or enter into solid solutions with the fiber of the cloth while others may be precipitated as insoluble substances within the fiber, but many others do not have either of these characteristics. Such dyes require a mordant, *i.e.*, a substance which will attach itself firmly both to the fiber and to the dye. Aluminum hydroxide is such a substance. The cloth to be dyed is first treated with a solution of an aluminum salt in such a condition that it contains a considerable amount of aluminum hydroxide; neutral alum, aluminum sulfate, acetate, or sodium aluminate serve well; and it is then boiled with the dye. Dyes more often require mordants with cotton than with wool or silk. Aluminum hydroxide even in the absence of the fiber will take up many dyes forming what are known as “lakes.”

**Aluminum Acetate.**—Aluminum acetate,  $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ , may be made by the action of the sulfate in solution upon lead or barium acetate, lead or barium sulfate being precipitated. Since it is a salt of a weak acid and of a weak base it is strongly hydrolyzed, and on this account is used in mordanting cloth. The same result may be secured at a lower cost by using aluminum sulfate and sodium acetate.

**Aluminum Sulfide.**—Aluminum sulfide,  $\text{Al}_2\text{S}_3$ , cannot be prepared in a wet way. It is formed by the action of finely divided aluminum on sulfides at a high temperature by practically the methods of the Goldschmidt process.

**Aluminum Silicate—Clay.**—The rocks which originally composed the earth's crust were very largely complex silicates and almost invariably contained aluminum as one of their constituents. By the action of the carbon dioxide of the air and of water, these rocks gradually decompose or weather as it is called, and aluminum silicate is one of the products. The aluminum silicate being practically insoluble and in an extremely fine state of division is carried by flowing water and deposited when the latter reaches a quiet lake or the ocean, forming the beds of clay. These evidently have a very good chance to become contami-

nated and are rarely pure. The purest clay, kaolin or china clay,  $H_2Al_2(SiO_4)_2 \cdot H_2O$ , has probably been formed by the decomposition of feldspar,  $KAlSi_3O_8$ , the potassium carbonate being carried away and the kaolin left where it was formed. Common clay contains some calcium carbonate, iron oxide, quartz, etc. When comparatively pure it is known as potters earth. Marl contains large quantities of calcium carbonate. Ocher, umber and sienna are clays colored by oxides of iron and manganese. They are used to some extent as pigments.

Clay as is well known becomes plastic when moist and may be easily worked into almost any shape desired. When dried and then heated to a high temperature it shrinks, becomes quite hard, and loses its power of becoming plastic with water. It also becomes resistant to chemical change and acquires considerable mechanical strength. Because of these properties it is used for making brick, pottery, and porcelain. The chemical change which takes place during the heating consists in the driving off of all of the hydrogen and part of the oxygen in the form of water. Pure kaolin cannot be melted in the furnace for working these articles, but the presence of compounds of the alkalis, calcium or magnesium carbonates or especially of oxide of iron causes the mixture to fuse partially and become more or less pasty while in the furnace, and stronger after the firing. The iron imparts the red color commonly associated with brick. Fire brick is made from nearly pure clay and has a high melting-point to which it owes its name. Articles made from clay are more or less porous after firing, and for many purposes they must be glazed. This is accomplished in various ways as will develop.

**Porcelain and Pottery.**—Porcelain is the name applied to the highest grade of ware made from clay. It is made by grinding together very pure kaolin and feldspar in the proper proportions, and making up into a plastic mass from which the desired articles are formed. After drying, these are fired at such a temperature that the feldspar melts and binds the burned kaolin together into a hard translucent mass which is nearly homogeneous but does not have a glaze. To secure the latter the articles are dipped into a suspension of very finely ground feldspar in water, the ware becomes coated with a thin layer of the feldspar, and after drying is fired once more at a high temperature and is

then allowed to cool slowly (annealed). The ware is then translucent and has a smooth glaze which is practically a glass. It is very difficultly fusible and decidedly resistant to chemical action, but is attacked by aqueous and fused alkalis.

Semiporcelain is made from a white plastic clay to which is added ground quartz, flint, or feldspar. After the first burning it is porous and is glazed with a mixture of borax, quartz, sodium carbonate, and oxide of lead. The ware is usually much thicker than porcelain and is not very suitable for chemical purposes.

Earthen ware is made from colored plastic clay, the impurities of which serve to frit or bind the kaolin together. It is glazed by throwing common salt into the kiln toward the close of the burning. At the high temperature, the salt volatilizes and reacts with the clay and the water vapor present so as to form an easily fusible silicate which fills the pores of the ware. Unglazed earthenware is largely used in the form of tile, bricks, flower pots, etc.

**Ultramarine.**—A double silicate of sodium and aluminum containing some sulfur is found in nature as the mineral lapis lazuli which has approximately the composition  $(\text{NaAlSiO}_3)_4 \cdot \text{Na}_2\text{S}_2$ . It has a very beautiful blue color and is used for ornamental purposes. When ground it forms the pigment known as ultramarine. This same pigment may be very cheaply made by heating together sodium sulfate, carbon, and clay. The resulting blue compound is ground and washed with water. Since it is very cheap and is stable toward light, air and alkalis it is much used as a pigment in water color paints, wall paper, laundry blue, etc. It was formerly used to disguise the faint yellow color of granulated sugar. It loses its color on contact with even very weak acids and the loss of color is accompanied by the evolution of hydrogen sulfide. The blue color of the compound is something of a puzzle because its components might naturally be expected to yield a colorless substance. By varying the methods of manufacture, green, violet, and red varieties may be obtained.

**Hydraulic Mortars and Cements.**—When a limestone containing something like 8 to 18 per cent. of clay is "burned" in the ordinary way the product will slake and form a mortar which will set and harden under water and hence is called hydraulic cement.

A much better product is made by burning a limestone which contains 20 per cent. or more of clay until the carbon dioxide is driven off. The substance so produced will not slake; but if finely ground and mixed with water, will set and harden out of contact with the air. This is known as *natural cement*.

**Portland cement** is the best hydraulic cement. *It is the finely pulverized product made by heating to incipient fusion a properly proportioned mixture of silica, aluminum silicate, and calcium carbonate to which an addition of not more than 3 per cent. of gypsum has been made after the heating.* The chemistry of Portland cement is not very well understood, and there is great disagreement on most of the points in connection with it. However, all are agreed that the essential constituents of Portland cement are lime, silica, and alumina, some of the alumina is always replaced by ferric oxide, and a little of the lime by magnesia. Most are agreed that calcium silicate or silicates and calcium aluminate or aluminates are present in the burned product. The product is not a chemical compound as shown by the variations in composition and properties, but the better cements correspond in composition to mixtures of tricalcium silicate,  $\text{Ca}_3\text{SiO}_5$ , and dicalcium aluminate,  $\text{Ca}_2\text{Al}_2\text{O}_5$ , in such proportions that there shall be in the whole 58 to 67 per cent. of lime, 19 to 25 per cent. silica, 5 to 10 per cent. of alumina, all these oxides, of course, being in combination. The iron oxide runs from 2 to 5 per cent. and takes the place of a part of the alumina. Of course, it does not necessarily follow that the compounds given above are present in the cement; in fact quite other compounds have their advocates. The following table gives the analysis of a few American Portland cements.

Where made	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	CaO	MgO	$\text{SO}_3$	Loss
Pennsylvania.....	22.20	2.27	6.69	62.61	3.00	1.32	1.56
Pennsylvania.....	21.94	2.37	6.87	60.25	2.78	1.38	3.55
Michigan.....	22.71	3.54	6.71	62.18	1.12	1.21	1.58
Michigan.....	22.10	2.35	7.95	61.81	2.15	1.71	1.34

Portland cement may be made from almost any materials which

give the proper mixture of calcium carbonate, silica, and aluminum silicate provided they do not contain more than 4 per cent. of magnesium carbonate and that the silica is in a very fine state of subdivision. The most widely used materials for the preparation of this cement are limestone and clay or shale; these are very finely ground and thoroughly mixed in such proportions that the mixture shall contain close to 75 per cent. of calcium carbonate and 20 per cent. silica, alumina and ferric oxide taken together, the remaining 5 per cent. being magnesium carbonate, alkalis, etc. Some limestones have approximately this com-

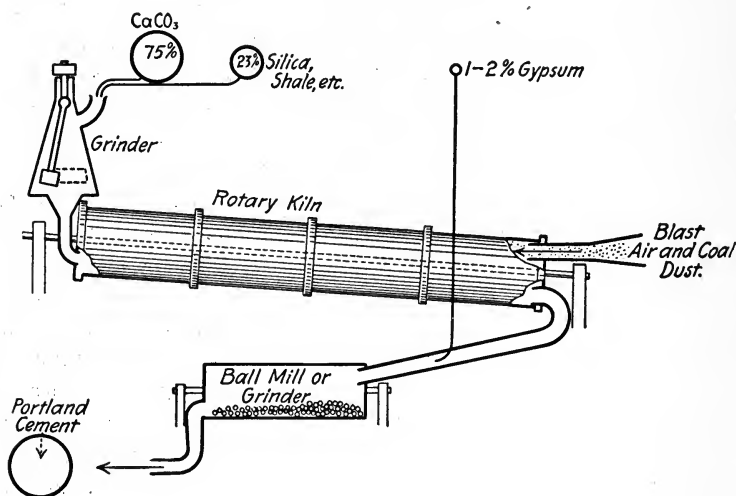


FIG. 42.

position, and are called "cement rock" since they require merely the addition of a little of a purer limestone or of a suitable clay to correct their composition.

After the components of the cement have been ground very finely and thoroughly mixed in the proper proportions, they are then fed into the upper end of a long, slightly inclined rotary kiln through which they gradually work their way against the flames and hot gases of a fire of powdered coal which is blown into the lower end of the kiln with a blast of air and which burns much as a gas would do (Fig. 42).

These kilns are 60 to 150 ft. in length and 6 to 9 ft. in diameter. Sometimes they are fired with crude oil, or natural gas, but coal is the usual fuel. The temperature reached (1500-1600°) is high enough to drive off the carbon dioxide and to heat the calcium silicate and aluminate formed, to incipient fusion. The product is termed clinker and comes out in hard lumps. It is then ground once more and mixed with 2 to 3 per cent. of calcium sulfate in the form of gypsum or plaster of Paris. This acts as a "retarder" and increases the time of setting. After being stored for some time, such a retarded cement may become quick setting once more, and may then be retarded by adding more plaster of Paris or by slaking a little lime in the water used. After the cement has set it gradually hardens and increases in strength for months, and even in some cases for years. The setting and hardening are due to the formation of interlaced crystals of substances formed by the reaction of water with the cement. But the different investigators are very far from agreement as to the composition of these crystals. The setting seems to be connected with the calcium aluminate and the hardening with the silicate. No one seems to know why the calcium sulfate acts as a retarder or why it loses its influence in the course of time, except that contact with the air has something to do with it, and it is of course impossible to say why the slaked lime will revive the retarding power of the sulfate.

A mixture in the proper proportions of Portland cement, sand, crushed stone and water will harden to a stone-like substance called concrete, the usefulness of which is well known to every one. In 1910 the United States produced 76,550,000 barrels of Portland cement.

### GALLIUM

Gallium has a combining weight of 69.9 and is the third member of the aluminum family. Its existence and some of its properties were predicted by Mendelejeff. The element is widely distributed but always in very small quantities. It is found in many samples of zinc blende, in some iron ores, and always in bauxite. The metal melts at 30.5°, has a bluish-white color and a density of 5.9. Toward air, water, acids, and bases it acts as aluminum does. It is mostly trivalent in the compounds,

although a dichloride,  $\text{GaCl}_2$ , is known. The hydroxide is both a base and an acid. The sulfate forms alums with the sulfates of the alkali metals. It is most easily detected by its spark-spectrum. No application of the element or compounds has as yet been made. It was discovered by Lecoq de Boisbaudran in 1875.

### INDIUM

Indium is the fourth member of the group and has a combining weight of 114.8. It occurs in small quantities, as the sulfide in certain zinc blends. The metal has a density of 7.1 and is white and easily malleable; it melts at  $176^\circ$ . It retains its luster in air and water. It is dissolved by dilute hydrochloric and sulfuric acids, and more readily by nitric acid. It is mostly trivalent in its compounds, but a mono- and dichloride are known. The hydroxide is soluble both in acids and in the strong bases. The sulfate forms alums. The spectrum contains a strong indigo blue line and a violet line. The element was discovered in 1863 by Reich and Richter.

### THALLIUM

Thallium was discovered in 1861 by Crooks in the flue dust of a sulfuric acid plant using pyrite as the source of sulfur. Such dust still constitutes the chief source of the metal since it is found in many varieties of iron and copper pyrites. It also occurs as an essential constituent of a few rare minerals. It is somewhat more abundant than gallium and indium. Its combining weight is 204.0. In a general way the metal resembles lead, except that it is much more readily oxidized. The density of the metal is 11.8. It melts at  $303^\circ$ , and boils at  $1280^\circ$ . The density of the vapor gives a molar weight of 220, from which it is concluded that there is one combining weight per mole. The metal dissolves readily in dilute and concentrated sulfuric acids, and less readily in hydrochloric. Thallium forms two series of compounds. In one it is trivalent and resembles aluminum to a certain degree, but the resemblance is not very marked. Thallic hydroxide is not soluble in bases and the sulfate does not form

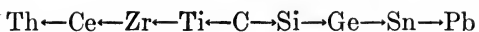


alums, although double sulfates with the alkali metals are known containing eight moles of water of crystallization, and crystals of ammonium alum have been obtained containing thallium sulfate.

The monovalent or thallose series presents a curious set of relationships. The hydroxide,  $\text{ThOH}$ , is soluble in water and is a strong base. The carbonate, phosphate, sulfate and oxalate are soluble. These properties are very remarkable for a heavy metal, and are like those of an alkali metal. This resemblance is further strengthened by the fact that the sulfate forms the compound  $\text{Tl}_2\text{SO}_4, \text{MgSO}_4, 6\text{H}_2\text{O}$ , isomorphous with the corresponding potassium salt, and also forms alum with the ferric, chromic, or aluminum sulfates, which are isomorphous with ordinary alum. The fluoride is easily soluble while the rest of the halides are but slightly soluble, the solubility decreasing from the chloride to the iodide. The chloride changes from white to violet in the light. The chromate is slightly soluble. In all these ways it is like silver. It resembles lead in that the chloride is not dissolved by ammonia but is by hot water.

## CHAPTER XXVI

### GROUP IV



The members of Group IV, like those of the preceding groups, divide themselves into two sub-groups, which may be named the titanium and the germanium sub-groups. There is not as marked a difference in the properties of the two as was the case with the preceding groups, and yet the same general relationship holds here. The basic character of the elements increases with the combining weight. The members of the titanium groups, which occupy the left hand column in the table as it is arranged, are, on the whole, stronger bases than those on the right-hand side, the germanium group. This, it will be recalled, has been the case in each of the preceding groups of metals. The gradual weakening in the basic properties, which has been noticeable in passing to each successive group, is continued with this and there is no really strong base formed by a member of the group, in fact the first two members, carbon and silicon, are distinctly non-metallic, and have been discussed among such elements. The maximum valence of the members of the group is four.

#### TITANIUM SUB-GROUP

The members of this sub-group are titanium,  $\text{Ti}=48.1$ ; zirconium,  $\text{Zr}=90.6$ ; cerium,  $\text{Ce}=140.25$ ; and thorium,  $\text{Th}=232.4$ . Titanium is a widely distributed and comparatively abundant element being present in almost all igneous rocks and forming a larger per cent. of the lithosphere than carbon. It does not occur free in nature, and its compounds are not collected in great beds like the coal beds, so it is not as available as carbon. It occurs in a number of minerals, such as rutile,  $\text{TiO}_2$  and titanite iron ore or ilmenite,  $\text{FeTiO}_3$ . The metal dissolves in acids with the evolution of hydrogen, and decomposes steam at a high

temperature. It forms three series of compounds in which it is di-, tri-, and tetravalent; the latter are the most stable. Titanic hydroxide is rather more of an acid than of a base but acts in both ways, forming titanates, such as potassium titanate  $K_2TiO_3$ , and the tetrachloride  $TiCl_4$ , or the sulfate  $Ti(SO_4)_2 \cdot 3H_2O$ . Metallic titanium has a great tendency to combine with nitrogen, oxygen and sulfur. An alloy of metallic titanium with iron, called ferrotitanium, is often used in the manufacture of steel. It improves the quality of the steel by removing nitrogen, reducing oxides and causing the slag to separate. Used in this way the titanium does not remain in the steel. Very recently alloy steels containing titanium have come into favor. The titanium increases the tensile strength and toughens the steel. The carbide is used in special kinds of flaming arc lamps, burning titanium carbide as cathode below a copper anode. Attempts have been made to use the metal as the filament in incandescent electric lamps.

#### ZIRCONIUM

**Zirconium** is a rare metal, which is found chiefly as zircon, the silicate  $ZrSiO_4$ . Its hydroxide is a weaker acid and a stronger base than titanium hydroxide. The dioxide  $ZrO_2$  is one of several of the oxides of the rarer elements which are used in making the glower of the Nernst electric lamp. This glower is a rod composed of the oxides and is a non-conductor at ordinary temperatures, but when heated it conducts and produces a greater amount of light for a given expenditure of energy than the carbon filament lamp which has been commonly used.

#### CERIUM

**Cerium** is a rare metal which is chiefly found in cerite, a hydrated silicate, which contains calcium, cerium, and lanthanum, and the other rare earths, which so closely resemble lanthanum. The metal burns more readily than magnesium and the small particles thrown off, when it is scratched with a hard object, take fire. This is probably connected with the fact that alloys of iron with cerium, lanthanum, and others of the rare earth metals will give brilliant sparks when rubbed with a piece of steel. These sparks will ignite tinder, gases, alcohol vapor, and certain explosives, and the alloys find a number of practical applications taking the place of matches for certain purposes. Cerium dioxide is used in connection with thorium dioxide in the

preparation of incandescent mantles, as will soon be described. Cerium forms two series of compounds, in one it is trivalent and strongly resembles the rare earths, while in the other it is tetravalent, and is like the other titanium metals.

### THORIUM

**Thorium** is a rather rare element, which is obtained chiefly from monazite, a phosphate of cerium and thorium. Thorium hydroxide is the strongest base of the titanium series. The nitrate,  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  is the most important salt. It is used in the formation of Welsbach incandescent gas mantles. These are made by dipping a woven cotton mantle into a solution of thorium nitrate along with about 1 per cent. of cerium nitrate,  $\text{Ce}(\text{NO}_3)_4$ . After drying, the cotton is burned away, and the nitrates are converted into the oxides which retain the form of the cotton mantle. This is then heated with a powerful gas burner until the oxides sinter together and acquire some little strength. They are then dipped into a solution of collodion, as it is called, made from soluble cotton, so that they may bear transportation. A mixture of the two oxides in the proportions given is very efficient as a light producer, while pure thorium dioxide, or a mixture containing more cerium, is not nearly so good. Other earths and basic oxides can be substituted for the cerium with more or less success.

Thorium and its compounds are radio-active, but nowhere near as highly so as the radium compounds. A discussion of this phase of the properties of thorium will be postponed until later, when all the radio-active elements may be treated together.

### GERMANIUM SUB-GROUP

The members of this sub-group are both di- and tetravalent. In their divalent compounds, they are more strongly basic than in the other series.

**Germanium**, 72.5, is a very rare element. Its properties agree very closely with those predicted by Mendelejeff for ekasilicon, germanium being then undiscovered. The element itself is distinctly metallic, but its compounds are much more like those of the non-metals than the metals. It bears a strong resemblance to carbon and silicon, as may be seen from the formulas of a few of its compounds,  $\text{GeH}_4$ ,  $\text{GeF}_4$ ,  $\text{GeCl}_4$ ,  $\text{GeCl}_2$ ,  $\text{GeHCl}_3$  (germanium

chloroform),  $\text{GeO}_2$ ,  $\text{GeO}$ ,  $\text{GeS}_2$ ,  $\text{GeS}$ . The dioxide has acid properties, but also dissolves in acids. The sulfide, like zinc sulfide, is white.

## TIN

The discovery of tin is prehistoric, the metal having been used by early man in making his bronze tools and weapons.

**Occurrence and Metallurgy.**—Very small quantities of tin are found native, but the chief ore is tin stone, or cassiterite,  $\text{SnO}_2$ . This is found in many places, but chiefly in the East Indies, Bolivia and Cornwall. This tin stone was among the first ore to be smelted by man. It is easily reduced to the metallic state by carbon, the greatest difficulty in the metallurgy of tin being the purification of the oxides before its reduction. This is done by crushing the ore and mechanically separating the granite or other rocky gangue. The concentrated ore is then repeatedly roasted and washed to remove the sulfides of arsenic, iron and copper. The roasting is done in revolving furnaces similar to the Portland cement kiln. The purified stannic oxide is then reduced in reverberatory furnaces with carbon in the form of anthracite coal. The tin so obtained contains some iron and arsenic. These combine with a little tin to form a compound having a higher melting-point than the pure tin, so that the latter may be purified by carefully heating the ingots to a very little above the melting-point of tin, and allowing the purer metal to run away from the iron arsenic alloy. This process is called liquation. The purest tin is that from Banca. The world's production of tin in 1910 was 115,589 tons, of which the United States produced about 40 tons and imported 52,528 tons valued at \$34,000,000.

**Physical Properties.**—Tin is a silvery white highly lustrous crystalline metal, which exists in several enantiotropic modifications. The one which is the most familiar is stable from  $20^\circ$  to  $175^\circ$  and is known as tetragonal, or ordinary tin. Below  $20^\circ$  it becomes meta-stable, and may pass over into a gray pulverescent modification, with a considerable increase in volume, since the density of the gray tin is 5.8, while that of the ordinary tin is 7.3. This is of course accompanied by the injury or destruction of any object made of the tin. The change is known as the

"tin disease" and has caused the gradual decay of organ pipes, etc., in the northern part of Europe where the temperature averages lower than  $20^{\circ}$ . This change is most rapid at  $-50^{\circ}$ . The transformation is very easily suspended and in the absence of the gray modification, ordinary tin will remain at temperatures somewhat below  $20^{\circ}$ , practically indefinitely. At  $175^{\circ}$ , tetragonal or ordinary tin changes into rhombic, which is stable up to the melting-point,  $233^{\circ}$ . Tin is very malleable and may be beaten or rolled into thin sheets, known as tin foil. Cast tin is crystalline and when bent gives out a peculiar sound known as the "cry of tin." Tin plate or "tin," as it is generally called, is made by dipping carefully cleaned sheets of mild steel into molten tin. The tin forms an alloy with the iron and this, in turn, becomes covered with a thin layer of practically pure tin. Such plate owes its usefulness to the fact that metallic tin is unaffected by air, water, or by weak acids in the absence of air. As is well known, very large quantities of tin plate are used in making cans and utensils. The greater part of these soon find their way to the rubbish heap and the tin is lost. This waste is regrettable because the supply of tin ore seems to be limited. Attempts are being made with somewhat encouraging success to recover the metal from such waste plate. One very serious drawback is the cost of collection.

There are in use two important methods for the recovery of tin. In one the tin plate is made anode in a solution of sodium hydroxide. The tin dissolves as sodium stannate and is deposited on the cathode. In the other, the plate is exposed to the action of chlorine which attacks the tin much more easily than the iron. Each of these methods works well on the clean scrap left in the manufacture of tinned articles and about one-fourth of the tin used in this country is recovered in these ways.

A piece of tin plate which has once got a hole scratched through the tin down to the iron will rust more rapidly at that place than a piece of pure iron. This is due to the fact that in the presence of water an electric battery is formed with the iron acting like the zinc in an ordinary cell with the result that it is rapidly corroded.

Tin is a component of many alloys; bronze has been given; soft solder contains 50 per cent. each of lead and tin; pewter, 25 per

cent. lead; Britannia metal 10 per cent. antimony and some copper. Tin amalgam was formerly used to back mirrors.

**Chemical Properties.**—Tin forms two series of compounds, the stannous, in which it is divalent, and the stannic, in which it is tetravalent. Stannous hydroxide is more basic than stannic and its salts are less hydrolyzed in water solutions than the stannic salts, but each hydroxide is soluble both in bases and in acids and therefore each is a weak base. Neither is a strong enough base to form a carbonate. The stannous salts are good reducing agents, passing readily into the stannic compounds.

The metal is not altered by air or water at ordinary temperatures, but oxidizes easily at higher temperatures. It dissolves readily in hydrochloric acid with the evolution of hydrogen and the formation of stannous chloride,  $\text{SnCl}_2$ . Hot concentrated sulfuric acid forms stannous sulfate,  $\text{SnSO}_4$ , and sulfur dioxide. Cold dilute nitric acid slowly acts upon it for the formation of stannous nitrate,  $\text{Sn}(\text{NO}_3)_2$ , and ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , while concentrated nitric acid acts rapidly, forming white insoluble meta stannic acid,  $\text{H}_2\text{SnO}_3$ , and nitrogen peroxide,



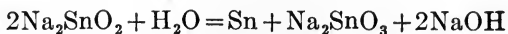
Tin will dissolve in the caustic alkalies, giving hydrogen and stannate, such as  $\text{K}_2\text{SnO}_3$ .

The combining weight of tin is 119.

#### STANNOUS COMPOUNDS

**Stannous Oxide, Hydroxide and the Stannites.**—Stannous oxide,  $\text{SnO}$ , is a black powder, which will burn in the air, forming stannic oxide. It is made by heating stannous oxalate,  $\text{SnC}_2\text{O}_4$ , which decomposes into the oxide, carbon monoxide and carbon dioxide. The corresponding hydroxide is precipitated from a solution of stannous chloride upon the addition of sodium hydroxide or carbonate. It is a white, gelatinous precipitate, which is soluble, both in acids and strong bases, forming in the latter case stannites, such as sodium stannite,  $\text{Na}_2\text{SnO}_2$ . These solutions are powerful reducing agents and will reduce the compounds of many of the metals to the metallic state. When a stannite

solution is boiled a part of the tin is reduced to the metal, while the remainder is oxidized to the stannate, as shown below for sodium stannite.



**Stannous Chloride.**—Stannous chloride, or tin salt,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , is the most important stannous salt. It is made by dissolving tin in hydrochloric acid. Like the other stannous salts, it is hydrolyzed and the presence of an excess of acid is necessary to prevent the formation of a basic salt,  $\text{Sn}(\text{OH})\text{Cl}$ . When the crystals are heated, they are partially decomposed, much as magnesium chloride is, with the formation of hydrochloric acid and the oxide. The anhydrous salt melts at  $250^\circ$  and boils at  $606^\circ$ . Solutions of stannous chloride are used by the dyers as mordants, and also as reducing agents, in the manufacture of dyes, etc. The use of it as a mordant depends upon the hydrolysis of the solution and the formation of the hydroxide, which has similar properties to aluminum hydroxide in its relation toward dyes. The action of the chloride as a reducing agent is due to the tendency of the stannous compound to pass into the stannic. Stannous chloride will reduce the compounds of mercury and of the noble metals to the metallic state, ferric and cupric salts to ferrous and cuprous salts. It will also be oxidized by the oxygen of the air; and it is necessary to keep some metallic tin in a stannous chloride solution to reduce any stannic chloride which may be formed in this way.

Stannous sulfate and nitrate are less stable than the chloride, and are of no practical importance.

**Stannous Sulfide.**—Stannous sulfide,  $\text{SnS}$ , is analytically important. It is formed as a dark brown precipitate when hydrogen sulfide is passed into a moderately acid solution of a stannous salt. It is soluble in concentrated hydrochloric acid and is reprecipitated upon diluting the solution. It is not soluble in solutions of the alkali sulfide unless they contain polysulfides which act by first oxidizing the stannous sulfide to stannic sulfide, which then dissolves, forming thiostannates, such as sodium thiostannate,  $\text{Na}_2\text{SnS}_3$ . This formation of soluble thio salts relates tin to gold and to arsenic and antimony, as will soon be seen.



## STANNIC COMPOUNDS

**Stannic Oxide and Hydroxide.**—Stannic oxide,  $\text{SnO}_2$ , as has been mentioned, occurs in nature and is the principal ore of tin. It is white when pure, but the natural compound is usually colored from impurities. It may be made by treating tin with concentrated nitric acid, when meta stannic acid will be formed, as noted above. This, when heated, decomposes into water and stannic oxide. When prepared at a low temperature, it is easily soluble in acids; but when ignited, it becomes very difficult to attack.

Two stannic hydroxides are known, each of which behaves as an acid. When dried they both pass into the dioxide. To distinguish them, one is called alpha and the other beta stannic acid. Alpha stannic acid is formed by precipitating stannic chloride solution with ammonium hydroxide, or by carefully acidulating an alpha stannate. It is a white gelatinous precipitate, which gives to water a faintly acid reaction, and which dissolves readily in dilute mineral acids and in solutions of sodium or potassium hydroxides, forming alpha stannates,  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ , for example. The sodium salt is much used as a mordant in calico printing and is called "preparing salt."

Beta or meta stannic acid is made by acting upon tin with concentrated nitric acid. It differs from the alpha acid in that it is entirely insoluble in nitric acid, that it swells up but does not dissolve in sulfuric acid, and when treated with hydrochloric acid forms a compound which is not soluble in hydrochloric acid, but which dissolves after the hydrochloric acid is removed and replaced by water. The solution so obtained is not like that of stannic chloride and gelatinizes when boiled. Sodium hydroxide dissolves beta stannic acid and yields a salt, sodium beta stannate,  $\text{Na}_2\text{Sn}_5\text{O}_{11} \cdot 4\text{H}_2\text{O}$ ; by acidulating this solution, beta stannic acid is precipitated. When beta stannic acid is fused with sodium hydroxide, the alpha stannate is formed.

When solutions of alpha stannic acid in hydrochloric or hydrobromic acid stand for a long time, beta stannic acid is gradually precipitated.

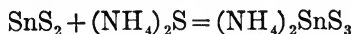
**Stannic Chloride.**—Stannic chloride,  $\text{SnCl}_4$ , is formed by the action of chlorine upon stannous chloride or upon the metal.

Use is made of this in recovering tin from scraps of the plate by the chlorine process. It is a colorless liquid, which freezes at  $-33^{\circ}$  and boils at  $114^{\circ}$  and has a density of 2.234. It fumes in contact with the air. It is a non-conductor of electricity; is a good solvent for sulfur, iodine, phosphorus, miscible in all proportions with bromine and carbon bisulfide. With water a number of hydrates are formed,  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{SnCl}_4 \cdot 8\text{H}_2\text{O}$ , for example. The pentahydrate is much used in dyeing as a mordanting agent, under the name of "oxymuriate of tin." It combines with hydrogen chloride to form chlorstannic acid,  $\text{H}_2\text{SnCl}_6$ , several salts of which are known. The ammonium salt,  $(\text{NH}_4)_2\text{SnCl}_6$ , was formerly much used as a mordant in dyeing under the name of "pink salt," not because it had a pink color but because it was used in dyeing pink. Stannic chloride will also combine with a great many other inorganic and organic compounds.

Solutions of the chloride in water are very poor conductors of electricity when first made. This is interpreted as indicating that the compound is only slightly ionized. The conductivity of the solution increases as it stands, as does also its acidity. This is evidently due to hydrolysis, which takes place slowly, but finally becomes nearly complete. The stannic hydroxide remains in solution in the colloidal state, and is gradually transformed into beta stannic acid. Stannic bromide,  $\text{SnBr}_4$ , is very much like the chloride. It melts at  $30^{\circ}$  and boils at  $201^{\circ}$ .

The sulfate and nitrate hydrolyze even more readily than the chloride and there is room for doubt as to whether it is possible to prepare a solution with any appreciable concentration of a stannic ion,  $\text{Sn}^{++++}$ .

**Stannic Sulfide.**—Stannic sulfide is precipitated as a yellow amorphous substance by passing hydrogen sulfide through a moderately acid solution of a stannic salt. It is soluble in concentrated hydrochloric acid, and is reprecipitated by diluting the solution. It is also soluble in solutions of ammonium sulfide or of the alkali sulfides, forming thiostannates,



Upon acidulation with dilute acids, thiostannic acid is formed,

which at once decomposes to give stannic sulfide and hydrogen sulfide.

By heating together finely divided tin, sulfur and ammonium chloride, stannic sulfide may be obtained in golden-yellow translucent scales which is called mosaic gold, and is used as a bronzing powder.

**Analytical Properties.**—The properties of stannous sulfide and those of stannic sulfide, which have just been given, put it in an analytical group with arsenic and antimony, which is distinguished from that containing mercury, copper, cadmium, bismuth, and lead by the fact that the sulfides of the last mentioned metals are not soluble in ammonium sulfide (copper is slightly soluble). In solution, both the stannic and stannous compounds are colorless. The stannous are distinguished from the stannic by the dark color of the sulfide and by the fact that the former are strong reducing agents.

#### LEAD

**Lead** is the member of the germanium sub-group with the highest combining weight, 207.1. Although it occurs free in nature in insignificant quantities, it is so easily smelted from its ores that it was well known to the ancients. It was used by the Romans for water pipes, a use to which it is still put.

The chemical relationships of lead are somewhat varied, as is often the case with the last member of a sub-group. It is both di- and tetravalent. In the divalent state, lead resembles barium in several ways, in others it is like silver and thallium. The hydroxide,  $\text{Pb}(\text{OH})_2$ , acts both as a base and an acid in that it dissolves and forms salts with both acids and bases. In this way lead is like zinc. The hydroxide is a stronger base than acid, so that its salts with the stronger acids are fairly stable in solution. The tetravalency of lead shows its relationship to the other members of this group, but the relationship is not very strong. The hydroxide,  $\text{Pb}(\text{OH})_4$ , is both basic and acidic; but is a very weak base, so that its salts, even with the strongest acid, are practically completely hydrolyzed. The tetravalent lead compounds tend to pass to the divalent state and are good oxidizing agents, so the oxidation relationships are the reverse of those between stannous and stannic tin.

**Occurrence.**—The principal ore of lead is galena, lead sulfide,  $\text{PbS}$ , which contains, when pure, 86.57 per cent. of lead. It is found in nearly all countries and very often carries silver, either as finely divided native silver, or as isomorphous sulfide, disseminated through it.

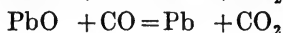
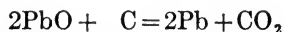
Other common ores of lead are the carbonate, cerussite,  $\text{PbCO}_3$ , and sulfate, anglesite,  $\text{PbSO}_4$ . They are formed as decomposition or oxidation products from galena, and are consequently found near the surface in mines which lower down yield galena almost exclusively.

**Metallurgy.**—Since lead sulfide is a chief form of lead ore, the extraction of lead from its ores is largely devoted to the treatment of this compound. This is accomplished entirely by smelting or dry processes, which may be classified according to the kind of furnaces used; as reverberatory, hearth, and blast-furnace processes.

Hearth and reverberatory smelting of lead ore have given place almost entirely to blast-furnace smelting. The lead blast-furnace is rectangular in shape and is from 15 to 25 ft. high, 10 to 20 ft. long and from 3 to 5 ft. wide at the bottom. The upper part is built of brick work, supported on iron columns and lined with fire brick; the lower part, which is exposed to the highest temperature is built of water jackets, hollow steel castings, cooled by water constantly circulating through them. By this means the excessive wearing away of the furnace walls by the hot charge is prevented. A row of blast pipes, or tuyeres, along each side of the furnace, serve to introduce the air blast, which has a pressure of 1 to 3 lb.

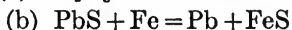
The lead ore mixed with coke to furnish heat for the smelting, and sufficient limestones to flux off the silica from the gangue, is charged into the furnace. A part of the lead ore is charged raw, that is, unroasted, while another portion is previously roasted to lead oxide in a separate roasting furnace. This roasted ore usually has in it a considerable quantity of iron oxide, which is utilized to furnish iron for reducing lead sulfide. In some cases, iron oxide ore is specially added for this purpose.

The reactions that take place in the furnace are somewhat complex, but the chief ones may be summarized as follows: First, lead oxide is reduced by carbon or by carbon monoxide to metallic lead,



Second: (a) Iron oxide is reduced by carbon monoxide to metallic iron.

(b) This iron, in turn, reduces lead from lead sulfide, forming metallic lead and ferrous sulfide,



Third, the iron sulfide formed, collects all the copper in the charge and part of the lead sulfide, forming a mixture called *lead matte*, which is similar to the copper matte already described under copper.

Fourth, the silica of the ore gangue unites with the calcium oxide from the limestone flux and iron oxide from the ore, forming a calcium iron silicate slag.

At the bottom of the furnace, the slag, matte, and metallic lead are tapped off together into a fore hearth somewhat like that used in copper smelting. Here they separate according to their density, and each is drawn off separately; the slag is thrown away, the matte is roasted and further smelted to remove the lead and concentrate the copper. Then it is smelted for copper as described under that metal.

The lead tapped from the blast furnace is far from pure. It is called *work lead* or *base bullion* and contains besides the gold and silver of the ore, considerable quantities of antimony, bismuth, copper, and other impurities. Most of the latter can be removed by melting the lead in large pots and keeping it molten for several hours, during which period it is frequently stirred. The impurities oxidize more readily than the lead and the oxides rise to the top as a scum or dross, which is easily skimmed off. Some lead is lost by this process, but the resulting refined product is quite soft and malleable.

This process does not remove gold and silver or all the copper. If these are in the lead, it is further treated by the Parke Process (see page 468) to recover the gold and silver.

Not only does the lead smelting process save the gold and silver occurring in the lead ores, but it also allows the smelting of other

gold and silver ores containing little or no lead, with the lead ores charged to recover the precious metals.

Lead is being successfully purified on a large scale by the Betts' electrolytic process. The anodes are made of work lead, the cathodes of pure lead and the electrolyte of lead fluosilicate,  $\text{PbSiF}_6$ , in solution to which a little glue has been added. This latter addition has the effect that the lead is deposited in a more coherent form than in its absence. The process produces very pure lead and at the same time recovers the precious metals in the work lead. The production of lead for 1910 was 372,000 tons in this country and 1,211,000 tons for the world.

**Physical and Chemical Properties.**—Lead is a bluish-gray metal which is very soft and has but little tensile strength; its density is 11.4 and its melting-point is  $327^\circ$ ; it volatilizes appreciably at the temperatures reached in ordinary furnaces, and boils rapidly in the oxy-hydrogen blowpipe. At temperatures a little below its melting-point, it softens enough so it can be forced by hydraulic pressure into the form of pipes which are used in plumbing and as a cover for electric cables. There are several valuable alloys containing lead; of these, solder, pewter, Britannia metal have already been given. Type metal and hard lead contain antimony, as does Babbit metal which has tin in addition. Shot usually contains a small amount of arsenic. Lead is decidedly resistant to chemical action and on this account is much used in chemical work, as for example in the construction of the lead chambers for the manufacture of sulfuric acid. It is but slightly acted upon by the oxygen of the air at ordinary temperatures, and soon becomes covered with a protecting coat of a basic carbonate. At higher temperatures it is rather rapidly oxidized, forming litharge,  $\text{PbO}$ , or red lead,  $\text{Pb}_3\text{O}_4$ . In the presence of air and pure water lead forms the hydroxide,  $\text{Pb}(\text{OH})_2$ , which is somewhat soluble. On this account lead pipes should not be used for carrying drinking water, because all compounds of lead are poisonous, and when taken, in repeated small doses, gradually accumulate in the system and produce a very serious condition known as chronic lead poisoning or "painter's colic." If the water contains carbonates or sulfates in solution, the pipes become coated with the difficultly soluble carbonate or sulfate of lead and the danger of using the water is diminished. However,

in modern plumbing the use of lead is almost entirely confined to the waste pipes.

Lead stands on the dividing line between the metals which are dissolved by the ordinary acids with the evolution of hydrogen and those which require an oxidizing agent stronger than hydrogen in the ionic state. It is not dissolved by cold dilute, but is by boiling concentrated hydrochloric acid. Sulfuric acid, hot or cold, is almost without action until the acid reaches a concentration of 80 per cent. or more when the lead is rather rapidly attacked, especially by the hot acid. Nitric acid dissolves lead readily forming the nitrate, but oxides of nitrogen are evolved rather than hydrogen. Acetic acid with the aid of oxygen of the air dissolves lead, a fact which is of importance in connection with the manufacture of white lead.

**Oxides and Hydroxides.**—Lead forms five oxides, having the following formulas,  $Pb_2O$ ,  $PbO$ ,  $Pb_2O_3$ ,  $Pb_3O_4$ , and  $PbO_2$ . Of these the first, the sub-oxide, and the third, the trioxide, are of but little importance. The others all serve some very useful purposes.

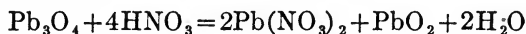
The monoxide or litharge is prepared by heating lead in the air. This is done at one stage in smelting of lead and silver ores; the process is called cupellation. Litharge is a crystalline substance of a reddish-yellow color. The reddish tinge is due to the presence of a little red lead,  $Pb_3O_4$ . The monoxide is the only stable oxide at temperatures above  $600^\circ$ , and all the others pass into it when heated to this temperature in the air. It is very easily reduced to the metal. Litharge is soluble in acids forming salts of divalent lead, which although somewhat hydrolyzed are in the main fairly stable in solution. It is also soluble in sodium hydroxide solution, forming sodium plumbite,  $Na_2PbO_2$ . These facts show that the hydroxide,  $Pb(OH)_2$ , which is undoubtedly formed before the oxide is dissolved either by the acids or bases, acts both as a base and as an acid. The hydroxide is, however, a stronger base than an acid and is strong enough to form a carbonate. The oxide is used in glazing pottery, making glass, and in preparing other compounds of lead.

Lead hydroxide,  $Pb(OH)_2$ , is a white substance slightly soluble in water. It is precipitated upon the addition of a solution of an alkali to a solution of a lead salt. It is as indicated above,

soluble in acids and bases, and yields the same compounds as the oxide of lead.

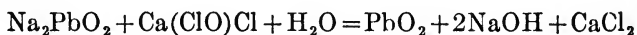
Red lead or minium,  $Pb_3O_4$ , is made by carefully heating finely powdered lead monoxide or carbonate in the air to a temperature not higher than  $545^\circ$ . It decomposes at higher temperatures into oxygen and monoxide. The system is one of two components, which are oxygen and monoxide; in three phases, gaseous (oxygen), and the two solids (red lead and monoxide); and, therefore, there is one degree of freedom, and at each temperature, there is a perfectly definite pressure of oxygen which is in equilibrium with the solids. This pressure is one atmosphere at  $636^\circ$ , but the partial pressure of the oxygen in the air is only one-fifth atmosphere, so red lead cannot exist in contact with the air at  $636^\circ$ , but only at and below  $545^\circ$ , which is the temperature at which the equilibrium pressure is one-fifth atmosphere.

When treated with acids, red lead yields lead dioxide and salts of divalent lead,



Because of its fine red color, red lead is used as a pigment; it also seems to have a specific action in protecting iron from corrosion. It is further used in the manufacture of glass.

**Lead Dioxide.**—Lead dioxide is the most stable and important of the tetravalent compounds of lead. It is a dark brown powder which may be formed as described above, but is usually prepared by the action of bleaching powder upon a solution of lead plumbite,



The dioxide is insoluble under these conditions and is precipitated. It has some tendency to act as an acid forming oxide as is shown by the following. When fused with sodium or potassium hydroxide, it yields soluble meta-plumbates such as  $K_2PbO_3 \cdot 3H_2O$ , analogous to the meta-stannates. Red lead is regarded as being lead ortho-plumbate, and on this basis should be written  $Pb_2PbO_4$ .

Lead dioxide is a strong oxidizing agent. It will react with sulfur dioxide so vigorously that its temperature will be raised to redness, forming lead sulfate. It sets fire to a jet of hydrogen sulfide and inflames when ground in a mortar with sulfur. When



heated with hydrochloric acid, it acts like manganese dioxide and liberates chlorine, lead chloride,  $\text{PbCl}_2$ , being formed at the same time. When the dioxide is dissolved, in cold hydrochloric acid, lead tetrachloride,  $\text{PbCl}_4$ , is formed. This decomposes into the dichloride and chlorine when heated, or into the dioxide and hydrochloric acid when diluted. Plumbic sulfate,  $\text{Pb}(\text{SO}_4)_2$ , may be prepared by the electrolysis of cold strong sulfuric acid, using lead as the anode. It is as easily hydrolyzed as the chloride and decomposes with water, forming the dioxide.

From the above it is seen that the dioxide is both basic and acidic, but is very weakly basic.

**Lead Chloride.**—Lead chloride,  $\text{PbCl}_2$ , is formed by dissolving litharge in hot hydrochloric acid, or, since it is but little soluble in cold water, 1.08 parts per 100 at  $25^\circ$ , it may be prepared by adding a soluble chloride to a solution of lead nitrate or acetate. It is a white crystalline compound which is about three times as soluble in boiling water as in water at room temperature. Advantage is taken of this in separating lead chloride from silver and mercurous chlorides, which are but slightly soluble in either hot or cold water.

**Lead Bromide.**—Lead bromide,  $\text{PbBr}_2$ , is very similar to the chloride and has about the same solubility.

**Lead Iodide.**—Lead iodide,  $\text{PbI}_2$ , is precipitated as a yellow substance upon the addition of an iodide to a solution of the lead salt. One hundred parts of water dissolve 0.0764 parts at  $25^\circ$ , and nearly six times as much at  $100^\circ$ . From the hot solution it separates as beautiful glistening yellow scales. The halogen compounds of lead show a tendency to form complex anions with the alkali halides similar to those formed by the mercuric compounds, so many complex salts are known.

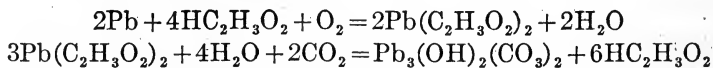
**Lead Nitrate.**—Lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , and acetate are almost the only lead salts of the common acids which are soluble in water. The nitrate is made by dissolving litharge or the metal in nitric acid, and crystallizing the product. It forms white anhydrous octahedra which are isomorphous with barium nitrate. One hundred parts of water dissolve 60.6 parts of the salt at  $25^\circ$ , and 138.8 at  $100^\circ$ . As is to be expected from the weakness of lead hydroxide, a solution of the nitrate is acid in reaction.

**Lead Acetate.**—Lead acetate, or sugar of lead,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , is a white crystalline salt, which is easily soluble in water; 100 parts of the latter dissolve 50 parts of the salt. The solution has a sweet taste, which gives to the salt its common name. By boiling a solution of lead acetate with litharge a soluble basic salt is formed,  $\text{Pb}(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)$ . This is alkaline in reaction. Both the normal and the basic salts, when in solution, yield precipitates of the carbonate when acted upon by carbon dioxide; the action is not complete and stops when the concentration of the acetic acid has reached a certain point. This reaction is of importance in connection with the preparation of "white lead."

**Lead Carbonate and White Lead.**—Normal lead carbonate,  $\text{PbCO}_3$ , is found in nature as the mineral cerussite and may be prepared in the laboratory, but the artificial product is usually a basic salt. Both the normal and basic salts are but very slightly soluble, 1 to 50,000 for the normal, and so may be formed by the precipitation of a solution of lead acetate by carbon dioxide, or a soluble carbonate. The carbonates are of course soluble in the acids, and more so in water containing carbon dioxide than in pure water. They are also soluble in sodium hydroxide solution, because of the formation of the plumbite ion.

White lead is a basic carbonate which has approximately the composition represented by the following formula,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ . It is much used as a pigment and is prepared in various ways. These nearly all consist in getting the lead in solution with acetic acid, and precipitating the carbonate with carbon dioxide, thereby recovering the acetic acid to be used to dissolve more lead and thus making it act as a catalyzer.

The white lead which is *claimed* to be the best is manufactured by what is known as the old Dutch process. In principle, the process consists in the solution of the lead in acetic acid, with the aid of the oxygen of the air, and the precipitation of the carbonate from this by carbon dioxide, the whole process taking place slowly at temperatures only a few degrees above that of the room. The equations are,



The lead to be "corroded" is cast into the form of perforated

disks called "buckles," and these are placed in the upper part of a glazed earthenware pot, about 8 inches across. In the bottom of the pot is some crude acetic acid, and about a third of the way up, the sides of the pot are pierced by a number of holes to allow circulation of air. A great number of these pots are placed side by side upon a layer of spent tan bark. They are then covered by boards and another layer of tan bark, and upon the whole another tier of pots is placed, which are covered in the same way. This is continued until a pile of many tiers of pots has been obtained. Bacteria grow in the tan bark and produce carbon dioxide from the oxidation of its materials, and the heat so generated warms the whole to a temperature favorable to the process. The vapors of the acetic acid, the oxygen of the air, and the carbon dioxide from the tan bark being in contact with the lead bring about the reactions given above. The process takes 5 or 6 weeks. At its close the heaps are taken down, the lead carbonate is separated from the unchanged lead by mechanical means and ground very fine while moist, dried, and then ground in linseed oil, making the pasty pigment known as white lead. Sometimes the white lead is not thoroughly dried before it is ground in the oil; the result is a slightly cheaper paint of distinctly inferior quality, which is much more rapidly attacked by atmospheric agencies than that made from the dry carbonate.

Other processes are in use which differ in their details from the one given above; in some the starting material is litharge, which is boiled with acetic acid to form the basic acetate, and then the carbonate is precipitated by carbon dioxide. In one process known as the "mild process" the metallic lead is first converted into the finest kind of powder, and then thoroughly agitated with air and water until it is converted into lead hydroxide. Carbon dioxide is then run in and the hydroxide is changed to the basic carbonate. No acids or alkalies are used in the process and there is nothing objectionable in the product, which must be removed by washing. Electrolytic processes have been devised which consist essentially in using a lead anode in a solution of sodium nitrate containing some bicarbonate; the white lead is formed on the anode.

White lead is costly, poisonous and hence dangerous to manufacture and use, and is so subject to atmospheric agencies, particu-

larly hydrogen sulfide, that it is not suitable for use in cities; and yet it has held its own against other white pigments which do not have these objections. The reason for this is that it has great covering power, *i.e.*, it is very opaque. This is due to the fact that the particles of white lead, although they are transparent, reflect a good deal of light from each of their surfaces, and any given layer of paint contains so many overlying particles, each one reflecting a part of the light which penetrated those above that practically all of the light is turned back, and the paint is decidedly opaque.

Some of the other white pigments are zinc oxide, silica, barium sulfate, powdered asbestos, and a basic lead sulfate, known as "sublimed white lead." Zinc oxide has the advantage over white lead that it is not darkened by hydrogen sulfide, but the thickness of a paint film is practically the diameter of the larger particles of the pigment, and zinc oxide is so very fine that when used alone a great many coats are necessary to cover the surface. The dried film is also so hard and inelastic that it cracks easily when exposed to the weather. For these reasons zinc oxide alone is not suitable for outside work, and is mainly used for interiors. A mixture of zinc oxide and white lead stands the weather well and is largely used outdoors. Silica, barium sulfate, and powdered asbestos have smaller covering powers than white lead, and call for a thicker paint film. Asbestos, because of its fibrous nature, is claimed by some to increase the strength of the paint, and to be a valuable addition to a mixture of white lead and zinc oxide. It is claimed for "sublimed white lead" that it is less poisonous than the carbonate, and has great covering power. This country uses yearly about 150,000 tons of white lead worth \$19,000,000.

It is a well established fact that a cheap red barn paint will last longer than a high-priced white house paint, when both are mixed with equally good oil. The explanation offered is that the pigment in the red paint is chemically inert, while the white lead in the house paint gradually converts the oil into a more or less soluble soap which washes off.

**Lead Chromate.**—Lead chromate,  $\text{PbCrO}_4$ , is a nearly insoluble substance, which is formed by bringing together in solution a soluble lead salt and a chromate. It has a fine yellow color

and is used as a pigment and as a dye. It is soluble in the stronger acids and in sodium hydroxide. In the latter case, lead hydroxide is first formed and is then converted into the plumbite.

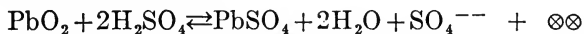
**Lead Sulfate.**—Lead sulfate,  $\text{PbSO}_4$ , is one of the few sulfates which are but slightly soluble; 100 parts of water dissolve 0.004 parts of the salt. In this respect lead resembles barium, and the naturally occurring lead sulfate is isomorphous with the natural barium sulfate or heavy spar. Since it is so slightly soluble, it is easily prepared by precipitation. It is less soluble in dilute sulfuric acid and in alcohol, but more soluble in dilute nitric and in concentrated sulfuric acid than in pure water. The decrease in solubility upon the addition of dilute sulfuric acid is, of course, due to the increase in the concentration of the sulfate ion. The increased solubility in concentrated sulfuric acid is probably due to the formation of the acid sulfate. The increase in solubility in nitric acid is ascribed to the fact that nitric acid is stronger acid than sulfuric, and hence the concentration of the sulfate ion is decreased. It is soluble in sodium hydroxide for the same reasons as the chromate and the chloride. Solutions of acetates, tartrates, and in fact of the salts of most organic acids, dissolve it, owing presumably, to the formation of the complex anion or slightly dissociated compounds; the latter seems to be the explanation in the case of the acetates.

The use of the basic lead sulfate  $(\text{PbSO}_4)_2\text{PbO}$  known as sublimed white lead for a pigment has been mentioned. This compound is made by putting a mixture of finely powdered galena,  $\text{PbS}$ , and carbon on a brisk coke fire in a furnace. The lead sulfide is oxidized to the basic sulfate which volatilizes at the temperature of the fire, condenses in the flue and is caught in bags. It is very fine and white, and is chemically much more inert than white lead.

**Lead Sulfide.**—Lead sulfide,  $\text{PbS}$ , occurs in nature in cubical crystals, which have a gray metallic luster. It is the principal ore of lead and is called galena. In the laboratory it may be prepared as a black precipitate by passing hydrogen sulfide into an acid solution of a lead salt. It is insoluble in cold dilute acid, in sodium hydroxide or the alkali sulfides. It is soluble in concentrated hydrochloric acid, being reprecipitated upon dilution, and also in boiling dilute nitric acid. In the latter case,

the solution results because of the oxidation of the sulfur ion to the element or to the sulfate.

**The Storage Battery.**—A storage battery is a voltaic cell, which, after it has worked for a time and produced electrical energy at the expense of the free energy of the reactions within the cell, may be restored to its original condition by passing a current of electricity through it in the reverse direction. It is a reversible cell. The most practical form consists of two sets of lead plates, the one coated with lead dioxide and the other with spongy lead, the plates being placed in dilute sulfuric acid. The oxidizing agent in this case is the tetravalent lead of the lead dioxide, which gives up two positive charges to the lead electrode, upon which it is placed, and these flow through the connecting wire to the other lead electrode and there oxidize the finely divided spongy lead, which is the reducing agent, to the divalent ion. The divalent lead ion is formed at each electrode and passes into the nearly insoluble sulfate as fast as it is produced. After the cell is discharged, each electrode is coated with lead sulfate, instead of lead dioxide, or spongy lead. The cell may now be "charged" by passing a current of electricity in the reverse direction. At the anode, or dioxide plate, the divalent lead ion receives two positive charges and is changed to plumbic sulfate, which at once hydrolyzes and gives the dioxide. At the cathode, or spongy lead plate, the divalent lead ion is reduced to the metal which comes out in a spongy condition, and after somewhat more electricity has been passed through than was taken out, the cell is restored to its original condition. The excess of electricity is due to unavoidable losses. The reactions may be represented by the following equations, at the positive or dioxide plate on discharge,



in which  $\otimes \otimes$  represents the two + charges given up by the tetravalent lead and passed through the wire to the negative or spongy lead plate, where the following reaction takes place,



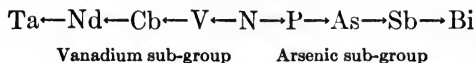
On charging, these equations are reversed.

**Analytical Properties of Lead.**—Divalent lead forms a difficultly

soluble chloride which puts it in an analytical group with silver and mercurous mercury; from these it is distinguished by the solubility of lead chloride in hot water. The very slight solubility of lead sulfide in dilute acid and in alkali sulfides places it in an analytical group with mercuric mercury, copper, cadmium and bismuth. From these it is distinguished by the very slight solubility of its sulfate, all the other sulfates of the group being easily soluble. The properties of the chromate, iodide and hydroxide are also of analytical importance.

## CHAPTER XXVII

### GROUP V



The members of Group V are polyvalent elements with a maximum valence of five. The group may be divided into two sub-groups, the first consisting of the rare and comparatively little known elements, vanadium, columbium, neodymium, and tantalum, is called the vanadium group, while the other containing the well-known elements nitrogen, phosphorus, arsenic, antimony, and bismuth may be called the arsenic group. The members of the arsenic sub-groups form a particularly well-marked family and change their properties in a very regular manner with increasing combining weight. The tendency observed with the preceding groups for the basicity to decrease from group to group is continued here. Nitrogen and phosphorus are entirely non-metallic in their chemical and physical properties; arsenic shows principally non-metallic characteristics with some few of the properties of the metal; antimony is both a base and an acid-forming element, while bismuth is almost exclusively base-forming.

Every member of Group V forms an acidic pentoxide; the lower oxides are more basic, or at least less acidic in their tendency.

#### VANADIUM SUB-GROUP

From the relations found in the other groups, it might be expected that the members of this family would be more basic than the corresponding ones in the arsenic group. Vanadium meets this expectation for it is distinctly more basic than arsenic; while columbium and tantalum are apparently rather more acid than base-forming elements, but their compounds have not been thoroughly studied.



These three metals all combine very vigorously with oxygen and have high melting-points.

**Vanadium** (comb. wt. = 51) forms five oxides,  $V_2O$ ,  $VO$ ,  $V_2O_3$ ,  $VO_2$ ,  $V_2O_5$ , analogous to the five oxides of nitrogen. The second and third of these are base-forming and yield the vanadous and vanadic salts, while the fourth and fifth are acid anhydrides and give the vanidites and vanidates respectively. It forms the following chlorides:  $VCl_2$ ,  $VCl_3$ ,  $VCl_4$ ,  $VOCl_2$  and  $VOCl_3$ . The Group  $VO$ , is very interesting because it acts like a complex di- and trivalent cation, forming, for example, vanadyl sulfate,  $VOSO_4$ , and di-vanadyl sulfate,  $(VO)_2(SO_4)_3$ .  $VO^{++}$  is called vanadyl and  $VO^{+++}$  di-vanadyl.

Columbium, Cb. (comb. wt. = 93.5) and tantalum, Ta, (comb. wt. = 181.5) are very rare and hard to separate. Their principal compounds are the columbates and tantalates. Metallic tantalum melts at  $2250^\circ$  to  $2300^\circ$  and may be drawn into very fine strong wire, which can be used in the construction of incandescent electric lamps. These are much more efficient than the carbon filament lamps. They have, however, been largely replaced at the present time by tungsten lamps which are even more efficient.

The combining weight of neodymium, 144.3, seems to place this element in this group but its properties are very much like those of cerium with which it is always found associated in nature. As yet neither the element nor its compounds have found any applications.

### THE ARSENIC FAMILY

The members of this family are very similar to nitrogen and especially to phosphorus; a proper grasp of their chemistry may be most readily obtained by comparison with these elements, noting the points of similarity and of difference. At the end of this chapter the whole family will be summarized in the form of a table.

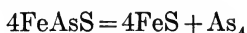
### ARSENIC

**General.**—The compounds of arsenic were known to the ancients. The element itself was familiar to the chemists of the

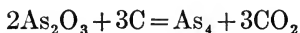
thirteenth century, but the history of its discovery is unknown to us.

**Occurrence.**—Arsenic occurs free in nature and also in combination, chiefly in the sulfide of the metals in which it replaces a part of the sulfur, arsenical pyrites,  $\text{FeAsS}$ , may be given as an example of such a compound. It is also found as the trioxide,  $\text{As}_2\text{O}_3$ , and as the two sulfides orpiment,  $\text{As}_2\text{S}_3$ , and realgar,  $\text{As}_2\text{S}_2$ . The ores of the metals very often contain arsenic, and the removal of this element is one of the serious problems connected with their metallurgy.

**Preparation.**—The element arsenic is obtained on a manufacturing scale by heating arsenical pyrites which decompose into ferrous sulfide and arsenic,



It may be prepared in the laboratory by reducing the trioxide with charcoal.



**Physical and Chemical Properties.**—Arsenic forms at least three solid modifications, ordinary or metallic arsenic, yellow arsenic, and a black so-called amorphous form. The ordinary modification is steel gray in color, is decidedly crystalline and very brittle. Its density is 5.73. It is volatile and at about  $450^\circ$  the vapor pressure reaches one atmosphere, but the arsenic sublimes without melting. If the pressure be increased sufficiently to raise the sublimation temperature to  $480^\circ$ , the arsenic will melt. The density of arsenic vapor at  $563^\circ$  corresponds to a molar weight of 305; at  $720^\circ$  it is somewhat lower, 293, and at  $1736^\circ$  it has fallen to 157. The combining weight is 74.96, so the molar weight at the lower temperatures indicates the formula  $\text{As}_4$ , and that at higher temperatures the formula  $\text{As}_2$  for the vapor. It will be recalled that the formula for the vapor of phosphorus is  $\text{P}_4$ . The ordinary form of arsenic is not soluble in carbon disulfide. Acids do not attack it with the evolution of hydrogen; but those which are among the better oxidizing agents will dissolve it with the formation of the reduction products of the acid and either arsenous or arsenic acid (which see). It is very stable toward dry air, but oxidizes in moist. When

heated in the air, it phosphoresces at temperatures near  $200^{\circ}$ , and finally burns with the formation of the trioxide. Arsenic combines directly with the halogens, sulfur and many of the metals.

The yellow modification is formed by rapidly cooling the vapors of arsenic in the absence of the ordinary form. It is distinctly crystalline, sulfur yellow in color, has a density of 3.9. It is soluble in carbon disulfide, and when a drop of this solution is evaporated on filter paper and exposed to the sunlight, the spot of yellow arsenic is almost instantly changed to a black mirror-like form. It volatilizes at temperatures but little above that of the room. Its molar weight in solution, in carbon disulfide, indicates the formula  $As_4$ . It is phosphorescent at ordinary temperatures and is even more poisonous than the other modifications. In all these ways the yellow modification is like yellow phosphorus, and the relation between these two forms of arsenic is strikingly similar to that between the red and yellow phosphorus.

The black mirror-like modification of arsenic, which is deposited upon cooling the vapors under such conditions that the yellow is not formed, is considered to be another modification of arsenic, and was formerly held to be amorphous, but it has been shown to be crystalline.

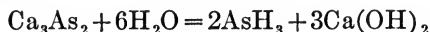
Arsenic forms two series of compounds; in the one it is trivalent, and in the other pentavalent. There are a few compounds in which it is apparently divalent.

#### TRIVALENT COMPOUNDS

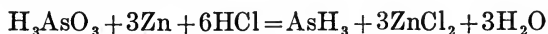
**Arsine.**—Arsenic shows another point of similarity to nitrogen and phosphorus in the formation of the hydrogen compound arsine,  $AsH_3$ , analogous to ammonia and phosphine. It will be recalled that ammonia has a great tendency to combine with acids for the formation of ammonium salt, but that in spite of this, these salts were practically completely dissociated when in the form of vapor. Phosphine showed a much smaller tendency to form such salts and only a very few were stable, even in the solid state. If this tendency toward instability of the salts should continue to increase with the combining weight, arsine could

scarcely be expected to form any compounds of this character, and as a matter of fact none is known. Ammonia is fairly stable, but is largely decomposed at higher temperatures into its elements; phosphine is less stable and arsine still less.

Arsine may be formed by the action of water upon calcium arsenide,  $\text{Ca}_3\text{As}_2$ ,

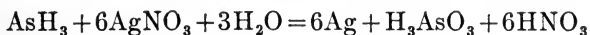


Or by the reduction of a soluble arsenic compound, arsenious acid,  $\text{H}_3\text{AsO}_3$ , for example, by zinc or magnesium, in the presence of hydrochloric or sulfuric acids,



Of course, in this case, a large amount of hydrogen is given off, but the arsine is easily obtained in the pure state by passing the mixture through a tube surrounded by liquid air. The arsine condenses to a solid, melting at  $-119^\circ$  and boiling at  $-55^\circ$ , while the hydrogen, of course, is not liquefied at this temperature.

Arsine either pure or mixed with hydrogen, may be almost completely decomposed into its elements by passing the gas through a red hot glass tube. The arsenic is deposited beyond the burner as a black mirror. Arsine kindles easily and burns with a pale blue flame, producing water and a white smoke of arsenic trioxide. Within the flame itself the arsenic is evidently in the free state, because if a piece of porcelain or other cold object be held in the flame, a mirror of arsenic will be deposited upon it. The mirror of arsenic formed on the cold porcelain, or deposited in the glass tube beyond the burner, is so very easily seen, even when only the merest trace of a soluble compound of arsenic is introduced into the hydrogen generator, that this test which is known as Marsh's test is an exceedingly valuable one. Antimony behaves in much the same way, but the two mirrors may be easily distinguished as will be seen. The zinc, acid, and even the glass used must be especially pure and a "blank" experiment run without the addition of the solution suspected to contain the arsenic, to establish their purity must be carried out. The test is almost too delicate for ordinary work. When arsine is passed into a silver nitrate solution metallic silver is precipitated and arsenous acid is formed,



Arsine is exceedingly poisonous, and the inhalation of even very small quantities has produced death.

**Arsenic Trioxide.**—Arsenic trioxide, or simply arsenic, as it is usually called, is the most important compound of arsenic. It occurs in nature in small quantities, but is generally obtained by the sublimation of the flue dust from smelters which roast arsenic ores. The amount produced in this country is about one-fourth of the consumption, and yet one smelter alone allowed 10,000 tons, worth \$600,000, to escape from its flues in 1 year.

There are two different crystalline forms of the trioxide, octahedral and monoclinic, and also an amorphous modification. In the process of purification by sublimation the arsenic trioxide collects as an amorphous glass-like substance, which, upon being kept for some time, gradually becomes milk white and looks very much like porcelain. The change in appearance is due to the passage of the amorphous into a crystalline (octahedral) modification. From the fact that the glass-like form appears first, it may be concluded that it is less stable than the crystalline. This is in accord with the general rule that the amorphous modifications are less stable and more soluble than the crystalline. The solubility of the crystalline is 0.3 while that of the amorphous is 1.0 parts per 100, which is in agreement with the rule. The transformation of the glassy into the crystalline form is hastened by the presence of moisture which helps, through the formation of a solution, which, when saturated with respect to the glassy, is supersaturated toward the crystalline.

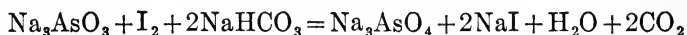
When the ordinary octahedral trioxide is rapidly heated, it sublimes without melting, but when kept for some time at a temperature near its point of sublimation, it finally melts and will solidify to an amorphous form.

The vapor density of the trioxide at temperatures near 600° corresponds to the formula  $\text{As}_4\text{O}_6$  and on this account it is sometimes called the hexoxide, but at 1800° the formula indicated is  $\text{As}_2\text{O}_3$ , and this simpler one is that generally used.

The trioxide is very easily reduced by charcoal or by potassium cyanide with the formation of the metal. It acts both as an acid and as a base-forming oxide, but is only slightly basic.

With concentrated sulfuric or hydrochloric acid, it forms complicated sulfates or the trichloride,  $\text{AsCl}_3$ . These salts are completely hydrolyzed upon dilution with much water.

**Arsenous Acid.**—A solution of arsenic trioxide in water is slightly acid, and is called arsenous acid. When attempts are made to obtain the acid in the anhydrous state, it decomposes into water and the trioxide. The trioxide is easily soluble in sodium hydroxide solution, and from this sodium arsenite,  $\text{Na}_3\text{AsO}_3$ , may be obtained. This sodium arsenite is an important article of commerce and is used for making sheep "dips" as well as for manufacturing and chemical purposes. Like all other arsenic compounds, it is very poisonous. The arsenites of most of the metals, other than the alkalis are but slightly soluble. London purple, impure calcium arsenite and arsenate, and Paris green, a copper acetate and arsenite,  $\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)(\text{AsO}_3)$ , are used as insecticides, and Scheele's green,  $\text{CuHAsO}_3$ , is sometimes, though rarely at the present day, used as a pigment. It is objectionable on account of its poisonous nature. Ferric hydroxide forms very difficultly soluble arsenites, and is used as an antidote in cases of poisoning with arsenic trioxide or its salts. The arsenites are easily oxidized to the arsenates and advantage is often taken of this in quantitative analysis, using standard solutions of sodium arsenite and of iodine, which react as follows in the presence of some sodium bicarbonate;



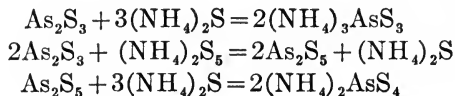
**The Halogen Compounds.**—Arsenic trichloride,  $\text{AsCl}_3$ , is the most important halogen compound of arsenic. It is a colorless, oily liquid, having a density of 2.2, melting at  $-16^\circ$  and boiling at  $130^\circ$ . It may be formed by the action of chlorine upon arsenic, or by hydrochloric acid upon the trioxide. When dissolved in water, it undergoes very extensive hydrolysis with the formation of hydrochloric acid and arsenous acid, which in turn is largely decomposed into the slightly soluble trioxide and water. This action is much like that between phosphorous trichloride and water, with the exception that the hydrolysis of the arsenic compound is reversed by the addition of concentrated hydrochloric acid. Because of this, the trioxide is more soluble in hydrochloric acid than in water. Because of the volatility of

arsenic trichloride, precautions have to be taken before the evaporation of an acid solution of arsenic containing chlorine as ion to see that the arsenic is oxidized to the pentavalent form, and that no reduction takes place during the process. These precautions are effective because there is no pentachloride. Sulfuric acid, containing arsenic, may be purified by reducing the arsenic to the trivalent form, warming the acid and then passing hydrogen chloride through it. Arsenic trichloride will be formed and volatilized. The tribromide is formed by the interaction of the elements and is a colorless solid, density 3.6, melting at  $31^{\circ}$  and boiling at  $220^{\circ}$ . The triiodide is formed by the union of the elements. It is a red crystalline substance, density 4.4, melting at  $146^{\circ}$ , and boiling between  $394$  and  $414^{\circ}$ . Arsenic trifluoride is a colorless liquid, density 2.7, melting-point  $-8.5^{\circ}$ , and boiling at  $73^{\circ}$ .

**Arsenic Trisulfide.**—Arsenic trisulfide,  $As_2S_3$ , is found in nature in the mineral called orpiment, which, upon being ground, yields a lustrous yellow powder, which was formerly used as a pigment. It may be prepared in the laboratory by passing hydrogen sulfide through an acid solution of an arsenite, or of arsenous acid. Under these conditions, it comes down promptly as a flocculent yellow precipitate, which is practically insoluble, even in the strongest hydrochloric acid. Use is made of this property in the preparation of hydrochloric acid free from arsenic by passing hydrogen sulfide through the acid and filtering off the arsenic sulfide formed. If the hydrogen sulfide is passed through a pure solution of arsenous acid, no precipitate will appear, but the solution becomes yellow in color, and contains the sulfide in colloidal solution in the form of very small particles, as is shown by the fact that the path of a ray of light through the solution is visible, and the solution polarizes light. The addition of acids and of neutral salts will cause the particles to gather into flocks and to precipitate. In bringing about this result, the salts are more active the higher the valence of the cation, but the anion is almost without influence.

As mentioned above, the sulfide is insoluble in cold hydrochloric acid, but it is slowly dissolved by boiling concentrated hydrochloric acid with a volatilization of arsenic trichloride. Strong HCl and  $KClO_3$  will dissolve it with the formation of

arsenic acid,  $\text{H}_3\text{AsO}_4$ , sulfuric acid and reduction products of the chlorate. It is soluble in the alkali sulfides, giving thioarsenites,  $(\text{NH}_4)_3\text{AsS}_3$ , if the sulfide is colorless; or thioarsenates,  $(\text{NH}_4)_3\text{AsS}_4$ , if a polysulfide is used. The equations are



The corresponding sulfides of sodium and potassium will, of course, give sodium or potassium thioarsenites, or thioarsenates. The extra sulfur of the polysulfide is the oxidizing agent, which changes the trisulfide to the penta, which is then dissolved to form the thioarsenate. When an acid is added to one of these solutions, thioarsenous or thioarsenic acid is formed. Each of these at once decomposes evolving hydrogen sulfide and precipitating a trisulfide from the thioarsenous acid, or the pentasulfide,  $\text{As}_2\text{S}_5$ , from the thioarsenic acid. This behavior of the sulfide toward alkali sulfides is very much like that of the sulfides of tin and puts arsenic and tin into the same analytical group.

The trisulfide is also soluble in solutions of the alkalis and their carbonates forming complex thio compounds, which contain both sulfur and oxygen in the anion. The trisulfide is reprecipitated from these solutions when they are acidulated.

#### PENTAVALENT COMPOUNDS

**Arsenic Pentoxide and Arsenic Acid.**—When arsenic or the trioxide is treated with concentrated nitric acid, a solution is obtained from which, after high concentration, orthoarsenic acid,  $\text{H}_3\text{AsO}_4$ , crystallizes. This acid is a white very soluble and deliquescent substance. Like phosphoric acid, to which it is analogous, it is tribasic and forms three series of salts. The soluble normal salts are like the corresponding phosphates in that they are largely hydrolyzed and their solutions are highly alkaline. When the orthoarsenic acid is carefully heated, it loses water in stages and passes successively into the pyroarsenic acid,  $\text{H}_4\text{As}_2\text{O}_7$ , the metarsenic,  $\text{HAsO}_3$  and finally into the pentoxide,  $\text{As}_2\text{O}_5$ . All these changes are like the corresponding changes for the phosphoric acid, except that they take



place more readily, and that metaphosphoric will not give the pentoxide when heated. The reverse change from the meta- to the orthoarsenic acid may also take place far more rapidly than the corresponding change of the phosphoric acid, and only orthoarsenic acid and the orthoarsenate are known in solution.

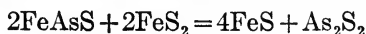
The orthophosphate and the orthoarsenates are isomorphous and have about the same solubilities, so that it is not altogether an easy matter to distinguish between the two groups of salts. The sharpest distinction rests upon the fact that arsenic forms a difficultly soluble sulfide with hydrogen sulfide in acid solutions, while phosphorus does not.

Sodium arsenate,  $\text{Na}_2\text{HAsO}_4$ , and the bi- or pyroarsenate,  $\text{Na}_4\text{As}_2\text{O}_7$ , have become important articles of commerce, being used to prepare the lead arsenates,  $\text{Pb}_3(\text{AsO}_4)_2$  or  $\text{PbHAsO}_4$ , which are extensively employed as sprays to protect fruit trees from the attacks of insects.

**Halogen Compounds.**—Arsenic pentafluoride,  $\text{AsF}_5$ , is a colorless gaseous substance, which condenses at  $-53^\circ$  and freezes at  $-80^\circ$ . The pentaiodide is a brown crystalline solid, melting at  $70^\circ$  and easily decomposing into the triiodide and iodine. The pentachloride and bromide are unknown.

**Pentasulfide.**—Arsenic pentasulfide is a yellow powder, which may be obtained as mentioned above by acidulating a solution of a thioarsenate. It is also prepared by passing hydrogen sulfide into a solution of arsenic acid in concentrated hydrochloric acid. It is a rather unstable substance, readily decomposing into the trisulfide and sulfur and having about the same solubilities as the trisulfide. In dissolving in the alkali sulfides, thioarsenates are formed whether the sulfide be colorless or yellow.

**Divalent Compounds.**—The best known of these compounds are the iodide,  $\text{AsI}_2$ , and the sulfide,  $\text{As}_2\text{S}_2$ . The latter occurs in nature and is known as realgar. It has a red color, melts easily, and burns to arsenic trioxide and sulfur dioxide. It may be made by heating together arsenical pyrite and pyrite,



#### ANTIMONY

**General.**—Metallic antimony, as well as some of its compounds was known to the ancients, as a Chaldean vase of pure antimony

has been discovered, and the old writings show that the sulfide has long been used by the oriental women to darken the eyebrows. There is a very close resemblance between antimony and arsenic. The difference being due to the fact that antimony is more of a metal than arsenic.

**Occurrence.**—Very small quantities of antimony are found free in nature. The principal ore is a trisulfide or stibnite,  $Sb_2S_3$ . From stibnite the metal is prepared either by fusion with metallic iron, which yields antimony and ferrous sulfide, or the ore is first roasted, forming sulfur dioxide and antimony tetraoxide,  $Sb_2O_4$ ; the latter is then reduced by carbon. The metal prepared by either of these processes is not pure and must be remelted with sodium sulfate and slag from previous operations and finally with potassium carbonate and slag.

**Properties.**—When pure, antimony is a silvery white, highly crystalline metal, which may be easily powdered and which has a density of 6.7. It melts at  $631^\circ$  and boils between  $1500^\circ$  and  $1700^\circ$ . The vapor density indicates a mixture of  $Sb_2$  and  $Sb_4$  in the vapor at  $1634^\circ$ . Besides the ordinary form which has just been briefly described, there is a very unstable yellow modification, prepared by the action of oxygen upon liquid stibine,  $SbH_3$ , below  $-90^\circ$ . This, like yellow phosphorus and arsenic is soluble in carbon disulfide. It is unstable, and even at  $-90^\circ$  passes into a black form, a transformation which is accelerated by light. The black modification is obtained by the action of oxygen on liquid stibine at  $-40^\circ$ , and also by rapidly cooling the vapor of the ordinary modifications. Its density is 5.3. It is more volatile and more active chemically than the ordinary modifications into which it passes rapidly at  $400^\circ$ . Besides these, there is an explosive form which is prepared by the electrolysis of the concentrated solution of the trichloride. It always contains 4 to 7 per cent. of the trichloride and passes into the metallic form with explosive rapidity when scratched, or heated to  $200^\circ$ ; at the same time 20 calories are evolved per gram. Antimony is a constituent of several important alloys. Type metal contains two parts of lead and one part each of tin and antimony. Like most of the alloys of antimony, it expands upon solidification and hence makes sharp castings. Babbit

metal contains 1.5 per cent. copper, 13 per cent. antimony, 45.5 per cent. tin and 40 per cent. lead.

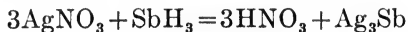
Antimony is stable in the air at ordinary temperatures, but burns when heated, forming the trioxide or tetraoxide,  $\text{Sb}_2\text{O}_4$ . It combines directly with the halogens and is oxidized by nitric acid to either the trioxide or antimonous acid,  $\text{H}_3\text{SbO}_4$ , with the formation of nitrogen peroxide. Hot concentrated sulfuric acid forms the sulfate  $\text{Sb}_2(\text{SO}_4)_3$  and sulfur dioxide. Dilute sulfuric acid and hydrochloric acid are without action upon the pure metal.

Antimony forms two series of compounds; in the one it is trivalent, and in the other pentavalent. The trivalent are the more numerous and important.

#### TRIVALENT COMPOUNDS

**Stibine.**—One strong point of resemblance between antimony and the preceding members of the group is the formation of the hydrogen compound, stibine,  $\text{SbH}_3$ . This is a colorless, gaseous substance, liquefying at  $-18^\circ$  and freezing at  $-91.5^\circ$ . It is very poisonous. It is formed by the action of zinc in acid solution upon a soluble antimony compound. The reaction is very similar to that for the preparation of arsine. Stibine is even more readily decomposed than arsine. It is formed from its elements with the absorption of 364 KJ., and hence belongs to the class of substances which readily act as explosives; in fact, it will explode upon the passage of a spark or when strongly heated. Its decomposition by oxygen at low temperatures has already been given. It is decomposed by heat even more readily than arsine, the decomposition going on rapidly at  $200^\circ$  and the antimony is deposited as a non-volatile mirror on both sides of the heated portions of the tube. The mirror differs from that of arsenic in that it is deposited on both sides of the heated portion, while the arsenic is always beyond; that it melts and is hard to volatilize while arsenic is readily volatilized, but does not melt; and that it is not soluble in solutions of hypochlorites, while arsenic is; and that with hydrogen sulfide the mirror of antimony turns red, while that of arsenic becomes yellow, the sulfides of the elements being formed.

When stibine is passed into silver nitrate a precipitate of silver antimonide,  $\text{Ag}_3\text{Sb}$  is produced.



It will be recalled that arsine will react with silver nitrate, forming arsenious acid and metallic silver. These reactions offer a means of separating arsenic and antimony since the arsenic is in the solution while the antimony goes into the precipitate.

**The Trioxide and Its Acids.**—The density of the vapor of antimony trioxide at  $1560^\circ$  corresponds with the formula,  $\text{Sb}_4\text{O}_6$ , analogous to that of phosphorus or arsenic trioxides at lower temperatures. In spite of this the formula of the substance is usually written  $\text{Sb}_2\text{O}_3$ , and it is called the trioxide, rather than the hexoxide. It may be obtained by acting upon antimony with nitric acid or by heating the metal in a limited supply of air. It is a white crystalline substance which exists in two different crystalline modifications isomorphous with those of the analogous compound of arsenic. The trioxide is white and is practically insoluble in water, dilute sulfuric or nitric acid; it is soluble in moderately dilute hydrochloric or tartaric acids and in concentrated sulfuric acid and in solutions of sodium or potassium hydroxides. These properties show that it is both basic and acidic, and therefore not strong in either way. Both series of salts are largely hydrolyzed.

The hydroxide,  $\text{Sb}(\text{OH})_3$  is a white solid which is very slightly soluble in water. It has the same solubilities as the trioxide and is probably formed as an intermediate stage in the solution of the latter in acids and bases. Whenever the oxide or hydroxide dissolves in sodium hydroxide, sodium meta-antimonite,  $\text{NaSbO}_2$ , is formed, potassium hydroxide yields the corresponding salt. Antimony hydroxide is soluble in potassium hydrogen tartrate  $\text{KHC}_4\text{H}_4\text{O}_6$  or "cream of tartar," as it is often called, owing to the formation of the complex salt tartar emetic, or potassium antimonyl tartrate,  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$ . This salt is important in medicine and also in the laboratory, since it is almost the only antimony compound which will form a clear, neutral solution. The explanation of this is found in the very small ionization of the ion,  $\text{Sb}^{+++}$  from the complex antimonyl tartrate ion,  $\text{SbOC}_4\text{H}_4\text{O}_6^-$ . The group  $\text{SbO}$  is called antimonyl and acts like

a monovalent cation. The solubility of the trioxide in tartaric acid is due to the formation of antimonyl tartrate ion. Because of the weakness of the basic properties of the hydroxide no carbonate is known and the chloride and sulfate are largely hydrolyzed with the precipitation of basic salts. When these basic salts are boiled with water, the hydrolysis becomes completed and the trioxide is formed.

**Halogen Compounds.**—The most important halogen compound is the trichloride,  $\text{SbCl}_3$ . This may be readily prepared by dissolving the trisulfide in strong hydrochloric acid and distilling. The water passes off first and then the trichloride. It is a white solid, melting at  $72.0^\circ$  and boiling at  $233^\circ$ . With a small quantity of water it gives a white precipitate of the oxychloride,  $\text{SbOCl}$ , which is sometimes called antimonyl chloride. With more water the compound  $\text{Sb}_4\text{O}_5\text{Cl}$  is formed, and when this is washed with hot water the oxide is left behind. Hydrochloric acid will reverse this hydrolysis even more readily than that of arsenic trichloride.

The trichloride is used in medicine as a caustic and technically for bronzing iron, and in dyeing for a mordant.

The trifluoride,  $\text{SbF}_3$ , forms colorless, rhombic crystals, which are deliquescent and whose solution may be dilute without precipitation, owing probably to slight ionization of the salt.

The tribromide,  $\text{SbBr}_3$ , forms colorless, rhombic crystals, melting at  $94^\circ$  and boiling at  $275^\circ$ . It is decomposed by water as is the chloride.

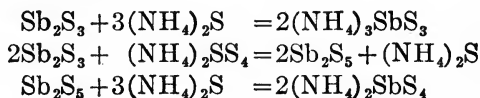
Antimony triiodide is prepared by warming the elements together. It forms three kinds of crystals. The most common form is red, the others greenish-yellow. The red form melts at  $167^\circ$  and boils at  $400^\circ$ . The vapor is orange red.

**Other Salts.**—The salts of the oxyacids in general are not very stable and are hydrolyzed even more readily than the halogen salts. The sulfate,  $\text{Sb}_2(\text{SO}_4)_3$ , and the nitrate,  $\text{Sb}(\text{NO}_3)_3$ , may be obtained in solution, but the latter will not stand dilution and soon decomposes on standing, in spite of an excess of acid.

**Antimony Trisulfide.**—Antimony trisulfide,  $\text{Sb}_2\text{S}_3$  is known both in the crystalline and amorphous state. The crystalline modification is black, melts at  $450^\circ$ , and has a metallic luster. It is found in nature and is known as stibnite; it may also be

formed by heating the red amorphous form to 220°. The amorphous modification is precipitated when hydrogen sulfide is passed into an acid solution of an antimony salt. It is orange red in color and is soluble in concentrated hydrochloric acid, but is reprecipitated upon dilution. A method for separating arsenic and antimony may be founded upon the difference in the behavior of their sulfides toward hydrochloric acid. Arsenic sulfide is completely precipitated in very strong hydrochloric acid, while antimony is unaffected. The solution is then filtered and diluted, when, upon the passage of more hydrogen sulfide, antimony is quantitatively precipitated as the sulfide.

Antimony trisulfide is soluble in solutions of sodium or ammonium sulfide, or polysulfide, with the formation of thioantimonites, with the sulfides and thioantimonates with the polysulfides, the reactions being strictly analogous to those for the arsenic compound;



The most familiar thioantimonate is that known as Schlippe's salt,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ .

When the solutions of the thio salts are acidulated, thioantimonious, or thioantimonie acids are formed. These acids are unstable and promptly break down into hydrogen sulfide which escapes as a gas, and antimony tri- or pentasulfides, which are reprecipitated. The solubility of the sulfide in ammonium sulfide and its reprecipitation by acids places antimony in the analytical group with tin and arsenic. The sulfide is soluble in NaOH and KOH, forming mixed thioantimonites, from which acids reprecipitate the sulfide.

#### PENTAVALENT COMPOUNDS

The pentavalent compounds are formed from the trivalent by the action of oxidizing agents.

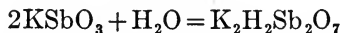
**Antimony Pentasulfide.**—The method for the formation of the pentasulfide has just been given in connection with the trisulfide. The oxidizing agent in this case is the polysulfide. The penta-

sulfide is a yellow-red substance which like the trisulfide is soluble in strong hydrochloric acid, the sulfides of ammonium, and of the alkalies, sodium or potassium hydroxides and in their carbonates. In all these ways it is like arsenic sulfide, but differs from the latter in that it is not soluble in ammonium carbonate. It is reprecipitated from the hydrochloric acid solution on dilution, and from the other solutions upon acidulation. The thioantimonates have already been mentioned in connection with the trisulfide.

**Antimony Pentachloride.**—Antimony pentachloride,  $\text{SbCl}_5$ , is formed when an excess of chlorine acts upon powdered antimony. The action is very vigorous and the metal takes fire spontaneously in contact with the chlorine. This chloride may also be obtained by the action of chlorine upon the trichloride. It is a colorless liquid, which freezes at  $-6^\circ$ . It boils without decomposition at  $79^\circ$ , under a pressure of 2.2 cm., but decomposes into the trichloride and chlorine at  $150^\circ$ , under atmospheric pressure. This behavior is very like that of phosphorus pentachloride.

When the pentachloride is treated with a little water, various hydrates are formed, while with more water it is completely hydrolyzed, giving antimonic acid, or its anhydride, the pentoxide.

**Antimonic Acids and the Pentoxide.**—As was the case with phosphoric and arsenic acid, there are three antimonic acids. Orthoantimonic,  $\text{H}_3\text{SbO}_4$ , pyroantimonic,  $\text{H}_4\text{Sb}_2\text{O}_7$ , and metantimonic,  $\text{HSbO}_3$  acids. When these acids are heated they pass into the pentoxide and water. The acids and also the pentoxide are sparingly soluble in water or acids, but dissolve in potassium hydroxide. These properties indicate that the pentoxide is a purely acid-forming oxide. Potassium metantimonate,  $\text{KSbO}_3$ , is formed by fusing potassium nitrate with powdered antimony. When boiled with water it forms the acid pyro salt,  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ ,



This potassium salt is easily soluble in water, but the corresponding sodium salt requires 350 parts of water for its solution, and hence is precipitated upon the addition of a concentrated solution of the potassium salt to a strong solution of a sodium salt. This is interesting as it is the least soluble inorganic sodium compound.

As a test for sodium, it is far less sensitive and characteristic than the flame-test.

Antimony tetroxide,  $\text{Sb}_2\text{O}_4$ , is formed by heating the trioxide to somewhere between  $400^\circ$  and  $775^\circ$  in the air. In the absence of reducing agents it is stable up to high temperatures. It is neither an acid nor a base. One large use for the substance is in the manufacture of enamel ironware for cooking purposes. In view of the highly poisonous character of antimony compounds, this use would not seem to be wholly free from objection.

### BISMUTH

**General.**—The metal bismuth, and some of its compounds have been known from the Middle Ages, but the circumstances of the discovery are lost. The element is far more metallic in its character than the other members of the group. The trivalent compounds are the only stable and important ones. It does not form a compound with hydrogen. Bismuth trihydroxide,  $\text{Bi}(\text{OH})_3$  is the strongest base in the family. It does not act as an acid, and does form carbonates, nitrates, phosphates, sulfates, etc. These salts are hydrolyzed by water so the hydroxide is not a really strong base. The trisulfide does not form thio salt with the alkali sulfides.

**Occurrence.**—Bismuth is found free in nature and to a smaller extent as a sulfide,  $\text{Bi}_2\text{S}_3$ , and oxide,  $\text{Bi}_2\text{O}_3$ . It is obtained from its ores by first roasting them to remove sulfur, and then heating in a crucible or reverberatory furnace, with carbon to act as a reducing agent, iron to reduce unchanged sulfide, and to combine with arsenic, and fluxing material to form an easily fusible slag. The metal so formed is purified by repeated fusion, first with bismuth oxychloride,  $\text{BiOCl}$ , to remove the lead, then with sodium and potassium carbonate and sulfur to remove the antimony, through the formation of the thioantimonate, and finally, with sodium hydroxide and nitrate to eliminate the arsenic.

**Properties.**—Bismuth is a hard, brittle, crystalline metal with a high luster and a distinct reddish tinge of color. It has a density of 9.75, melts at  $269^\circ$  and boils between  $1600^\circ$  and  $1700^\circ$ . Its molar weight lies between that required for the formulas  $\text{Bi}$  and  $\text{Bi}_2$ . The combining weight is 208. Several alloys of



bismuth, lead, tin and cadmium have been prepared, which have a melting-point below the boiling-point of water. Lipowitz metal containing 15 parts bismuth, 8 parts lead, 4 parts tin, and 3 parts cadmium, melts at 60°. Higher melting alloys are used as safety plugs in steam boilers and in making automatic fire extinguishers. Bismuth alloys expand on solidification and make good castings. Some of them are used as stereotype metal.

The metal is but very slightly acted upon in the air at ordinary temperatures, but when heated it is slowly oxidized to the trioxide. It requires a fairly strong oxidizing agent to transform it into ion, so it is not dissolved by hydrochloric acid in the absence of air. It is dissolved by hot concentrated sulfuric acid with the evolution of sulfur dioxide and also in the cold by nitric acid or aqua regia. In every case, salts of trivalent bismuth are formed.

**Bismuth Trioxide.**—Bismuth trioxide,  $\text{Bi}_2\text{O}_3$ , is found in nature as bismuth ocher. It is made in the laboratory by heating the hydroxide, carbonate or nitrate. It is a yellow substance, which melts at 820° and crystallizes upon cooling. Three different crystalline modifications are known, two of which are isomorphous with modifications of antimony trioxide. The trioxide has the same solubility in acids as the hydroxide, which is given below, and forms the same salts. It is not soluble in bases. The trihydroxide,  $\text{Bi}(\text{OH})_3$ , is a white amorphous powder and is prepared by precipitating a bismuth salt with ammonium or sodium hydroxide. It is not soluble in excess of the base and in this way differs radically from antimony hydroxide. Acids dissolve the hydroxide with the formation of salts, such as the trichloride,  $\text{BiCl}_3$ , or nitrate,  $\text{Bi}(\text{NO}_3)_3$ . When solutions of the salts are diluted, basic salts are precipitated, such as the oxychloride,  $\text{BiOCl}$ . In fact, clear solutions of bismuth salts can be prepared only in the presence of an excess of acid.

**Bismuth Salts.**—The salts of bismuth may be formed by dissolving the hydroxide in acids, or in the case of the nitrate and sulfate, by the solution of the metal in the corresponding acid. The nitrate,  $\text{Bi}(\text{NO}_3)_3$ , is the most important salt. It forms clear colorless crystals which are soluble in dilute nitric acid, but upon dilution the solution deposits the basic salt,  $\text{BiONO}_3$ . This salt is called bismuth subnitrate and is largely used in medi-

cine. The trichloride is colorless and is soluble in dilute hydrochloric acid. It forms the very slightly soluble oxychloride upon dilution, which is so difficultly soluble that it is used in the identification and separation of bismuth. It is promptly formed upon the addition of a solution of a chloride to a dilute but clear solution of bismuth nitrate. The bromide is much like the chloride, except that it has a yellow color. With water it forms the white oxybromide,  $\text{BiOBr}$ . The triiodide,  $\text{BiI}_3$ , is a blackish-red substance which is not very soluble in water and is precipitated when an iodide is added to a solution of bismuth chloride. It is not decomposed by cold water, but is changed to the oxyiodide by hot water. The triiodide is soluble in potassium iodide solution, forming the complex ion,  $\text{BiI}_4^-$ , and from this the salt  $\text{KBiI}_4$  may be obtained. Many other salts of this type are known. The sulfate,  $\text{Bi}_2(\text{SO}_4)_3$  is a white substance, formed by the action of the concentrated acid upon the metal. It decomposes with water for the formation of the basic salt,  $\text{Bi}_2(\text{OH})_4\text{SO}_4$ . The hydrolysis of the bismuth salt may, of course, be reversed by acids.

**Bismuth Trisulfide.**—Bismuth trisulfide,  $\text{Bi}_2\text{S}_3$ , is formed by the direct union of the elements, or by the action of hydrogen sulfide upon a moderately acid solution of a bismuth salt. It is brownish-black and is not soluble in water, cold dilute acids, the soluble sulfides, or polysulfides. It is soluble in concentrate hydrochloric and hot dilute nitric acids; in the latter case the sulfur is either liberated or oxidized to the sulfate. These properties place bismuth in the analytical group containing mercuric mercury, lead, copper, and cadmium. It is distinguished from mercury by the fact that its sulfide is soluble in hot dilute nitric acid, while that of mercury is not; from lead by the slight solubility of lead sulfate in dilute sulfuric acid; and from copper and cadmium by the fact that the hydroxide of bismuth is not soluble in an excess of ammonium hydroxide, while those of the other two metals are. It is finally identified by dissolving a little of the hydroxide in a few drops of dilute hydrochloric acid and pouring the solution into water, when a white precipitate of the oxychloride will form.

**Other Compounds.**—Besides the trioxide, bismuth forms the monoxide,  $\text{BiO}$ , the tetroxide,  $\text{Bi}_2\text{O}_4$ , and the pentoxide,  $\text{Bi}_2\text{O}_5$ .

The latter is almost indifferent. It does not form salts with acids, but when fused with the alkalis it forms bismuthates, which quickly decompose upon contact with water. A monosulfide,  $\text{BiS}$ , analogous to the monoxide, is known. Bismuth dichloride and dibromide have been prepared, but no pentachloride or bromide.

COMPARISON OF THE PROPERTIES OF THE ARSENIC FAMILY OF ELEMENTS

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Comb. wt .....	14.01	31.04	74.96	120.2	208.0
Formulae.....	$\text{N}_2$	$\text{P}_4$	$\text{As}_4\text{-As}_2$	$\text{Sb}_4\text{-Sb}_2$	$\text{Bi}_2\text{-Bi}$
Melt.-point.....	$-205^\circ$	$+44.0^\circ$	$+480.0^\circ$	$631^\circ$	$269^\circ$
Boil.-point.....	$-194^\circ$	$286^\circ$	$450^\circ$	$1600^\circ$ app.	$1700^\circ$ app.
Density.....	0.89	1.8-2.3	3.9-5.7	6.7	9.75
Occurrence.....	Fr.-Cb.	Cb.-never free.	Fr.-Cb.	Fr.-Cb.	Fr.-Cb.
Hydrides.....	$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	$\text{SbH}_3$	.....
B. p. of hydro com.	$-33.5^\circ$	$-86^\circ$	$-55^\circ$	$-18^\circ$	.....
Comb. with acids..	Salts	Salts	.....	.....	.....
Halides.	.....	$\text{PI}_2$	$\text{AsI}_2$	.....	$\text{BiCl}_2$
A = any.....	$\text{NA}_3$	$\text{PA}_3$	$\text{AsA}_3$	$\text{SbA}_3$	$\text{BiA}_3$
halogen.....	.....	$\text{PA}_5^*$	$\text{AsF}_5$	$\text{SbA}_5^\dagger$	$\text{BiF}_5$
Oxides.	.....	.....	.....	.....	.....
(ous).....	$\text{N}_2\text{O}^1$	.....	.....	.....	.....
(ic).....	$\text{NO}$	.....	.....	.....	$\text{BiO}$
(tri).....	$\text{N}_2\text{O}_3^1$	$\text{P}_4\text{O}_6^1$	$\text{As}_4\text{O}_6^{1, 2}$	$\text{Sb}_4\text{O}_6^{1, 2}$	$\text{Bi}_2\text{O}_3^2$
(tetr).....	$\text{N}_2\text{O}_4$	$\text{P}_2\text{O}_4$	.....	$\text{Sb}_2\text{O}_4$	$\text{Bi}_2\text{O}_4$
(pent).....	$\text{N}_2\text{O}_5^1$	$\text{P}_2\text{O}_5^1$	$\text{As}_2\text{O}_5^1$	$\text{Sb}_2\text{O}_5^1$	$\text{Bi}_2\text{O}_5^1$
Acids.	.....	.....	.....	.....	.....
hypo-ous.....	$\text{H}_2\text{N}_2\text{O}_2$	$\text{H}_3\text{PO}_2$	.....	.....	.....
meta-ous.....	$\text{HNO}_2$	.....	$\text{HASO}_2^3$	$\text{HSbO}_2$	.....
ortho-ous.....	.....	$\text{H}_3\text{PO}_3$	$\text{H}_3\text{AsO}_3$	$\text{H}_3\text{SbO}_3$	.....
meta-ic.....	$\text{HNO}_3$	$\text{HPO}_3$	$\text{HASO}_3$	$\text{HSbO}_3$	$\text{HBiO}_3^3$
pyro-ic.....	.....	$\text{H}_4\text{P}_2\text{O}_7$	$\text{H}_4\text{As}_2\text{O}_7$	$\text{H}_4\text{Sb}_2\text{O}_7$	.....
ortho-ic.....	.....	$\text{H}_3\text{PO}_4$	$\text{H}_3\text{AsO}_4$	$\text{H}_3\text{SbO}_4$	.....
Sulfides.	.....	.....	.....	.....	.....
tri.....	$\text{N}_4\text{S}_4$	.....	$\text{As}_2\text{S}_2$	.....	$\text{Bi}_2\text{S}_2$
penta.....	.....	$\text{P}_2\text{S}_3$	$\text{As}_2\text{S}_3$	$\text{Sb}_2\text{S}_3$	$\text{Bi}_2\text{S}_3$
.....	$\text{N}_2\text{S}_5$	$\text{P}_2\text{S}_5$	$\text{As}_2\text{S}_5$	$\text{Sb}_2\text{S}_5$	$\text{Bi}_2\text{S}_5$

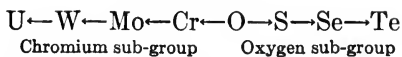
\* Except  $\text{PI}_5$  which is unknown.

† Except  $\text{SbBr}_5$  which is unknown. 1 = acid forming. 2 = base forming. 1, 2 = both acid and base forming. 3 = known only in salts.

From the facts collected in this table, it will be seen that nitrogen and bismuth differ more from the other three elements than these do from one another, but that the elements taken as a whole form a well-defined family with fairly regular changes in properties as the combining weight is increased. Some of the more striking of these changes may be summarized as follows: As the combining weight increases, the elements change from non-metals to metals; the melting-point, boiling-point, and density of the element rises; the boiling-point of the hydrides (except ammonia) rises; the stability of the hydrides decreases; the basic properties of the hydrides decrease; the acid properties of the oxides decrease; the basic properties of the oxides increase.

## CHAPTER XXVIII

### GROUP VI



The members of Group VI fall naturally into two well marked families or sub-groups; the first is called the oxygen or sulfur group and is made up of oxygen, sulfur, selenium, and tellurium. These are non-metals although tellurium possesses some of the characteristics of the metals. Their melting- and boiling-points are comparatively low and rise regularly with the combining weight. These elements all form compounds with the metals which are closely analogous, that is to say the oxides, sulfides, selenides, and tellurides are much alike. They all form compounds with hydrogen which are readily volatilized.

The members of the chromium family are chromium, molybdenum, tungsten, and uranium. These are all distinctly metallic, have very high boiling-points, are exceedingly hard, and do not form hydrogen compounds analogous to water, hydrogen sulfide, etc. The two sub-groups then differ markedly in some respects and the points of dissimilarity are about what would be expected from what has been noticed in the other groups. The elements of the chromium sub-group are more metallic than those of the sulfur family, have greater densities, and higher melting-points. The members of the whole sixth group have this in common that with the exception of oxygen they each have a valence of six and form the oxide  $\text{RO}_3$ , in which R stands for any member of the group. The oxide is in each case the anhydride of an acid. But the strength of the acid decreases as the combining weight increases until with tellurium and uranium distinctly basic properties appear. Sulfur, selenium, and tellurium form dioxides,  $\text{SO}_2$ ,  $\text{SeO}_2$ ,  $\text{TeO}_2$ . The first two are acid-forming exclusively, the last is both acidic and basic. Most of the members of the chromium group form the oxides  $\text{RO}$ ,  $\text{R}_2\text{O}_3$ ,  $\text{RO}_2$ . These are in general base-forming, but are often both basic and acidic.

The members of the oxygen-sulfur family have been discussed among the non-metals and it now remains to take up a part of the chemistry of the chromium sub-group. The members of this family form so many complex compounds that anything like a detailed treatment in a book of this kind is out of the question.

## CHROMIUM

**General.**—Chromium is di-, tri-, hexa- and possibly heptavalent, and has a very tangled relationship, because every time it changes its valence, it takes on points of similarity to different elements. In the hexavalent state, it is acid-forming, and resembles sulfur in sulfates; while in the trivalent condition, it is very much like aluminium and ferric iron. Chromium was discovered in 1797 by Vauquelin, and was given its name because all its compounds are highly colored.

**Occurrence.**—Chromium does not occur free in nature and the only important ore is chrome-ironstone which is a mixture of chromium trioxide,  $\text{Cr}_2\text{O}_3$ , and ferrous oxide,  $\text{FeO}$ , to which the formula  $\text{Fe}(\text{CrO}_2)_2$  is usually given. This mineral is somewhat uncommon although by no means rare.

**Preparation.**—Pure chromium may be most readily prepared by the Goldschmidt process, reducing the trioxide with powdered aluminium. The necessary high temperature for starting the reaction is obtained in the usual way by using a pellet of barium peroxide and aluminium which is ignited with a fuse of magnesium ribbon. The action once started goes on very rapidly, and the temperature reached is high enough to yield the metal as a button. The pure metal may also be secured by the electrolysis of salts in solution. The oxide is readily reduced by carbon at the temperature of the electric furnace, but the products contain some carbon. An alloy of chromium and iron containing 60 per cent. of the former known as ferro chrome, is made on a large scale in electric furnaces by the reduction of chrome-ironstone. The product is used in the preparation of chromium alloy steels which are very hard.

**Properties of Metal.**—Chromium is a tin white, very hard and brittle metal. Its density is 6.9 and its melting-point about  $1500^\circ$ . It may be distilled at the temperature of the electric

arc furnace. The metal is apparently not attacked by the air at ordinary temperature, but burns brilliantly at the temperature of the oxyhydrogen blowpipe. It dissolves in cold concentrated or hot dilute hydrochloric, sulfuric and oxalic acids, but is not attacked by nitric, chromic, chloric, or perchloric acids. This is surprising, because these latter acids are more active oxidizing agents than the others, and curiously enough a piece of chromium that has been in nitric acid will not dissolve when placed in hydrochloric acid. This is expressed by saying that chromium becomes passive in the oxidizing acids, and that this passivity persists when it is placed in other acids. Contact with the air or with free chlorine or bromine as well as with the oxidizing acids will make chromium passive, while reducing agents in general will render it active. For example, if a piece of passive chromium in hydrochloric acid be touched with a stick of zinc, cadmium, copper or even active chromium, it will at once begin to dissolve with the evolution of hydrogen. There is a difference of potential of about 1.6 volts between the active and the passive forms.

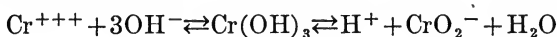
This change back and forth from active to passive in the presence of reducing or oxidizing agents suggests that the passivity may be due to a layer of oxide; but this explanation is not entirely free from objection. A chromium anode dissolves either as the chromous or chromate ion according to the current density.

**Chromous Compounds.**—The divalent or chromous compounds may be prepared by dissolving the metal in acids; by the reduction of the chromic salts with metallic zinc; or by heating chromic chloride in a stream of hydrogen. In the solid state they are red, blue, or yellow, but in solution are always blue which seems to be the color of the chromous ion,  $\text{Cr}^{++}$ . They change so easily to the trivalent or chromic compounds, that they will even be oxidized by water with the evolution of gaseous hydrogen, and are therefore very unstable. The principal ones are the hydroxide,  $\text{Cr}(\text{OH})_2$ , chloride,  $\text{CrCl}_2$ , sulfate,  $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ , and acetate,  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2$ . The latter is a dark red crystalline salt which is not very soluble in water, but is dissolved by strong acids. It is about the most stable of the chromous compounds.

**Chromic Compounds.**—Chromium in the chromic compounds

is trivalent, and the properties of the chromic ion are very much like those of aluminum, and the trivalent iron and manganese ions. All the chromic compounds are highly colored; in solution most of them are violet and this is said to be the color of the chromic ion  $\text{Cr}^{+++}$ . Some solutions are green, but these have different chemical properties from the violet, and apparently contain complex ions. Chromium hydroxide  $\text{Cr}(\text{OH})_3$  is very difficultly soluble, and is precipitated when a soluble base is added to a chromic solution.

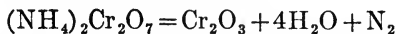
Like aluminum hydroxide, it acts as a base and as an acid, and so dissociates as follows:



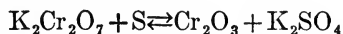
It is soluble both in acids and in excess of sodium or potassium hydroxide, forming in the first case chromic salts, and in the second chromites such as  $\text{NaCrO}_2$ . Upon standing or more quickly when boiled, a green partially dehydrated form of the hydroxide is deposited from the chromite solutions.

Ammonium hydroxide is too weak a base to dissolve chromium hydroxide with the formation of chromite, but it does dissolve it slightly owing to the formation of complex ammonia ions. Chromic hydroxide is a very weak base, and its salts, especially those of the weaker acids, are largely hydrolyzed, so the soluble sulfides precipitate chromic hydroxide instead of the sulfides. Carbonates usually precipitate the hydroxide, but under some conditions basic carbonates may be obtained. This action is precisely like that of aluminum salts.

Chromic oxide  $\text{Cr}_2\text{O}_3$  may be made by heating the hydroxide or ammonium dichromate,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .



and also by igniting a mixture of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and sulfur



The oxide has a fine green color and is used as a pigment under the name of chrome green.

**Chromic Chloride.**—Anhydrous chromic chloride is made by heating the metal in a stream of chlorine. It sublimes as peach-



blossom-colored scales which are so slowly soluble in water that they are apparently insoluble; but in the presence of minute quantities of a powerful reducing agent, for example, a very little chromous chloride, solution begins and goes on so rapidly that the temperature of the system is raised several degrees, and a large amount of the chloride goes in solution where it exists in the chromic state. Alternate reduction to the chromous and oxidation to the chromic suggests itself as an explanation for the action of the reducing agent.

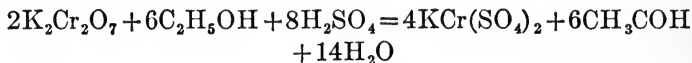
The solution obtained in this way is green, and upon the addition of silver nitrate, only two-thirds of the chlorine is precipitated as silver chloride. The remainder is evidently present in a complex ion, and since the solution is acid in reaction, the ion is probably  $\text{CrCl}(\text{OH})^+$ . When a dilute solution of the chloride is allowed to stand for some time, it becomes violet; and then the whole of the chlorine may be precipitated by silver nitrate. The violet solution is also a better conductor of electricity than the green. By carefully evaporating a solution of the chloride, green crystals of a hexahydrate,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , may be obtained; under other conditions, two more modifications, one blue and the other green, each containing six moles of water, may be prepared. When a hexahydrate is heated, it decomposes into the oxide  $\text{Cr}_2\text{O}_3$ , hydrogen chloride and water.

**Chromic Sulfate.**—The normal sulfate,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ , is violet in color, and its solution contains both the chromic and sulfate ions; but when heated, either dry or in solution, it turns green, and under certain conditions, passes into a state in which it will give reactions for neither chromic nor sulfate ions. Upon allowing the solution to stand at ordinary temperature, it slowly passes back into the violet modification. The electrical conductivity of the violet solution is much greater than that of the green under like conditions.

Chromic sulfate combines with potassium or ammonium sulfate to form the corresponding alums,  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  or  $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

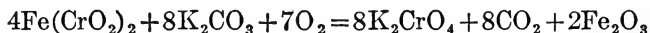
These are violet in color and are isomorphs with ordinary alum. When a solution of potassium chrome alum is boiled, it turns green and will then refuse to deposit crystals upon cooling until it has stood for some days and changed back into the violet.

Potassium chromic alum is most readily prepared by adding the necessary amount of sulfuric acid and alcohol to potassium dichromate, and boiling until the solution becomes green. The equation for the reaction is as follows:



The solution is green when first prepared and will not form crystals until it turns violet.

**Chromic Acid and the Chromates.**—Strong oxidizing agents in the presence of the alkalies or their carbonates will change the di- or trivalent chromium to hexavalent with the formation of chromates. Of these, perhaps, the potassium salt,  $\text{K}_2\text{CrO}_4$ , is the most important although the sodium salt is cheaper and very largely used. Potassium chromate is made by heating a mixture of chrome-ironstone, potassium carbonate and limestone in contact with the air. The equation is



The limestone is added to render the mixture porous and so assist the oxidation. The product is extracted with water, and any calcium chromate which may have formed is decomposed by the addition of potassium carbonate or sulphate.

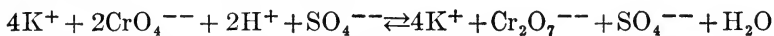
The sodium salt is prepared in the same way using the sodium instead of the potassium carbonate. The chromates are nearly all yellow in color and have about the same solubilities as the corresponding sulfates with which they are usually isomorphous. Lead chromate is very difficultly soluble, has a brilliant yellow color and is the pigment named chrome yellow. When attempts are made to prepare chromic acid, red crystals of the anhydride,  $\text{CrO}_3$ , are obtained and apparently the acid,  $\text{H}_2\text{CrO}_4$ , cannot exist in the pure state.

**Dichromates.**—Chromic anhydride is made by adding concentrated sulfuric acid to a solution of potassium dichromate; it crystallizes out and is washed with nitric acid. It will be recalled that sulfuric acid combines with sulfuric anhydride  $\text{SO}_3$  to form pyrosulfuric acid,  $\text{H}_2\text{S}_2\text{O}_7$ , and that this acid yields a series of salts called the pyrosulfates. In much the same way, chromic anhydride will combine with chromates for the formation

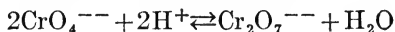
of the dichromates as they are, or pyrochromates, as they might be called.



So easily does this reaction take place and so readily is chromic anhydride formed in solution, that dichromates are made by simply acidulating solutions of the chromates. This equation may best be written ionically:



or omitting the ions which are unchanged



The reaction being reversible, it will at once be seen that acids by increasing the concentration of the  $\text{H}^+$  will cause it to go toward the right, and transform chromates into dichromates, while bases which will decrease the concentration of  $\text{H}^+$  will cause dichromates to change into chromates. The above equation will also make it clear why the difficultly soluble chromates such as barium or lead are precipitated from their soluble salts upon the addition of potassium dichromate. As fast as the chromate ion which always exists to a certain extent in any dichromate solution is used up, more is formed from the dichromate until the latter is finally practically all used up. The dichromate ion is orange red in color while the chromate is yellow; and the change of color may be used as a rough indicator of the presence of  $\text{H}^+$  or  $\text{OH}^-$ .

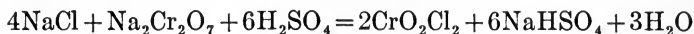
The tendency of chromic anhydride to combine with chromates is not exhausted with the formation of dichromate as is shown by the existence of such compounds as ammonium trichromate,  $(\text{NH}_4)_2\text{Cr}_3\text{O}_{10}$ , and the tetrachromate,  $(\text{NH}_4)_2\text{Cr}_4\text{O}_{13}$ .

This tendency for the formation of complex compounds is much more highly developed in molybdenum and tungsten.

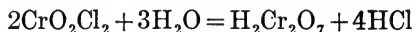
Chromates and dichromates are good oxidizing agents going to the chromic compounds and giving up three positive charges in the transfer for each combining weight of chromium.

Dichromates in acid solution will oxidize alcohol to aldehyde; oxalate to carbon dioxide; ferrous salt to ferric; and liberate chlorine, bromine or iodine. In either acid or alkaline solution, they will change sulfur as ion to free sulfur.

**Chromyl Chloride.**—When a mixture of a dichromate and a chloride is treated with concentrated sulfuric acid, a dark red fuming liquid distils over which bears a striking resemblance to bromine. This is chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ :



This chromyl chloride is analogous to sulfuryl chloride and like it is decomposed by water;



From this, it is seen that chromyl chloride is an acid chloride but it is interesting to note that the corresponding uranium compound,  $\text{UO}_2\text{Cl}_2$ , is a salt. This is in accord with the increase in the basic properties with the combining weight.

**Photochemical Reactions.**—When gelatine or glue is treated with a compound of trivalent chromium, it is rendered insoluble in hot water. Use is made of this in tanning leather which contains a sort of gelatine. The chromates or dichromates do not act in this way, but if a mixture of a dichromate and glue is exposed to the sunlight, the dichromate is slowly reduced and then tans the glue. Several technically important photochemical processes are founded upon this. If a metal plate coated with a mixture of glue and ammonium dichromate is exposed under an especially prepared negative and then washed with hot water, the glue is washed away where the plate has been protected from the light, but not in the other portions. The metal plate is then treated with acids, and the parts not protected by the tanned glue are partially dissolved away. Such a plate may be inked and printed from in a regular printing press and the dark spots in the object will come dark in the print.

**Perchromic Acid.**—When hydrogen peroxide is added to an acid solution of a dichromate, a very deep blue solution is obtained which soon evolves oxygen and turns green. The deep blue solution is supposed to contain perchromic acid which is thought to have the formula  $\text{HCrO}_4$ . The appearance of this blue color is a delicate test for either hydrogen peroxide or a chromate.

**Analytical Reactions of Chromium.**—All the compounds of chromium are strongly colored; chromous, generally blue;

chromic, violet or green; chromate, yellow, and dichromate orange red. Chromous compounds are too unstable to require much attention. Chromic compounds are so much like those of aluminum that they fall into the same analytical group, and are precipitated by ammonium hydroxide in the presence of ammonium salts. Chromium is most readily distinguished from iron and aluminum by the fact that its hydroxide is oxidized to sodium chromate in aqueous solution by sodium peroxide. The chromate may be recognized by its strong yellow color, by the formation of barium or lead chromate or by the blue color obtained on the addition of hydrogen peroxide to its acid solution.

### MOLYBDENUM

The rather rare element molybdenum is the second member of the chromium family. It was discovered in 1778 by Scheele. It does not occur free in nature and is found chiefly as molybdenite, the sulfide,  $\text{MoS}_2$ , and also as wulfenite or lead molybdate,  $\text{PbMoO}_4$ . When the sulfide is roasted in the air molybdenum trioxide,  $\text{MoO}_3$ , is formed. This may then be reduced to the metal by carbon in an electric furnace, by hydrogen at a high temperature, or by aluminum using the Goldschmidt process. It is a silvery white metal which is about as hard as iron. Its density is 9.0. It resembles iron in that it can be forged when hot, takes up carbon and then can be tempered like steel. It is used in the form of ferro-molybdenum alloys in the manufacture of special alloy steels. The metal is scarcely affected by oxygen up to  $600^\circ$  when it forms the trioxide. It is insoluble in dilute acids, except nitric.

Molybdenum forms three oxides: the sesquioxide,  $\text{Mo}_2\text{O}_3$ ; the dioxide,  $\text{MoO}_2$ ; and the trioxide,  $\text{MoO}_3$ . The first two are basic although their salts outside of the halogen compounds have been but little studied. The chlorides of molybdenum are  $\text{MoCl}_2$  or  $\text{Mo}_3\text{Cl}_6$ ,  $\text{MoCl}_3$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_5$ . The trioxide is the anhydride of molybdic acid,  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ . This forms a series of molybdates which are similar to the sulfates and the chromates not only in formula but also in solubility. Perhaps the most important of these salts, besides the naturally occurring lead compound, are the sodium and ammonium molybdates,  $\text{Na}_2\text{MoO}_4 \cdot 10\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{MoO}_4$ . The latter is much used as a

reagent. Molybdic acid and its salts have a great tendency to combine with the trioxide for the formation of complex compounds and a very large number are known. The formula of one of the sodium salts will serve to show something of the complexity of these compounds,  $\text{Na}_2\text{Mo}_{10}\text{O}_{31}\cdot 21\text{H}_2\text{O}$ .

Molybdenum trioxide will combine with other acids than molybdic acid to form complex salts. For example, it forms a series of such compounds with phosphoric acid, and these in turn form yellow crystalline very slightly soluble salts with ammonium, potassium, rubidium and cesium in the ionic state and also with many of the alkaloids. Because of this, a solution of phosphomolybdic acid is used as a reagent for the alkaloids. The most important use made of this property, however, is in the detection and separation of phosphoric acid, or rather of the phosphate ion.

For this purpose a dilute nitric acid solution of ammonium molybdate is added in excess to the solution of the phosphate and the whole kept warm for some time to favor the formation of the complex phosphomolybdate ion. Under these conditions a yellow precipitate of ammonium phosphomolybdate separates. The composition of this precipitate varies with the conditions and may be represented by the formula  $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_n$ , in which  $n$  may be 10, 11, or 12. Perhaps the most usual form is  $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{11}\cdot 6\text{H}_2\text{O}$ . These precipitates are soluble in excess of phosphoric acid or in alkalis, but are not soluble in dilute acids which implies that the phosphomolybdic acid is a strong acid. Arsenic acid and the arsenates react with the molybdates to form compounds which are very much like the phosphomolybdates in appearance and solubility.

When an acid solution of a molybdate is acted upon by a reducing agent such as hydrogen sulfide, sulfur dioxide or dilute stannous chloride, a blue solution which deposits a blue precipitate is formed. The composition of the precipitate is in doubt, but by some it is regarded as the molybdate of tetravalent molybdenum,  $\text{Mo}(\text{MoO}_4)_2$  or  $\text{Mo}_3\text{O}_8$ .

#### TUNGSTEN

The existence of the element tungsten was first established by Scheele in 1781 when he prepared tungstic acid from the naturally

occurring calcium tungstate which we now call scheelite,  $\text{CaWO}_4$ . Tungsten is a rather rare element which has recently become of great economic importance. It occurs principally in wolfram, an iron-manganese tungstate,  $(\text{FeMn})\text{WO}_4$ . In the preparation of the metal from wolfram, the ore is first heated with sodium carbonate to form sodium tungstate which is then dissolved in water. When the solution of sodium tungstate is acidulated, tungstic acid is precipitated. By gently heating the acid, it is converted into the trioxide which may be reduced to the metal in a number of ways; by carbon, hydrogen, zinc, or aluminum at rather elevated temperatures. Because of the very high melting-point of tungsten which is about  $3267^\circ$ , the element is usually obtained in the form of a powder; but a homogeneous mass of the metal may be secured by reducing the oxide with aluminum, if an excess of powdered aluminum is used and the mixture is wet down with liquid air rich in oxygen before it is set off. The extra high temperature necessary for the fusion of the tungsten is furnished by the powdered aluminum burning in the oxygen of the liquid air. The almost instantaneous change of temperature in this case from  $-182.5^\circ$  to over  $3200^\circ$  is to say the least striking. The metal prepared in this way is darker colored than zinc, is crystalline, harder than glass, very brittle, not ductile at any temperature, and has a density of 16.6. The powdered metal prepared in other ways has a density of from 17 to 18. One of the modern applications of tungsten is in the construction of high efficiency incandescent electric lamps, a use for which its very high melting-point renders it well adapted. The preparation of very fine wires required for such filaments was a matter of some difficulty, because of its hardness and lack of ductility. But the General Electric Co. has recently prepared ductile tungsten which may be drawn into filaments suitable for incandescent lamps. The details of the process are kept secret. Lamps prepared from this tungsten are very durable and because of their high efficiency will doubtless be very popular. The old style standard 16 candle-power carbon lamp consumed about 60 watts. The corresponding tungsten lamp uses 25 watts and gives about 20 candle-power, so the tungsten lamp gives  $1/4$  more light on less than half the energy which means that it converts the electrical energy more efficiently into light

and produces less heat. It is estimated that if the average price of electrical energy is 10 cents per kilowatt, the replacement of all the carbon lamps in the country by tungstens would effect a saving of \$240,000,000 per year.

Another important application of tungsten is in the preparation of special steels such as "high speed steel." For this purpose a ferrotungsten is often prepared in the electric furnace. High-speed steel through increasing the rate at which machines and machinists can work, has lowered the cost of automobiles on an average of \$200 per machine. Hence tungsten is economically very important.

The metal is fairly resistant to chemical action, but when powdered it will burn at a red heat to the trioxide. The ordinary acids act upon it very slowly; aqua regia dissolves it readily, and the powdered metal will also dissolve in potassium hydroxide with the evolution of hydrogen. At about 300° it reacts with chlorine for the formation of the hexachloride,  $WCl_6$ , from which the chlorides,  $WCl_2$ ,  $WCl_4$  and  $WCl_5$ , may be obtained by reduction. In addition to the trioxide already mentioned, a dioxide,  $WO_2$ , is known. Tungstic acid and sodium tungstate have been spoken of before. The sodium salt,  $Na_2WO_4 \cdot 2H_2O$ , is used as a mordant and for rendering cotton fabric fireproof, for which purpose it is dissolved in the starch with which the articles are treated. Very complex tungstic acids and the tungstates are formed by the union of the trioxide in varying quantities with the acid or the tungstates. Compounds very similar to the phosphomolybdates are formed by the interaction of tungstic acid with phosphoric, arsenic, antimonie, iodic, boric, and vanadic acids which makes the chemistry of tungsten very complex. In the formation of these complex acids, the basicity of the acid other than the tungstic is not altered, but its strength is considerably augmented. By the partial reduction of tungstates, metal-like appearing substances are formed which are called "tungsten bronze" and are used as bronzing powders.

The combining weight of tungsten is 184.0.

## URANIUM

Uranium, which is the last element of the chromium family, has the highest combining weight, 238.5, of any known element.



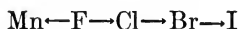
It was discovered in 1789 by Klaproth. It occurs in a number of rather rare minerals, but is chiefly obtained from pitchblende which contains the oxid,  $U_3O_8$ , and a little of almost everything else. This ore is interesting as furnishing the principal source of radium compounds. But all uranium minerals always contain radium. The metal may be prepared from the tetrachloride by reduction with metallic sodium, or from the oxide by reduction with carbon in a carbon tube at the temperature of an electric furnace. It may also be obtained in the form of a button containing a little aluminum by reducing the trioxide with aluminum in the presence of liquid air. Pure uranium is much like iron. It has a white color, takes a high polish, has a density of 18.7, and melts at about  $1500^\circ$ . The powdered metal is rather easily attacked chemically. It is oxidized in the air and burns in oxygen and the halogens at moderately elevated temperatures. There are two well-known oxides of uranium, the dioxide,  $UO_2$ , and trioxide,  $UO_3$ . The former of these has a good many metallic properties and was mistaken for the metal for many years. When treated with acids, it gives a series of salts called uranous salts such as uranous chloride,  $UCl_4$ , uranous sulfate,  $U(SO_4)_2 \cdot 8H_2O$ , etc. The trioxide is both basic and acidic. With acids it forms a series of salts called uranyl salts. These contain the group  $UO_2^{++}$  which acts like a complex divalent cation. These salts have a yellow color and many of them have a greenish-yellow fluorescence. The most important of the uranyl salts and in fact the most important of the uranium compounds is uranyl nitrate,  $UO_2(NO_3)_2 \cdot 6H_2O$ . When a solution of uranyl nitrate is added to an acetic acid solution of a phosphate containing ammonium acetate a precipitate of uranyl ammonium phosphate,  $UO_2NH_4PO_4$ , is formed which is insoluble in acetic acid. Use is made of this in the volumetric determination of phosphoric acid. The addition of an excess of a soluble hydroxide to a uranyl salt produces a precipitate of a diuranate analogous to the dichromates. The sodium salt,  $Na_2U_2O_7$ , is difficultly soluble and has a fine yellow color. It is an article of commerce under the name uranium yellow and is used to color uranium glass which like many other uranium preparations has a greenish-yellow fluorescence. This phenomenon is due to the absorption of the invisible ultra-violet rays of the sunlight by

the uranium compound and their conversion into visible greenish rays. Any substance which is able to become luminous, while under the excitation of some form of energy, without becoming heated to incandescence is said to be fluorescent. Fluorescence was first observed in connection with fluorspar and from this, received its name. Fluorescence differs from phosphorescence in that the former exists during the continuance of an exciting cause while the latter persists after its removal.

Metallic uranium and all of its compounds are radioactive and in fact the phenomena of radioactivity were first discovered by Becquerel in 1898 in the uranium compounds. The radioactivity of these substances is far less than that of the radium compounds and is about the same as that of the thorium salts. Again we shall have to postpone a full discussion of the subject to a later point.

## CHAPTER XXIX

### GROUP VII



Manganese      Halogen sub-group

Fluorine, the first member of the halogen family, shows a valence of one only, but the others have a variety of valencies from one up to seven. Each member of the family forms a compound with hydrogen in which the halogen is monovalent. They are typically non-metallic elements.

Manganese is the only member of the family which occupies the left-hand column of Group VII in the periodic system. It continues the regularities which have been noticed in the preceding groups in that it is much more basic than the right-hand family; it is unmistakably a metal. It does not form a compound with hydrogen analogous to the hydrohalogen acids nor is it monovalent in any compound. The strongest resemblance between manganese and the halogens is found in the heptoxide,  $\text{Mn}_2\text{O}_7$ , and the corresponding permanganic acid,  $\text{HMnO}_4$ . These are analogous to chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ , and perchloric acid, in fact potassium permanganate,  $\text{KMnO}_4$ , is isomorphous with potassium perchlorate,  $\text{KClO}_4$ .

Manganese has a rather large number of valencies. It is di-, tri-, tetra-, hexa-, and heptavalent and with each alteration of valence, it changes its chemical relationship, and points of similarity to additional elements become prominent. This makes the chemistry of manganese somewhat complicated. It will be seen in what follows that in the divalent form it is closely related to magnesium; in the trivalent state to chromium and iron; in the tetravalent condition to tetravalent lead and tin; while the hexavalent manganese is like sulfur in the sulfates and the heptavalent resembles chlorine in the perchlorates. The compounds of manganese have been known for centuries,

They were confused with those of iron until the latter part of the but v

18th century when they were differentiated, and the existence of the element manganese was established by the combined efforts of Pott, Kaim and Winterl, and Scheele working with Bergman. The element was first isolated by Gahn.

**Occurrence.**—Manganese is a fairly abundant and widely distributed element. Reference to the table on page 333 will show that it stands between barium and strontium in its abundance. It is found chiefly in the form of the dioxide, pyrolusite,  $MnO_2$ , to which frequent reference has been made in the past since it is a much used substance. Other less abundant ores are braunite,  $Mn_2O_3$ , manganite,  $Mn_2O_3 \cdot H_2O$ , hausmanite,  $Mn_3O_4$ , manganese blende,  $MnS$ , and manganese spar,  $MnCO_3$ . The metal is obtained by the reduction of its oxides with carbon in an electric furnace or more readily by their reduction with aluminum by the Goldschmidt process. Alloys of manganese with iron containing from 10 per cent. to 90 per cent. of manganese may be prepared in blast furnaces or in electric furnaces. Those containing up to 20 per cent. are called spiegeleisen while from 20 per cent. to 90 per cent. they are known as ferromanganese. These alloys are much used in the manufacture of steel. One alloy of manganese and copper containing about 30 per cent. manganese is known as manganese bronze. It possesses great tensile strength and is very hard.

**Properties.**—Pure manganese is a reddish-gray metal which is very brittle and is so hard that it will scratch glass. Its density is 7.2 and the melting-point is  $1245^\circ$ . It is readily volatilized in the electric furnace. It holds its luster in the air but is easily dissolved by acids, even by acetic, with the evolution of hydrogen and the formation of the divalent or manganous salts. When heated to a little over  $1200^\circ$  in a stream of nitrogen it takes fire and burns, forming a nitride. In this respect it is much like magnesium.

**Divalent or Manganous Compounds.**—The manganous salts are very much like the salts of magnesium. In many cases the two series have about the same solubility and are isomorphous. The manganous salts may be prepared by dissolving the metal, the carbonate, or any of the oxides in the acid of the salt desired and heating. The manganous salts are the only ones which are stable in acid solutions and all the others pass into permanganic acid.

Nearly all of them have a delicate pink color which is much more pronounced in the crystals than in the solutions. The hydroxide,  $\text{Mn}(\text{OH})_2$ , is thrown down as a white precipitate when a soluble hydroxide is added to a manganous salt solution. It has about the same solubility and strength as a base as the corresponding magnesium hydroxide, and like the latter, it is soluble in ammonium salts because of the decrease in the concentration of the hydroxyl through the formation of ammonium hydroxide. This solution quickly darkens because of the oxidation of the manganous ion to the manganic,  $\text{Mn}^{+++}$ , by the oxygen of the air and the precipitation of manganic hydroxide,  $\text{Mn}(\text{OH})_3$ , which is too weak a base to be dissolved by ammonium salts since it is even weaker than aluminum hydroxide. Manganous oxide may be prepared by gently heating the hydroxide in the absence of air. Manganous carbonate,  $\text{MnCO}_3$ , is formed as a white precipitate when a soluble carbonate is added to a manganous salt solution. It occurs in nature where it is often found in isomorphous mixture with magnesium carbonate. The precipitated carbonate like magnesium carbonate is soluble in ammonium salts and the explanation is the same as that given under magnesium carbonate (see p. 421).

**Manganous sulfate**,  $\text{MnSO}_4$ , usually crystallizes with  $4\text{H}_2\text{O}$ , but below  $6^\circ$  it has  $7\text{H}_2\text{O}$  and is isomorphous with ferrous sulfate while from  $7^\circ$  to  $20^\circ$ , the hydrate contains  $5\text{H}_2\text{O}$ , and is isomorphous with copper sulfate. It forms the double salt,  $\text{K}_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ , with potassium sulfate which is isomorphous with the corresponding salt of magnesium and in fact with the whole series of these double salts.

**Manganous Sulfide**,  $\text{MnS}$ , is the most soluble of the sulfides of the heavy metals. Its solubility product is so great that it cannot be precipitated by hydrogen sulfide except in the presence of hydroxyl or a very large amount of an acetate such as sodium acetate. It is usually precipitated by ammonium sulfide and comes down as an amorphous flesh colored substance which is readily soluble in all acids. Under conditions which are not well understood, it is sometimes precipitated as a green powder. When exposed to the air, the sulfide oxidizes rapidly and passes back into solution as the sulfate. These properties of the sulfide

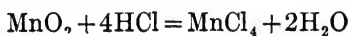
are of analytical importance because manganese is often separated from other metal by precipitation as the sulfide. This puts it in an analytical group with zinc, nickel, and cobalt whose sulfides are not precipitated in acid solutions while they are in alkaline. Manganese is distinguished from these and all other elements by its oxidation to the strongly colored permanganic acid (see p. 567) when boiled with lead dioxide and sulfuric acid.

**Manganous Ammonium Phosphate**,  $\text{MnNH}_4\text{PO}_4$ , is formed under similar conditions to those for the formation of magnesium ammonium phosphate, and has closely the solubility and appearance of the latter so that it is not difficult to confuse the two.

**Manganous Borate**,  $\text{MnH}_4(\text{BO}_3)_2$ , is a salt which is of technical importance because it acts as a catalytic agent in the drying of oils and varnishes.

**Trivalent Manganese.**—The trivalent compounds of manganese or the manganic compounds as they are usually called are not as numerous nor as stable as the manganous. A solution of the chloride may be obtained by dissolving manganic hydroxide,  $\text{Mn}(\text{OH})_3$ , in cold hydrochloric acid, but it soon evolves chlorine and passes into manganous chloride. The sulfate,  $\text{Mn}_2(\text{SO}_4)_3$ , is formed as a violet-red powder by heating precipitated manganese dioxide with concentrated sulfuric acid to  $138^\circ$ . The powder is then drained on a porous plate and washed with nitric acid. It is very deliquescent and hydrolyzes with extreme ease with the precipitation of the hydroxide. It forms alums with rubidium and cesium sulfates. A few slightly dissociated salts, such as the fluoride,  $\text{MnF}_3$ , and the phosphate,  $\text{MnPO}_4$ , have been prepared which are not hydrolyzed. These salts give reddish-violet solutions. Manganese sesquioxide,  $\text{Mn}_2\text{O}_3$ , which is the oxide corresponding to the manganic salts occurs in nature as the mineral braunite.

**Tetravalent Manganese.**—Manganese dioxide is the principal tetravalent compound of manganese and is, in fact, the most important compound of the element. Like lead dioxide which it resembles in a number of ways, it is both feebly basic and acidic. When treated with cold hydrochloric acid it is dissolved to form the tetrachloride,  $\text{MnCl}_4$ ,



This hydrolyzes upon dilution with the precipitation of the dioxide. When heated, the tetrachloride decomposes into the dichloride and chlorine,



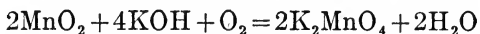
It was with the aid of these reactions that the chlorine of the world was formerly prepared, and large quantities are still made in this way although the processes involving the electrolysis of the chlorides have largely replaced it. The tetrahydroxide,  $\text{Mn}(\text{OH})_4$ , may be prepared by the action of powerful oxidizing agents upon manganous salts in neutral or alkaline solutions. Chlorine, bromine, hypochlorites, or permanganates may be used as the oxidizing agent or even under some conditions, the oxygen of the air. In acid solutions the manganese compounds all tend to pass into the divalent state, while in alkaline solutions they tend to become tetravalent and to be precipitated as the dioxide or its hydroxide. This hydroxide is a weak acid and forms salts called the manganites of which calcium manganite,  $\text{CaMn}_2\text{O}_5$ , may be taken for example.

If no other base than manganous hydroxide is present during the oxidation, manganous manganites are formed and it is thought by some that hausmanite,  $\text{Mn}_3\text{O}_4$ , and perhaps braunite,  $\text{Mn}_2\text{O}_3$ , may be such compounds. If this is the case hausmanite corresponds to red lead.

Like lead dioxide, manganese dioxide is a conductor of electricity and is used as an oxidizing agent in the ordinary form of salammoniac battery known as the Leclanche cell as well as in the slightly modified type called the dry cell. In each of these, the oxidizing agent is the dioxide and the reducing agent is metallic zinc. The dioxide is reduced to the manganous ion and the zinc oxidized to the zinc ion. The electrolyte is ammonium chloride solution containing some zinc chloride. The manganese dioxide is very slightly soluble, so it is necessary to have a very large area for the positive electrode which is of carbon packed around with the dioxide. Because of the slight solubility of the dioxide, the cell "polarizes" rapidly owing to the exhaustion of the dioxide which is in solution and in contact with the carbon electrode. It is then necessary to let the cell stand until more of the dioxide is dissolved. For this reason, the cell must be

used on an open circuit. Some idea of the magnitude of the dry cell industry may be obtained from the fact that about 50,000,000 of these cells are made in this country per year.

**Hexavalent Manganese.** *Manganates.*—By fusing manganese dioxide or, in fact, almost any manganese compound with potassium hydroxide in contact with the air, or more rapidly by the addition of a nitrate or chlorate, a dark green mass containing potassium manganate,  $K_2MnO_4$ , is formed;



This is soluble in water giving a green solution from which crystals may be obtained which are isomorphous with potassium sulfate. If sodium hydroxide is used instead of the potassium hydroxide, sodium manganate is formed which crystallizes from solution with ten moles of water,  $Na_2MnO_4 \cdot 10H_2O$ , and is isomorphous with the decahydrate of sodium sulfate. From these two examples, it will be seen that the manganates are analogous to the sulfates, and consequently hexavalent manganese to hexavalent sulfur. Solutions of manganates have an exceedingly intense green color, but are stable only in the presence of a hydroxide. Manganic acid cannot be prepared because it at once decomposes into permanganic acid and the dioxide, but its anhydride,  $MnO_3$ , has been obtained as a reddish deliquescent powder which is very unstable.

**Heptavalent Manganese.** *The Permanganates.*—When a solution of a manganate is diluted or acidulated, the color changes through blue and violet to purple and at the same time manganese dioxide is precipitated. This rather remarkable series of color changes gives to potassium manganate the name chameleon mineral. The change is due to the oxidation of a portion of the manganate to the permanganate at the expense of the remainder which is reduced to the dioxide,

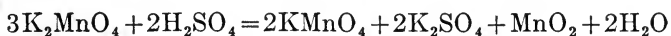


This reaction can be easily understood if the equation be written in the ionic form omitting the ions which do not enter directly into the reaction,



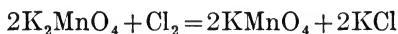


Since  $H^+$  is consumed in the reaction and  $OH^-$  produced, this reaction will take place much more readily when the solution is acidulated, and upon the addition of sulfuric acid the equation becomes,

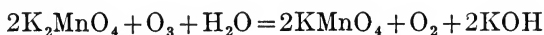


Even a very weak acid will bring about this change, so a solution of a manganate gradually becomes purple upon exposure to the air from the absorption of carbon dioxide and the formation of carbonic acid.

The transformation of the manganate into the permanganate is oxidation and may be brought about by passing chlorine into the solution of the manganate. In this case, the chlorine is reduced to the ion  $Cl^-$  and the whole of the manganate is oxidized to the permanganate so that manganese dioxide is not precipitated,



The oxidation may also be accomplished by ozone as shown below,



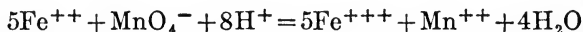
In the permanganate ion  $MnO_4^-$ , since each oxygen carries two negative charges, the manganese must have seven positive charges while in the manganate,  $MnO_4^{--}$ , on the same basis the manganese carries six, and in the dioxide,  $MnO_2$ , four positive charges. Then when one gram ion of the manganate is reduced to the dioxide the manganese gives up two + charges in passing from +6 to +4 and these two + charges are just sufficient to raise the manganese in two gram ions of the manganate from +6 to +7 or in other words, to oxidize them to the permanganate. Reference to the equations given above will show that this is the case, and three gram moles of manganate yield two gram moles of permanganate to one of manganese dioxide. Each combining weight of chlorine gives up a + charge in passing into the chlorine ion  $Cl^-$ , and hence a mole of chlorine can oxidize two moles of manganate.

The permanganates are powerful oxidizing agents and disinfectants and are manufactured in large quantities for such pur-

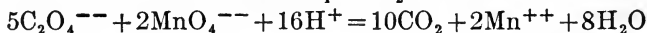
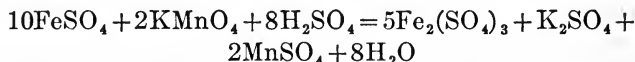
poses. The sodium salt is the cheapest if a pure article is not demanded. It is so very soluble that it is not easily obtained pure. For laboratory purposes the potassium salt is generally used. This crystallizes well in purple crystals with a greenish luster, and is isomorphous with potassium perchlorate. One hundred grams of water will dissolve 7.53 grm. of the salt at 25° and 25.03 grm. at 100°.

Solutions of potassium permanganate of known concentration are much used in the laboratory in the volumetric determination of ferrous iron, oxalic acid, and nitrous acid, as well as of manganous salts, since the permanganate acts in a rapid and definite manner with these substances. In carrying out the operation, the permanganate is added from a burette to the solution to be tested and the volume necessary to give to the solution the purple color of the permanganate is noted. The operation is especially convenient since owing to the strong color of the permanganate no other indicator is necessary. When the permanganate is used in this way, it is reduced to the manganous ion in acid solutions or to manganese dioxide in neutral or alkaline solutions. The titration of ferrous ion, oxalic acid, and of nitrous acid is carried out in acid solutions so the manganese in passing from the heptavalent to the divalent state gives up five + charges, and hence one mole of permanganate is able to oxidize five moles of a reducing agent which takes up one + charge per mole, or two moles of the permanganate can oxidize five moles of reducing agent which takes up two + charges as is the case with the oxalate ion.

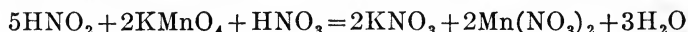
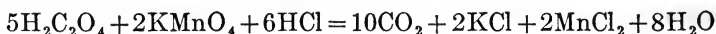
The following equation represents the reactions mentioned above,



or



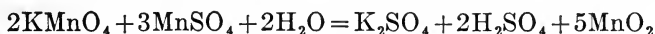
or



Hydrochloric acid cannot be used in the titration of the iron

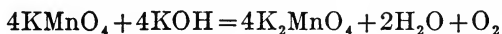
with the permanganate without taking rather elaborate precautions, because there is a slow reaction between the permanganate and hydrochloric acid which is catalyzed by ferric salts. Oxalates, however, may be titrated in the presence of hydrochloric acid without difficulty.

As has been mentioned, the permanganate is reduced to manganese dioxide in neutral or alkaline solutions, and also in these same solutions, the manganous ion tends to oxidize to the tetravalent condition and to be precipitated as the dioxide. The result of these tendencies is that manganous compounds may be titrated by permanganate in neutral solutions. In going from the permanganate to the dioxide, the manganese gives up three + charges, and the manganous in going to the dioxide takes up two + charges; hence two moles of permanganate will oxidize three moles of manganous salt as shown in the following equation,



The solution tends to become acid which would interfere with the reaction, so the titration is carried on in the presence of an excess of zinc oxide which neutralizes the acid as it is formed. The behavior of permanganate as an oxidizing agent can be readily kept in mind by remembering that in acid solutions it gives up five plus charges and goes to the manganous state, while in neutral or alkaline solutions it gives up three charges and becomes manganese dioxide.

Solutions of potassium permanganate when made highly alkaline turn green from the formation of the manganate;



When the dry salt is heated to 240° it yields oxygen, the manganate and manganese dioxide. This gives purer oxygen than the decomposition of the chlorate which generally yields some chlorine.

A solution of permanganic acid may be prepared by the second general method for the preparation of acids, using barium permanganate and sulfuric acid. It has the deep purple color of the permanganates and decomposes upon boiling or exposure to the light. An impure solution of the acid is also formed whenever a manganese compound is boiled with moderately dilute

sulfuric or nitric acid and red lead or lead dioxide. The equation in the latter case is,



Because of the strong and very characteristic color of the permanganate ion, this constitutes one of the best tests for manganese. It is necessary, however, to have the solution highly acid and to use a very small quantity of manganese as otherwise the action stops with the formation of the dioxide. Manganese heptoxide,  $\text{Mn}_2\text{O}_7$ , is formed by dissolving potassium permanganate in cooled concentrated sulfuric acid and carefully adding water when the oxide separates as a dark reddish-brown liquid which decomposes with the evolution of oxygen and explodes at the slightest provocation.

**Analytical Properties of Manganese.**—The solubility of manganese sulfide in acids and its precipitation by ammonium sulfide puts this element in an analytical group with zinc, cobalt, and nickel. From these it is distinguished by the pink color of its sulfide, by the formation of permanganic acid as described just above, by the green mass of manganate which is formed by fusion with an alkali and a nitrate, or by the amethyst color which all manganese compounds give in a borax bead heated in the oxidizing flame.

## CHAPTER XXX

### GROUP VIII

Fe—Co—Ni

Ru—Rh—Pd

Os—Ir — Pt

An examination of Group VIII of the periodic system will show that it differs radically from the other groups in that it is made up of three families of closely related metals in which the similar elements occur side by side, and have about the same combining weight, instead of forming a perpendicular column with widely different combining weights. There is, however, some similarity in the perpendicular columns, particularly between the last two families.

The three sub-families of the group are:

The iron sub-group; iron (Fe=55.84), cobalt (Co=58.97), and nickel (Ni=58.68).

The ruthenium sub-group: ruthenium (Ru=101.7), rhodium (Rh=102.9), and palladium (Pd=106.7).

The platinum sub-group: osmium (Os=190.9), iridium (Ir=193.1), and platinum (Pt=195.2).

All the members of the group are true metals and are somewhat remarkable for the number of complex compounds which they form.

From the gradual increase in the maximum valence which has been observed in the preceding groups, it might be anticipated that the valence of the members of this group would reach eight. The only known compounds of this kind are the tetraoxides of ruthenium and osmium,  $\text{RuO}_4$  and  $\text{OsO}_4$ .

### THE IRON FAMILY

Iron forms three series of compounds: the ferrates in which it is hexavalent and resembles manganese, and chromium in the manganates and chromates; the ferric salts in which it is trivalent and is like aluminum, and trivalent chromium or mangan-

ese; and the ferrous salts in which it is divalent and resembles the metals of the magnesium groups as well as cupric, chromous, and manganous compounds. Cobalt forms two series of salts similar to the ferric and ferrous, but the cobaltous are, in general, the more stable. Nickel forms only one series of salts, the nickelous, but shows some tendencies toward higher valence in the oxide,  $\text{Ni}_2\text{O}_3$ . The members of this family are all magnetic, have high melting-points and decompose steam at a high temperature.

## IRON

**General.**—This is truly the age of iron, as may be seen from the fact that the United States alone produces yearly about 27,000,000 long tons of the metal. A moment's thought will show that our present civilization would be very different if we did not have iron and steel in such abundance. Iron has been known and used from prehistoric times. Many meteors are composed chiefly of metallic iron, and the earliest tools and weapons were probably made from this source. The ores of iron are easily reduced by carbon, and even very primitive peoples have known how to do this in a small way, but the production on anything like the modern scale has only been possible since the invention of the blast furnace.

**Occurrence.**—Native iron is found in meteorites, and in certain deposits in Greenland; but all that is used is obtained from compounds. The principal ores are hematite, ferric oxide,  $\text{Fe}_2\text{O}_3$ ; brown iron ore or hydrated ferric oxide,  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , this is also called brown hematite, bog ore or limonite; magnetite, magnetic iron oxide,  $\text{Fe}_3\text{O}_4$ ; and siderite, spathic iron or kidney ore, ferrous carbonate,  $\text{FeCO}_3$ . Hematite furnishes about nine-tenths of the ore. Another iron mineral is pyrite,  $\text{FeS}_2$ ; this is mined in large quantities and burned as a source of sulfur dioxide in the manufacture of sulfuric acid. The residue consists principally of  $\text{Fe}_2\text{O}_3$ , but is too finely powdered and contains too much sulfur to use as an ore of iron. It has recently been found that this material may be sintered in a rotary kiln similar to that used in the manufacture of Portland cement, and brought into a suitable mechanical state; at the same time the sulfur content is reduced to a point where it is no longer

objectionable. This will make what was a waste product, a valuable source of iron. More than 50,000,000 tons of iron ore are mined per year in this country, the greater part of this comes from a region around the south and west of Lake Superior. It is mined in great open pits with steam shovels, loaded directly into cars and taken to the harbors on the lake, transferred to ships and carried to the lower lakes, where it is either unloaded and smelted on the spot, or taken by train to the great iron smelters around Pittsburg which are conveniently located with respect to the coal fields and manufacturing centers. Within very recent times a number of mammoth iron and steel plants have been located on the shores of the Great Lakes, so it looks as though Pittsburg might lose its pre-eminence in this industry. Another important iron-producing region is around Birmingham, Alabama, which has near at hand both iron ore and coal. Everything must be done as cheaply as possible because the average price of pig iron is about \$15 per long ton.

**Metallurgy of Iron.**—The manufacture of all forms of iron and steel begins with the making of cast iron in a blast furnace. This depends for its usefulness upon the fact that by properly selecting and proportioning the materials put into the furnace, the impurities in the ore and the products of the reactions may all be removed as gases or liquids, and the operation made continuous for a long time. The materials used are coke, iron ore, and limestone. The coke burns and gives the necessary high temperature, and also furnishes the requisite reducing agent, carbon monoxide. The limestone is changed to lime which reacts with the silicious impurities in the ore to form an easily fusible slag consisting of calcium and aluminum silicates which are removed from the bottom of the furnace in the liquid state. If the slag is basic, that is, contains an excess of lime, it will react with the greater part of the sulfur of the ore and fuel and so yield purer iron.

A modern blast furnace is a very large affair; 80 to 100 ft. in height by about 22 ft. in greatest diameter. Its shape is approximately that of two truncated cones set base to base. It is made of steel plates and lined with very infusible silicious fire brick. Toward the lower part where the temperature is highest, the furnace is cooled by spraying water upon the outside and also





in at the top. A blast of hot dry air is blown in through 8 to 16 tuyeres near the bottom. The coke nearest the tuyeres burns to carbon dioxide, which is then reduced by that farther away to carbon monoxide, which passing up through the iron oxide reduces it first from  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ , then to  $\text{FeO}$  and finally to the metal. The latter then takes up enough carbon to lower

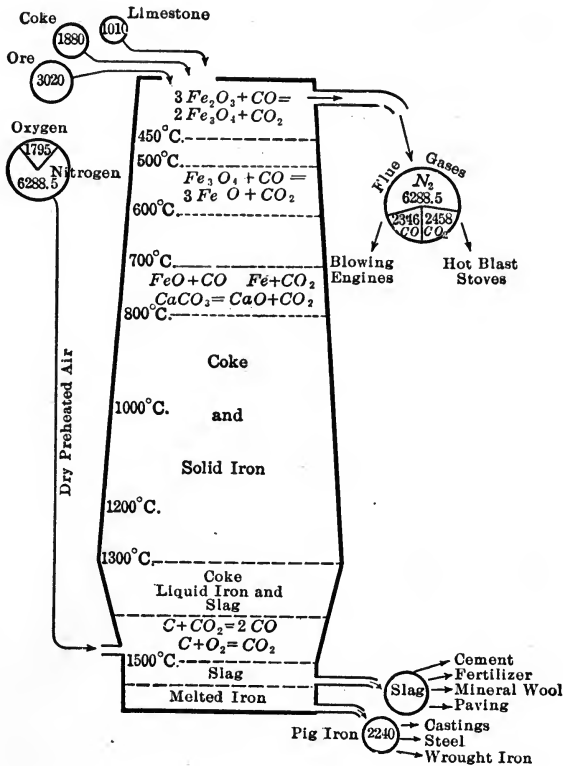


FIG. 44.

its melting-point from 1600, that of pure iron, to 1200, that of cast iron, and melts and collects in the lower part of the cylindrical portion of the furnace which is known as the hearth. The slag collects in the fused state just above the iron and is tapped off once in a while. The iron is also removed from the furnace through a tap hole at intervals, and either cast into bars called

pigs, or kept in the molten state in large mixers until it is needed for the conversion into steel in Bessemer converters or open hearth furnaces. Fig. 44 shows the substances and their weights used to produce a long ton of pig iron; the equations for the reactions which take place; where they occur; the temperature at the various parts of the furnace; and the disposal of the products. It should, therefore, receive careful study. The gases that escape from the top of the furnace contain under the best conditions approximately 16 per cent.  $\text{CO}_2$ , 24 per cent.  $\text{CO}$  and 60 per cent.  $\text{N}_2$ . The carbon monoxide is combustible and the gas produced in a furnace represents thousands of horse-power. About one-third of it goes to the stoves for heating the blast; the rest is used to develop the power needed around the plant being burned under boilers or better in gas engines. Heating the blast saves a great deal of fuel; another great saving is made by drying the air, before it is heated, by cooling it to a low temperature with an ammonia refrigerating plant, thus freezing out the water. This helps, because the water vapor in the air would react with the coke for the formation of carbon monoxide and hydrogen and the absorption of much heat. The saving in fuel caused by drying amounts to 20 per cent. and the output of the blast furnace is increased by the same amount.

The cast iron as it comes from the blast furnace is impure and contains from 4 to 11 per cent. of foreign substance, chiefly carbon, silicon, manganese, sulfur and phosphorus. These substances lower the melting-point of the iron and make it crystalline and brittle over all ranges of temperature. Cast iron, therefore, is not suitable for any purpose which requires considerable tensile strength, but may be used for casting which will be subjected to compression without much impact. There are two varieties of cast iron—white and gray. The white kind is made by rapid cooling; it contains the carbon in chemical combination and is very hard and brittle. The gray iron is made by slowly cooling. It is tougher and softer than the white and contains a large part of the carbon in the form of crystals of graphite scattered through the mass.

By removing these impurities more or less completely, the iron may be converted into steel or wrought iron and thereby

acquires much more valuable properties. More than three-quarters of the pig iron manufactured is subjected to such purification processes. The first step in each of these is to take advantage of the fact that the impurities mentioned are more easily oxidized than the iron, and hence will be eliminated before the latter is attacked in case the crude substance is exposed to oxidation. This oxidation is done either by the oxygen of the air or by that from iron oxide. It is difficult to draw the line between wrought iron and steel because the division is arbitrary, but the following is in common usage. Wrought iron is slag-bearing, contains less than .12 per cent. carbon, and does not harden materially when suddenly cooled. It is made in puddling furnaces. Steel is iron which is malleable at least over some range of temperature, contains from .12 to 2.2 per cent. of carbon, and which when suddenly cooled, is materially hardened. It is made in Bessemer converters, open hearth furnaces, or in crucibles.

**Bessemer Process.**—Kelly, an American, invented and patented in 1852 the process of purifying molten pig iron by blowing air through it. Bessemer, an Englishman, patented in 1855 the converter or vessel best adapted to carry out the process. After litigation, the Kelly interest sold out to the Bessemer, and the process now bears the name of the latter.

The converter used is a pear-shaped vessel built of boiler plate and lined with silicious material so mounted on trunions that it may be tipped through a very large angle, and provided with about 250 small holes in the bottom through which air may be blown (see Fig. 45). To start the blow, the converter is turned on its side and ten to fifteen tons of molten pig iron poured in. The air is turned on and the converter straightened up so that the air passes through the molten iron, burning first the silicon to  $\text{SiO}_2$ , then the manganese to  $\text{MnO}$ , and lastly the carbon to  $\text{CO}$ . This burns at the mouth of the converter forming a great flame which gradually dies down and disappears at the end of the blow. The whole process is completed in from six to ten minutes. The heat produced raises the temperature some  $300^\circ$  which is favorable to the success of the operation, because removing the impurities raises the melting-point of the iron. By the time that the carbon is burned out, much of the iron is oxi-

dized to  $\text{FeO}$ . This makes the product brittle and unfit for use. This fault is overcome by adding at the end of the blow such a quantity of spiegeleisen (an alloy of iron, manganese and carbon) as will furnish the manganese and carbon necessary to reduce the ferrous oxide and to bring the manganese, silicon,

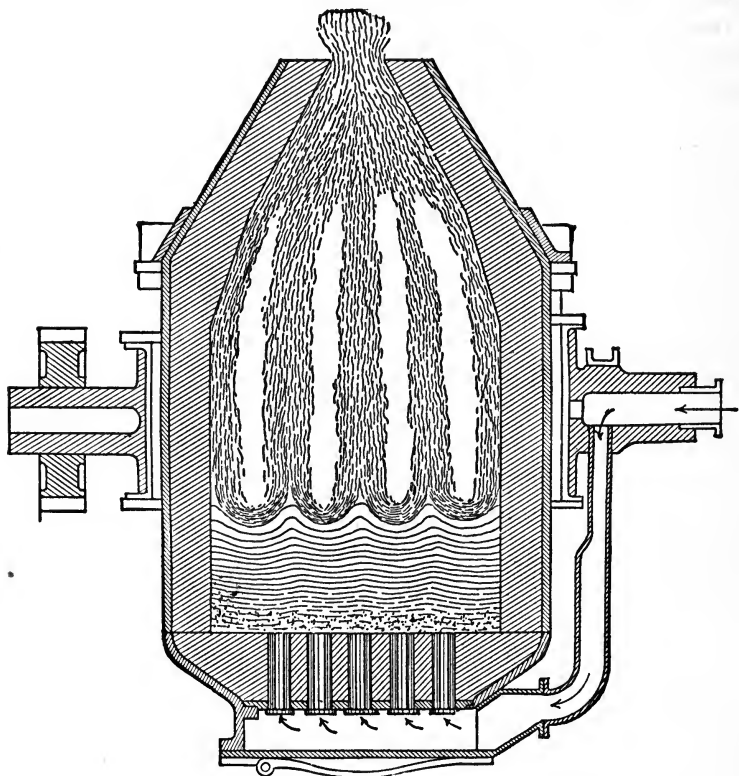


FIG. 45.

and carbon content of the whole mass to that required in the grades of steel desired.

This process using the acid or silicious lining leaves in the steel all the phosphorus and sulfur present in the pig iron. But by using basic linings made of lime or calcined dolomite,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ , and adding lime with the charge, it is possible to remove the phosphorus and a part of the sulfur as calcium or magnesium



steel may be cheaply made from pig iron which contains too much phosphorus for the acid Bessemer converter.

The furnace used (see Fig. 46) is of the type known as regenerative because the air and the producer gas which is used as fuel are preheated by the waste heat of the escaping products of combustion, with the result that the temperature reached is very high. This type of furnace was invented by Siemens Brothers and applied to steel-making by Martin; hence the name Siemens-Martin process.

The materials used are pig iron, soft scrap steel, iron ore and in the basic process, lime. The purification of the pig iron is effected partly by an excess of air in the flame which plays over the charge, but more by the oxidizing action of the iron oxide in the ore. When the oxide is reduced, it of course increases the amount of iron present. The scrap steel is added to dilute the impurities and so hasten the process. The lime makes a very basic slag in the presence of which calcium phosphate and calcium sulfide are formed with the elimination of phosphorus and sulfur. Lime can be used only when the lining is made of calcium and magnesium oxide or the latter alone. The process is much slower than the Bessemer, requiring from six to ten hours, but the capacity of the furnace is large, usually 50 to 75 tons. Because of its slowness the changes can be followed by physical and chemical tests, and hence a more uniform and higher grade product can be produced than by the Bessemer converter. After the purification, the charge is tapped out into a ladle, slag is removed as completely as possible, and the iron recarburized to the desired degree by the addition of ferromanganese, an iron alloy rich in manganese, and anthracite coal or charcoal. It is then cast into ingots and worked up as in the other process.

The acid process is used to make about 1,200,000 tons of the 16,500,000 tons produced in the open hearth. It differs mainly in using a silicious lining and omitting the lime from the charge. The materials used must be very low in phosphorus and sulfur.

**Crucible Steel.**—By melting wrought iron with a proper amount of charcoal or cast iron in large clay or graphite crucibles, a very fine grade of high carbon steel is made which is especially desirable for making tools, knives, springs, and other special uses.

The steel made by this method usually has a carbon content of from 0.75 to 1.50 per cent. and is called crucible steel.

By mixing with the iron and carbon, other metals or alloys, special alloy steels can be made, some of which have very valuable properties.

Electric furnace steel is practically the same as crucible steel. The main difference being that melting is carried out in an electric furnace instead of a crucible, and that larger charges can be worked at a lower cost. Because of the high temperature obtainable in these, they are often used to give Bessemer or open-hearth steel a super-refining which removes phosphorus and sulfur, and greatly improves the quality. The electricity simply serves as a source of heat and there is no electrolysis in the process.

Within recent years, it has been found that the addition of one or more of the following metals to steel will increase its valuable qualities, or impart new ones; nickel, manganese, chromium, vanadium, molybdenum, tungsten, titanium, and silicon; such steels are called alloy steels, and are extensively used. Manganese steel is very tough. Nickel increases the tenacity and elastic limit. Chromium increases the hardness.

**Wrought Iron.**—A third method of purifying pig iron is the puddling process, invented by Henry Cort in 1784 and greatly improved by Joseph Hall in 1830. This consists in melting pig iron in small lots of 500 to 1500 lb. in a reverberatory furnace heated by coal or gas.

The hearth of the furnace is lined with roll scale or other material rich in iron oxide which with the excess oxygen in the furnace gases, serves to oxidize silicon, manganese, carbon, phosphorus and sulfur. The silica, manganous oxide, and phosphorous pentoxide produced, unite with some iron oxide formed by oxidation of iron, making a very basic slag, and effectually removing them from the iron. The melting-point of the iron which is about 1200° in the impure state at the beginning, gradually rises as the impurities are eliminated and finally becomes so high that the pure iron cannot remain liquid at the highest temperature of the furnace. It separates, therefore, as a spongy plastic mass, honey-combed with slag. This is gathered together and worked into balls weighing about 125 lb., which are then

removed from the furnace and passed through a mechanical squeezer to expel slag. The iron is rolled into rough bars, which are cut up, piled together, reheated to welding temperatures, and rolled into bars and other shapes.

The product of the puddling furnace, called wrought iron, is very nearly free from impurities, other than slag, and is the purest commercial iron.

It is very soft and malleable, welds easily, and is characterized by a fibrous structure, which easily distinguishes it from low carbon steel, which is rolled into form from cast ingots nearly free from slag. This structure is due to particles of slag enclosing those of iron and causing the iron particles to stretch separately during the rolling process. The fibrous structure, it is thought, increases the strength of the iron.

**Physical Properties of Iron.**—Pure iron has a density of 7.8, is silvery white, takes a high polish and is very ductile and malleable. It may be welded at a bright red heat and melts at 1550 to 1600°. It exists in three modifications;  $\alpha$  ferrite, magnetic, and stable up to 785°;  $\beta$  ferrite, non-magnetic and stable from 785° to 915°;  $\gamma$  ferrite, non-magnetic and stable when pure from 915° to 1600°, or when saturated with carbon from 725° up. Pure iron is not hardened by heating to a high temperature and sudden cooling but steel is. Iron forms a carbide,  $\text{Fe}_3\text{C}$ , known as cementite. This is soluble in solid  $\gamma$  ferrite to the extent of 2.2 per cent. of carbon at 1145°, and 0.9 per cent. at 725°. It is not soluble in alpha or beta ferrite. If a steel containing between .9 and 2.2 per cent. carbon be heated to 1145° all of the carbon will pass into a solid solution in  $\gamma$  ferrite. If now this be suddenly cooled, it will be hard and all the harder the more carbon it contains, in the form of cementite in solid solution in supercooled  $\gamma$  ferrite. This is glass hard steel and is very brittle. When this is warmed, the cementite separates if the steel contains more than .9 per cent. of carbon. As the cementite in solution decreases, the steel softens. This is called tempering and is controlled either by the temperature to which the steel is heated or by the colors formed on the surface of the steel which are rough measures of the temperature. Tungsten and molybdenum have the property of causing the  $\gamma$  ferrite to remain stable down to



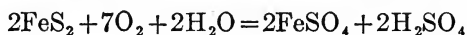
ordinary temperature, and hence the cementite stays in solution and the steel does not soften upon reheating. This is the property upon which the usefulness of tungsten and molybdenum depends in high speed steel tools.

**Chemical Properties of Iron.**—Iron is stable in dry but is attacked by moist air and gradually becomes covered with iron rust,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , which does not protect the underlying metal from further action. Something of a discussion of the mechanism of the rusting of iron will be given at the close of the treatment of this metal. When heated in the air or steam, iron becomes converted into the magnetic oxide,  $\text{Fe}_3\text{O}_4$ , which when formed under certain conditions clings tightly to the surface of the metal and protects it from further oxidation (Baruff's process for the prevention of rust). Dilute hydrochloric or sulfuric acids dissolve iron with the evolution of hydrogen and the formation of ferrous salts: the hydrogen usually contains some hydrocarbons as well as compounds of phosphorus and sulfur and has a disagreeable odor. When the iron dissolves in cold dilute nitric acid, ferrous nitrate and ammonium nitrate are formed; while with somewhat more concentrated acid, ferric nitrate and oxides of nitrogen are produced. When iron is dipped into very concentrated nitric acid, it almost instantly becomes passive, that is passes into a condition in which it is not attacked by nitric acid, dilute or concentrated, and does not precipitate copper from solutions of the latter. In fact, it acts as though it were moved in the potential series to a position near that of platinum. Potassium dichromate, chloric, bromic, iodic acids and other powerful oxidizing agents will also induce the passivity of iron. There is no visible change in the iron. The passivity is destroyed by contact with reducing agents, scratching the surface or even by simply placing the iron in a very strong magnetic field. An entirely consistent and satisfactory explanation of this phenomenon is lacking.

**Ferrous Compounds.**—The ferrous compounds are very much like those of magnesium and especially like manganous salts with the exception that the trivalent compounds of iron are more stable than the divalent either in acid or alkaline solution, while the reverse is true for manganese in acid solution. The ferrous salts even in acid solutions are oxidized in the air to ferric; in

alkaline solutions, the change takes place more readily. When a perfectly pure ferrous salt solution is acted upon by a soluble base in the entire absence of oxygen, a white precipitate of **ferrous hydroxide**,  $\text{Fe}(\text{OH})_2$ , is obtained. On exposure to the air, it becomes first dirty green and finally brown from oxidation to ferric hydroxide. Ferrous hydroxide has about the solubility and strength of magnesium and manganous hydroxides, and hence, like these is soluble in an excess of ammonium salts and for the same reason. It is not soluble in excess of the alkalis or of ammonium hydroxide, but is, of course, in acids. From its solubility in ammonium salts, it follows that it is a strong base and that its salts are but little hydrolyzed, so those of even as weak an acid as carbonic can be easily prepared. Ferrous oxide,  $\text{FeO}$ , corresponding to the hydroxide is most easily made by heating the oxalate in the absence of air. It has a black color.

**Ferrous Sulfate.**—Ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , is the best known and most largely used of the ferrous salts. In its crude form it is often called green vitriol or copperas. It is made on a very large scale by the oxidation of moist pyrite.



The ferrous sulfate and sulfuric acids which are formed are leached out, the acid is allowed to act on scrap iron, and the solution concentrated to crystallization. The hepta hydrate is dimorphous. When left to itself, it separates in monoclinic crystals; but in the presence of crystals of magnesium or zinc sulfates, it takes on the rhombic shape of these substances and forms isomorphous mixtures with them. A pentahydrate isomorphous with copper sulfate, and a tetrahydrate isomorphous with the corresponding manganous sulfate may be obtained. When exposed to the air, it effloresces and also oxidizes with the formation of a yellowish-brown basic ferric salt,  $\text{Fe}(\text{OH})\text{SO}_4$ . It combines with sulfates of the alkali metals and ammonium to form double salts of the type formed by the other vitriols. The ferrous ammonium sulfate,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , is especially important, and is much used in the laboratory since it is the most stable ferrous salt.

The sulfate is used as a deodorant and disinfectant, in the

manufacture of dyes, in tanning, in the making of inks, and in the clarification of water.

**Ferrous Sulfide.**—Ferrous sulfide,  $\text{FeS}$ , is formed by the direct union of the elements. This takes place very readily when the two are heated together. The sulfide has a slight metallic luster. It is readily dissolved by hydrochloric or sulfuric acids with the formation of hydrogen sulfide and the corresponding ferrous salt. The usefulness of hydrogen sulfide as a reagent makes ferrous sulfide important also. It is precipitated by ammonium sulfide as a black powder easily soluble in acids, but is not precipitated by hydrogen sulfide from acid solutions.

**Other Ferrous Compounds.**—Ferrous chloride,  $\text{FeCl}_2$ , is much more soluble than ferrous sulfate, and on this account it is advisable to use hydrochloric acid instead of sulfuric in the generation of hydrogen sulfide, as the apparatus is not so likely to become clogged with crystals of the salt. There is nothing especially noteworthy concerning the bromide and the iodide except that ferrous iodide is the only stable iodide of iron, the ferric salt decomposing into the ferrous and free iodine. Ferrous carbonate occurs in nature as spathic iron ore. As it is obtained in the laboratory, it is partially hydrolyzed and is easily oxidized to the ferric hydroxide. It is more soluble in water containing carbon dioxide in solution than in pure water.

**Ferric Compounds.**—As has been mentioned, the ferric compounds are formed from the ferrous by oxidation. This takes place more readily in alkaline than in acid solutions, but the oxygen of the air is able to bring about the change in either case.

Any ferric salt in solution will be reduced to the ferrous state by the stronger reducing metals such as zinc, magnesium, iron, etc.; or by hydrogen sulfide or stannous chloride. The metals, of course, yield the corresponding cations; hydrogen sulfide gives free sulfur, stannous chloride becomes stannic. Some of these properties are made use of in the quantitative determination of iron, it being reduced to the ferrous state and then titrated with permanganate.

**Ferric Hydroxide.**—Solutions of bases when added to a solution of a ferric salt, produce a brown precipitate of ferric hydroxide,  $\text{Fe}(\text{OH})_3$ . This precipitate is very slimy when formed in the cold, but becomes more compact upon boiling. It has a marked

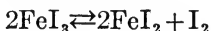
tendency to pass into colloidal solution especially in the presence of ferric chloride. By separating such a solution from pure water by parchment paper, dialysis will take place and the ferric chloride will gradually diffuse into the water leaving a pure solution of colloidal ferric hydroxide. This is called dialyzed iron and has a strong red color. Like other colloides it has practically no effect upon the boiling-point of the water, and is precipitated by many neutral salts. Ferric hydroxide is soluble in acids, but not in excess of dilute alkalies; or in ammonia or ammonium salts. It is a very weak base, and its salts are as highly hydrolyzed as the salts of aluminum; hence, their solutions are decidedly acid. The ferric ion appears to be colorless, but the ferric salt solutions are usually colored, presumably, in most cases, from the hydroxide formed by hydrolysis.

When the hydroxide is dried and heated, it passes into ferric oxide,  $\text{Fe}_2\text{O}_3$ , which in finely divided condition is known as "rouge" and "venetian red," and is used as a polishing material and pigment. Although ferric hydroxide will not dissolve in dilute alkalies it is somewhat soluble in very concentrated solutions of sodium or potassium hydroxides, forming unstable ferrites. The dark colored substance formed during the early stages of the oxidation of ferrous hydroxide is probably a hydrated ferrous ferrite; and magnetic iron oxide,  $\text{Fe}_3\text{O}_4$ , is in all probability the anhydrous compound and should be written  $\text{Fe}(\text{FeO}_2)_2$ . This is a valuable iron ore and remarkable because of its being attracted by magnets. Some specimens act as magnets and are then known as lodestone. Calcium, magnesium, and zinc ferrites of the general formula  $\text{M}(\text{FeO}_2)_2$ , are known. These like the ferrous ferrite are magnetic.

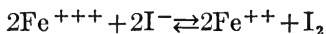
**Ferric Chloride.**—When chlorine is passed over heated iron, anhydrous ferric chloride,  $\text{FeCl}_3$ , sublimes and crystallizes in dark green scales which have a metallic luster and are red by transmitted light. It dissolves in water with the evolution of heat and from the solution, a number of hydrates may be obtained, the most common one is  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . This is most readily prepared, by oxidizing ferrous chloride with chlorine, evaporating the solution until it has the composition of the hexahydrate and allowing it to cool. The hydrate melts at  $37^\circ$  and is very soluble and deliquescent. Solutions of ferric

chloride are considerably hydrolyzed and react strongly acid. The hydrolysis increases with dilution and also with rising temperature as is shown by the deepened color of a hot solution which fades slowly on cooling. When attempts are made to prepare the anhydrous salt by heating the hydrates, decomposition takes place and hydrochloric acid and basic chlorides or even ferric oxide are formed. The chloride is soluble in alcohol and ether as well as in water. It is used in medicine.

**Ferric Bromide and Iodide.**—Ferric bromide is so much like the chloride that nothing in addition need be said about it, but the iodide is of interest because of its reversible decomposition into ferrous iodide and free iodine,

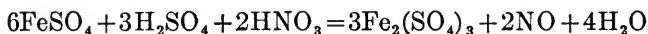


Because of the reversibility, the action is incomplete unless one of the substances is removed, which may be done by boiling the solution. Advantage is sometimes taken of this in the separation of iodine from chlorine and bromine. An excess of a ferric salt is added and the solution boiled until all the iodine is expelled. From the equation given above, it looks as if only one-third would be liberated, but by writing the equation in the ionic form the action may be readily understood,



**Ferric Fluoride.**—Ferric fluoride is noteworthy for the fact that it is practically undissociated and shows neither the reactions of the ferric salts nor of the fluorides. It forms compounds with the alkali fluorides of the type,  $\text{M}_3\text{FeF}_6$ .

**Ferric Sulfate.**—Ferric sulfate,  $\text{Fe}_2(\text{SO}_4)_3$ , may be prepared by adding the proper amount of sulfuric acid to ferrous sulfate in solution and then oxidizing with nitric acid,



and evaporating to dryness. The yellowish-white residue dissolves very slowly in water, but finally forms a fairly concentrated solution. With potassium and ammonium sulfates, it forms alums such as ammonium iron alum,  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . When pure it is almost colorless, but generally has a violet tint due perhaps to the presence of a trace of manganese. The

ammonium alum is often used in the laboratory when a ferric salt of definite composition is wanted. Basic ferric sulfates are known and are used in medicine to stop the flow of blood from wounds.

**Ferric Thiocyanate.**—Ferric thiocyanate,  $\text{Fe}(\text{CNS})_3$ , is a slightly dissociated salt which is formed by the interaction of a ferric salt and a soluble thiocyanate. It has a most intense blood red color which is visible even at high dilutions. The appearance of this color upon the addition of potassium thiocyanate is a very delicate test for ferric iron. Pure ferrous compounds give no color.

**Ferric Sulfide.**—Ferric sulfide,  $\text{Fe}_2\text{S}_3$ , is thrown down as a black precipitate when a ferric salt is added to an excess of ammonium sulfide, but when the ferric salt is in excess, reduction takes place with the formation of ferrous sulfide and sulfur. Ferric sulfide is also formed by the direct union of the elements.

**Pyrite.**—Pyrite or "Fool's gold,"  $\text{FeS}_2$ , is the most stable of the sulfides of iron at ordinary temperatures. It is found in very large quantities in nature and is an important source of the sulfur for sulfuric acid. It occurs in golden colored crystals which appear in a great variety of forms belonging to the regular system, cubes and octahedrons being common. It is not dissolved by dilute acids but is slowly changed by concentrated hydrochloric acid into ferrous chloride, hydrogen sulfide and sulfur. It is easily soluble in nitric acid with the liberation of sulfur.

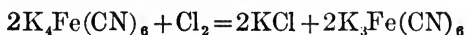
**Ferric Acetate.**—When a soluble acetate is added to a ferric salt in solution, a dark red coloration is produced owing partly to increased hydrolysis and partly to the formation of undissociated ferric acetate. When this solution is heated to boiling, all of the iron is precipitated as a basic ferric acetate and so may be removed from a slightly acid solution. This is analytically important, for use is made of it in the separation of iron from some other metals. If the solution be allowed to cool in contact with the basic acetate, the latter slowly passes back into solution and the red color is restored. The explanation for the precipitation is found in the increase in hydrolysis at high temperatures due to the greater dissociation of water.

**Ferric Phosphate.**—Ferric phosphate,  $\text{FePO}_4$ , is so slightly

soluble that it is precipitated upon the addition of sodium phosphate to a ferric solution even in the presence of acetic acid in which most phosphates are soluble. Advantage is sometimes taken of this property to remove phosphoric acid from solutions. It is a white slimy precipitate soluble in strong acids.

**Cyanogen Compounds.**—When potassium cyanide is added to a ferrous solution a yellow precipitate is formed which is ferrous cyanide. It dissolves in an excess of potassium cyanide, forming the typical complex salt, potassium ferrocyanide or yellow prussiate of potash,  $K_4Fe(CN)_6$ . This is easily soluble in water and the solution shows the properties of other potassium salts, but not those of either the ferrous salts or the cyanides; on the contrary, it has an entirely different set of properties. The salt for example is nothing like as poisonous as potassium cyanide. This is expressed by saying that it dissociates into potassium as ion and the complex ferrocyanogen ion,  $Fe(CN)_6^{--}$ . This ferrocyanogen ion is formed whenever the ferrous ion is boiled with the cyanogen in alkaline solution. The greater part of the ferrocyanides of commerce are obtained as by-products in the manufacture of coal gas, which contains small quantities of hydrocyanic acid and other cyanogen compounds. These are absorbed in sodium or potassium hydroxides, to which a ferrous salt has been added and the resulting ferrocyanide is purified by crystallization. The potassium salt has the composition,  $K_4Fe(CN)_6 \cdot 3H_2O$ , and the sodium,  $Na_4Fe(CN)_6 \cdot 10H_2O$ . Many of the ferrocyanides are insoluble and may be prepared by precipitation. Ferric ferrocyanide,  $Fe_4(Fe(CN)_6)_3$ , has a dark blue color and is known as "Prussian blue." The formation of this dark blue precipitate is a very delicate test for ferric iron and it is indeed remarkable that a solution containing iron can be used as a reagent for iron. When potassium ferrocyanide is added to a ferrous salt solution in the absence of oxygen, a white precipitate having the composition,  $K_2FeFe(CN)_6$ , is formed which quickly oxidizes and becomes blue.

**Ferricyanides.**—Ferricyanides may be easily formed from the ferrocyanides by the action of oxidizing agents. The potassium salt,  $K_3Fe(CN)_6$ , for example is made by passing chlorine through a solution of potassium ferrocyanide,



It crystallizes in dark red prisms and is known as "red prussiate of potash." It is the potassium salt of the complex ferricyanogen ion,  $\text{Fe}(\text{CN})_6^{--}$ , which differs from the ferrocyanogen in that it carries one less — charge. Sodium ferricyanide is prepared in the same way as the potassium salt; most of the others are made by precipitation. The free acid is unstable. Ferricyanides are powerful oxidizing agents and in alkaline solution will oxidize ferrous hydroxide to ferric, divalent lead and manganese to the tetravalent state, the ferricyanogen being reduced in all cases to ferrocyanogen. Ferric salts do not give any precipitate with ferricyanides, but the solution becomes somewhat dark brown. Ferrous salts, however, react and produce a dark blue precipitate of Turnbull's blue which is very similar to Prussian blue. From its mode of formation, it should be ferrous ferricyanide,  $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$ ; but some consider it identical with Prussian blue and think that the ferricyanogen ion oxidizes the ferrous ion to the ferric, and is itself reduced to the ferrocyanogen before they combine. This change certainly takes place in alkaline solution and may in acid.

When solutions of potassium ferricyanide and ammonium ferric citrate are mixed, a yellowish-brown liquid results. If this be spread over paper and the latter dried in the dark, sensitized blue print paper results. When it is exposed to sunlight under a tracing or negative, it turns blue wherever the light strikes the paper, from the formation of insoluble blue compounds like Prussian blue. This may be due to the reduction of the ferric salt to the ferrous or of the ferricyanogen ion to the ferrocyanogen and then their interaction. After the printing, the picture is "fixed" by washing in water which dissolves the unchanged mixture, leaving white lines on a blue ground.

**The Oxalates.**—Ferrous oxalate,  $\text{FeC}_2\text{O}_4$ , is precipitated as a yellow salt by the addition of oxalic acid to a ferrous solution. It is soluble in potassium oxalate owing to the formation of the complex salt,  $\text{K}_2\text{Fe}(\text{C}_2\text{O}_4)_2$ , which has a yellowish-red color not unlike that of many ferric salts. Ferric oxalate, unlike other ferric salts, has a green color remotely like that of the ferrous salts. It forms a stable complex salt with potassium oxalate,  $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ , which also has a green color and gives the complex ion  $\text{Fe}(\text{C}_2\text{O}_4)_3^{--}$ . The usefulness of oxalic acid and of



acid potassium oxalate in removing rust and ink spots from fabrics is due to the formation of this complex ion. Solutions of ferric oxalate and of its complex compounds are very sensitive to the light and are quickly reduced to ferrous oxalate with the evolution of carbon dioxide.

**Ferrates.**—When ferric hydroxide is suspended in potassium hydroxide solution and chlorine passed in, a red solution of potassium ferrate,  $K_2FeO_4$ , is formed. This may be obtained as crystals isomorphous with potassium sulfate and chromate. It is very unstable. Other salts have been prepared by precipitation.

**The Corrosion of Iron.**—It is of course well known to everyone that iron when exposed to air and water will gradually be converted into partially dehydrated ferric hydroxide which is called iron rust. The importance of an understanding of the conditions which influence this change is obvious, owing to the almost universal use of iron in our modern structures. There is a good deal of dispute concerning many of the facts in connection with this and still more as to their interpretation, but the following observations are generally accepted as facts: First, iron will be rapidly dissolved and corroded by practically all dilute acids including carbonic, solutions of ferrous salts and hydrogen gas being the usual products; Second, iron will slowly dissolve in pure water even in the absence of oxygen or carbon dioxide. The action is not very extensive, but hydrogen gas is evolved and the solution becomes distinctly alkaline from the ferrous hydroxide which is dissolved. In the entire absence of air, the solution of ferrous hydroxide formed by the action of distilled water upon iron will remain clear; but if air be passed through it, the whole solution will take on the color of iron rust and will deposit it; Third, that the corrosion of iron will be greatly increased by the presence of oxygen; Fourth, that the iron is more readily attacked the more impure and non-homogeneous it is; Fifth, that in alkaline solution the corrosion is greatly hindered or suppressed; Sixth, that in certain strong oxidizing agents, such as concentrated nitric acid, dichromates, and red lead, the iron becomes "passive" and will retain this condition for some time after the removal of the oxidizing agent.

The most consistent interpretation of these facts seems to be

the following: That the oxidation of the iron takes place in two stages; first, to the ferrous and then to the ferric condition; That the oxidizing agent which dissolves the iron to the ferrous state is hydrogen as ion either from acids or from water, and that the oxidation to the ferric is brought about by the oxygen of the air. Since an oxidizing agent is the more active the more concentrated it is, the more rapid solution in acids than in water is readily understood as being due to the smaller concentration of the ionized hydrogen in the latter. The protective action of alkaline solutions may be ascribed to the concentration of the hydrogen as ion having been so far reduced by the increase in the concentration of the hydroxyl that it is not a strong enough agent to oxidize the iron, and so the first stage of the rusting cannot take place.

If the iron is non-homogeneous, voltaic couples will be set up at various points on the surface and local electrolytic action will result. Hydrogen gas will be deposited at those points where the metal for any cause is acting as cathode, and since this hydrogen has a tendency to pass back into solution as ion, the local cells will be polarized and the action hindered. If oxygen is present, it will act as a depolarizer and hence increase the rate of electrolytic corrosion, and then in addition will oxidize the ferrous ion so produced to the ferric, and so complete the rusting process. There seems to be no satisfactory explanation for the passivity of iron.

**Analytical Properties of Iron.**—Because of the precipitation of ferric hydroxide by ammonium hydroxide in the presence of ammonium salts, iron is placed in an analytical group with aluminium and chromium. Ferrous salts give a deep blue with ferricyanides, while ferric compounds give the same color with ferrocyanides and also a blood red with thiocyanates. With the borax bead, iron compounds give green colorations in the reducing flame and a faint yellow or brown in the oxidizing flame.

#### COBALT

Cobalt has a slightly higher combining weight than nickel, but it is more closely related to iron than nickel is, so it is usually placed ahead of the latter in the periodic system. The

compounds of cobalt have been known and used, for centuries, for coloring glass blue, but the metal was first prepared in 1735 by Brandt. Cobalt occurs in nature in rather small quantities chiefly as smaltite,  $\text{CoAs}_2$ , and cobaltite,  $\text{CoAsS}$ , and is commonly associated with iron, nickel, and manganese. It is almost always a constituent of meteoric iron and is present in the sun as indicated by the spectrum. The metal may be obtained by the reduction of the oxide at a high temperature with carbon or hydrogen, by the Goldschmidt process, or by the electrolysis of a solution of the sulfate. It is magnetic and has the color of polished iron becoming pink on exposure to the air, has a density of 8.8 and melts at  $1530^\circ$ . It slowly oxidizes when heated and burns at a high temperature. It is attacked by dilute acids, but tends to become passive as iron does. Cobalt forms two series of compounds corresponding to ferrous and ferric. The simple cobaltous compounds are more stable than the simple cobaltic, but the case is the other way around with the complex compounds.

**Cobaltous Compounds.**—When sodium hydroxide is added to a cobaltous solution, a blue precipitate of basic salt is formed which on standing becomes pink and is changed to the **hydroxide**,  $\text{Co}(\text{OH})_2$ . This like the corresponding ferrous, manganous, and magnesium compounds is soluble in ammonium salts. In addition, it is soluble in ammonium hydroxide presumably because of the formation of complex ammonia ions. The ammoniacal solution absorbs oxygen, and a series of complex cobaltic ammonia salts are formed which will be treated briefly a little later. When heated, cobaltous hydroxide gives the oxide,  $\text{CoO}$ . The cobaltous salts in dilute solution have a red color and so do most of the fully hydrated solid salts, but the partially or completely dehydrated compounds are generally blue and often the hot concentrated solutions have the same color, particularly in the presence of large amounts of hydrochloric acid, sodium chloride, or glycerin. **Cobalt chloride**,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , is especially sensitive in this respect. One may prepare a dilute solution of cobalt chloride and write with it upon paper; after drying, the delicate pink of the salt is scarcely visible, but when heated it loses water and the characters become distinctly traced in the blue of the less hydrated salt. Upon standing in the air at ordinary temperatures,

the salt takes up water once more and the writing disappears. This is the basis of the so-called "sympathetic ink."

**Cobalt Sulfate.**—Cobalt sulfate,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , is isomorphous with magnesium sulfate and forms double sulfates with ammonium and potassium sulfates,  $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , which are isomorphous with the other double sulfates of the same type.

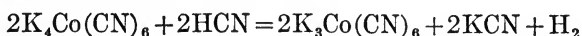
**Cobalt Nitrate.**—The nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , is perhaps the most used cobalt salt, being employed in blowpipe analysis and in making other cobalt preparations.

**Cobalt Sulfide.**—Cobalt sulfide,  $\text{CoS}$ , is black and is precipitated by ammonium sulfide. It is peculiar in that it is not precipitated by hydrogen sulfide in acid solutions, except in the presence of a large amount of sodium acetate; but after the precipitate has once been obtained it is scarcely appreciably dissolved by cold dilute acids. It probably forms a much more stable modification soon after precipitation.

**Cobalt Glass.**—Compounds of cobalt color the borax bead a beautiful blue and impart to fused silicates the same color. Smalt is a kind of glass which is made by fusing together sand, crude cobalt oxides and potassium carbonate. When ground very fine it is used as a pigment and for coloring glass and porcelain blue. When aluminum oxide or a salt of aluminum is heated with cobalt oxide or one of the cobalt salts, a blue compound is produced which is used as a paint. In making enameled iron ware, the first coat is usually a sort of cobalt glass as this seems to stick better than other mixtures.

**Cobaltic Compounds.**—Cobaltic hydroxide,  $\text{Co}(\text{OH})_3$ , is formed when a hypochlorite is added to a cobaltous salt. It is brownish-black and is soluble in cold hydrochloric acid, but the solution quickly decomposes with the evolution of chlorine and the formation of cobaltous chloride. The corresponding oxide,  $\text{Co}_2\text{O}_3$ , may be prepared by gently heating the nitrate; when more strongly heated it goes to the oxide,  $\text{Co}_3\text{O}_4$ . A cold acid solution of cobaltous sulfate may be oxidized at the anode of an electrolytic cell to cobaltic sulfate,  $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ . The crystals are blue and give in dilute sulfuric acid a greenish-blue solution which rapidly decomposes with the evolution of oxygen. Ammonium, potassium, rubidium or cesium sulfates form alums with this sulfate.

**Complex Compounds.**—When potassium cyanide is added to a cobaltous solution, a precipitate of cobalt cyanide is formed,  $\text{Co}(\text{CN})_2$ , which dissolves in excess of potassium cyanide with the formation of potassium cobaltocyanide,  $\text{K}_4\text{Co}(\text{CN})_6$ , analogous to potassium ferrocyanide. This is a very powerful reducing agent and in acid solutions will take up oxygen from the air or when boiled will liberate hydrogen gas and rapidly pass into potassium cobalticyanide  $\text{K}_3\text{Co}(\text{CN})_6$ ;



The complex ion so formed is very stable and does not give the reactions of the  $\text{Co}^{+++}$  ion. The corresponding acid is also very stable. Reference to the behavior of nickel under similar conditions will show differences upon which a method for the separation of these two elements may be based.

When acetic acid and a nitrite are added to a cobaltous salt, the latter is first oxidized to the cobaltic state and then the cobaltic ion combines with the nitrite to make the complex ion,  $\text{Co}(\text{NO}_2)_6^{---}$ . This yields very difficultly soluble compounds with potassium and ammonium ions, and in the form of a solution of the sodium salt, it is much used as a reagent for potassium. Since nickel does not form any corresponding compound, this furnishes a means for the separation of the two elements.

When cobaltous hydroxide is dissolved in ammonia and the solution exposed to the air or to the action of oxidizing agents, cobaltic ammonia compounds are formed. These act as though they were compounds of the complex cation  $\text{Co}(\text{NH}_3)_n^{+++}$ , in which  $n$  is 3, 4, 5, or 6, with three combining weights of a monovalent anion so that the general formula of the compounds might be written,  $\text{Co}(\text{NH}_3)_n\text{A}_3$ , in which A represents any monovalent anion. The following rules will give a slight idea of the behavior of these compounds. When " $n$ " is 6, all three combining weights of A are easily and equally ionizable. When " $n$ " is 5, two combining weights of A are easily ionizable while the third is far less so. When " $n$ " is 4 one combining weight of A is easily ionizable and the other two are but slightly so. When " $n$ " is three the substance is practically undissociated. These compounds may contain a mixture of anions in the same salt, and the ammonia may be replaced wholly or in part by water or a large number

of organic compounds. These things make the chemistry of these salts so complex that several hundred of the compounds are known.

## NICKEL

Nickel was discovered in Europe in 1751 by Cronstedt, but an alloy of copper, nickel, and zinc has been used for centuries by the Chinese in their coinage. It occurs associated with cobalt, iron, manganese, etc., in nicollite, NiAs, nickel glance, NiAsS, and genthite,  $Mg_2Ni_2H_4(SiO_4)_3 \cdot 4H_2O$ . The chief source of the mineral is Ontario, and New Caledonia. Nickel is more abundant than cobalt and hence is cheaper and has more applications. The commercial extraction of nickel from its ores is a very complex process and will not be described here, but something will be said of one method in connection with nickel carbonyl.

**Properties.**—Nickel is a silvery white metal with a tinge of yellow. It takes a high polish and is hard but malleable and may be rolled into thin sheets or drawn into fine wire. The pure metal melts at  $1484^\circ$  and has a density of 8.9. It is magnetic. Nickel is a component of a number of important alloys; German silver contains approximately 60 per cent. copper, 25 per cent. zinc, and 15 per cent. nickel, but the composition varies widely. Nickel coins usually contain 75 per cent. copper, and 25 per cent. nickel. Nickel steel has very valuable properties because of its increased strength and toughness. A steel containing about 36 per cent. of nickel has a very small temperature coefficient and is known as "invar." It is used in making standard meters because their length will vary but slightly with the temperature. Another nickel iron alloy containing 42 per cent. nickel has the same coefficient of expansion as glass and is used in making the so-called wire glass and in sealing the wires into electric light bulbs, thus taking the place of the precious metal platinum for this latter purpose. It is called "platinite." Monel metal is a nickel-copper alloy obtained by the direct smelting of the nickel copper ores mined at Sudbury, Ontario. It can be cheaply produced and has the very valuable properties of corroding less easily than brass or bronze and of being nearly as strong as steel. Nickel may be readily deposited electrolytically from a solution of the

double sulfate with ammonia,  $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , using anodes of cast nickel containing some carbon because they dissolve more readily than the pure metal. Iron or steel articles are first coated with copper and then with nickel. Nickel plate takes a high polish and protects the iron effectually from rust. Nickel does not rust in the air and is but slowly attacked by steam even at a red heat. It is slowly dissolved by dilute acids with the exception of nitric which acts upon it rapidly. Concentrated nitric acid, however, renders it passive.

**Nickel Compounds.**—Nickel forms only one series of salts which correspond to the ferrous and cobaltous salts. These may be considered to be derived from the oxide,  $\text{NiO}$ , or the hydroxide,  $\text{Ni}(\text{OH})_2$ , both of which are well-known. In addition there is a well defined oxide,  $\text{Ni}_2\text{O}_3$ , and a hydroxide,  $\text{Ni}(\text{OH})_3$ , corresponding to ferric oxide and hydroxide and also an oxide  $\text{Ni}_3\text{O}_4$ , analogous to magnetite, but no salts of these are known. The nickel salts both in the crystalline form and in solution are usually green.

**Oxides and Hydroxides.**—Nickelous hydroxide,  $\text{Ni}(\text{OH})_2$ , is an apple green precipitate which is formed upon the addition of a soluble base to a nickel salt solution. When heated, it readily decomposes into water and the oxide,  $\text{NiO}$ . The hydroxide is not soluble in an excess of sodium or potassium hydroxide, but does dissolve in ammonium hydroxide and the solution has a strong blue color not unlike that of copper ammonia solution. This is due to the formation of nickel ammonia ions which probably have the composition,  $\text{Ni}(\text{NH}_3)_4^{++}$ , and  $\text{Ni}(\text{NH}_3)_6^{++}$ . The hydroxide is also soluble in ammonium salts. Nickelic oxide,  $\text{Ni}_2\text{O}_3$ , may be obtained by carefully heating the nitrate. When this or any of the other compounds of nickel is heated in oxygen, the oxide  $\text{Ni}_3\text{O}_4$  is formed. Nickelic hydroxide,  $\text{Ni}(\text{OH})_3$ , is a black precipitate which is formed by the action of a hypochlorite on any nickel salt in solution. When nickelic hydroxide or any of the oxides, higher than the monoxide, is dissolved in hydrochloric acid, chlorine is evolved and nickelous chloride,  $\text{NiCl}_2$ , is formed.

**Edison Storage Cell.**—The Edison storage battery is a reversible, electrical cell in which the oxidizing agent is nickelic hydroxide,  $\text{Ni}(\text{OH})_3$ ; the reducing agent finely divided iron and

the electrolyte 21 per cent. potassium hydroxide. While it is discharging, the nickel is reduced to the divalent state, and the iron oxidized to the ferrous. On charge the nickel is oxidized to the nickelic, and the ferrous reduced to the metallic state, thus restoring the cell to its original condition. Its electromotive force is lower and its internal resistance higher than the corresponding magnitudes for the lead storage cell, so it is less efficient, but it is lighter and more durable than the latter.

**Salts.**—Anhydrous nickel chloride is brown, but the hexahydrate,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , is green like most of the nickel salts. The sulfate usually crystallizes as a hexahydrate,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , but it may be obtained as heptahydrate isomorphous with magnesium sulfate. The double sulfate with ammonium sulfate, mentioned in connection with nickel plating, is isomorphous with the other double sulfates of this same type. It is manufactured on a large scale and is one of the important salts of nickel. Nickel cyanide,  $\text{Ni}(\text{CN})_2$ , is a green precipitate which is thrown down by potassium cyanide from a nickel salt solution. It is soluble in an excess of the potassium cyanide forming the complex salt,  $\text{K}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ . This is not analogous to ferro- and cobaltocyanides and is much less stable, so much so that hypochlorite will precipitate from it the black nickelic hydroxide. It is not oxidized to anything which corresponds to the ferri- or cobalticyanides; and since the cobalticyanide is not affected by hypochlorites, this furnished the basis of one of the methods for the separation of the two elements. Nickel does not form a salt corresponding to potassium cobaltinitrite, and this may also be taken advantage of for the separation of nickel and cobalt. These reactions, together with the fact that nickel salts color the borax bead brown while cobalt compounds give a very intense blue enable the two elements to be recognized and separated. That they are not entirely satisfactory is indicated by the fact that a great many other tests have been devised and used. Nickel sulfide,  $\text{NiS}$ , is formed under the same conditions as that of cobalt and has the same solubility.

**Nickel Carbonyl.**—Nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , is formed below  $80^\circ$  by the action of carbon monoxide upon finely divided nickel. It is a colorless liquid which boils at  $43^\circ$ . Its vapor decomposes explosively at  $60^\circ$ . When diluted with carbon monoxide



it decomposes gradually and its decomposition is not complete below 180°. Cobalt does not form any similar compound. A process based upon this property of nickel has been used for its extraction from the ores. One difficulty in its application is that the carbon monoxide is partially decomposed with the deposition of carbon and the formation of the dioxide.

## THE PLATINUM METALS

The remaining members of Group VIII, the ruthenium and platinum sub-groups may conveniently be considered together under the heading of the platinum metals. These metals are found associated in the native platinum ores which are obtained by placer mining or dredging, chiefly in the Ural Mountains, although Columbia furnishes a small per cent. of the world's output. They are also found in certain copper ores and in the nickel copper ores of Sudbury, Ontario. In the following table these metals are arranged as they are in the periodic system and under each is given some of its more prominent properties and the formulas of a few typical compounds.

	<i>Ruthenium</i>	<i>Rhodium</i>	<i>Palladium</i>
Density	12.0	12.1	11.5
Melt.-point	2000.0°	2000°	1541°
Oxides	RuO Ru <sub>2</sub> O <sub>3</sub> RuO <sub>2</sub> RuO <sub>4</sub> (volatile liquid)	RhO Rh <sub>2</sub> O <sub>3</sub> RhO <sub>2</sub> —————	PdO ————— PdO <sub>2</sub> —————
Salts	RuCl <sub>2</sub> RuCl <sub>3</sub> , K <sub>2</sub> RuCl <sub>5</sub> ————— RuCl <sub>4</sub> , K <sub>2</sub> RuCl <sub>6</sub>  K <sub>2</sub> RuO <sub>4</sub> , KRuO <sub>4</sub>	————— RhCl <sub>3</sub> , Rh <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ————— —————	PdCl <sub>2</sub> ————— ————— PdCl <sub>4</sub> , K <sub>2</sub> PdCl <sub>6</sub> —————
	<i>Osmium</i>	<i>Iridium</i>	<i>Platinum</i>
Density	22.5	22.4	21.4
Melt.-point	2500°	2200°	1753°

Oxides	OsO	—————	PtO
	Os <sub>2</sub> O <sub>3</sub>	Ir <sub>2</sub> O <sub>3</sub>	—————
	OsO <sub>2</sub>	IrO <sub>2</sub>	PtO <sub>2</sub>
	OsO <sub>4</sub> (vol. liq.)	—————	—————
Salts	OsCl <sub>2</sub>	IrCl <sub>2</sub>	PtCl <sub>2</sub> , K <sub>2</sub> PtCl <sub>4</sub>
	OsCl <sub>3</sub> , K <sub>3</sub> OsCl <sub>6</sub>	IrCl <sub>3</sub> , K <sub>3</sub> IrCl <sub>6</sub>	—————
	—————	Ir <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (alums)	—————
	OsCl <sub>4</sub> , K <sub>2</sub> OsCl <sub>6</sub>	IrCl <sub>4</sub> , K <sub>2</sub> IrCl <sub>6</sub>	PtCl <sub>4</sub> , K <sub>2</sub> PtCl <sub>6</sub>
	K <sub>2</sub> OsO <sub>4</sub>		

An inspection of this table will show strong resemblances between the elements in each horizontal row and vertical column. All these elements form complex compounds with ammonia which are so numerous and varied that larger works must be consulted for their discussion.

Ruthenium and osmium are iron gray metals which are not dissolved by any single acid, and are but very slowly attacked even by aqua regia. They are dissolved by fusion with alkalis and nitrates. When finely divided and heated in oxygen they form the tetraoxide and volatilize. Osmium tetraoxide is not the anhydride of any acid, but is called osmic acid. It is used for staining and hardening histological specimens. It has a very disagreeable odor and is exceedingly irritating to the mucous membrane owing to its reduction to metallic osmium. The formation of osmates and ruthenates establishes a connection with iron and manganese.

Rhodium and iridium are white metals which are not attacked by aqua regia. They will form very hard, chemically resistant alloys with platinum. Iridium especially is used for this purpose.

Palladium and platinum are white metals. Platinum dissolves in aqua regia and palladium even in nitric acid, and is the only metal in the two sub-groups which will do so. Both platinum and palladium are remarkable for their ability to absorb gases, especially hydrogen, of which palladium will take up as much as 1000 times its volume. The hydrogen and the palladium form a solid solution which has greater volume than the metal. The hydrogen in this solution will readily reduce silver and copper to the metals, and ferric salts to ferrous as would be expected from the position of hydrogen in the potential series.

which, of course, is not materially altered by its solution in palladium.

**Platinum.**—Platinum is by far the most important member of this group. Not only is it indispensable to the chemist, but it also touches our daily life in many ways, especially in our electrical appliances. It is almost the only metal which has the proper coefficient of expansion, melting-point, and chemical resistivity to enable it to be fused through glass. This comes into play in many ways, particularly in the making of incandescent electric bulbs. It is used in the form of wire, foil, crucibles, and dishes in the laboratory, and it is hard to conceive of what we should do without it.

Platinum ware must be handled with care because it is ruined by contact when hot with easily fusible metals, alkalies, phosphorous, carbon, and silicon. The carbonates of the alkalies may be heated in it without danger. Aqua regia or anything which will evolve chlorine should not be allowed in contact with platinum.

As has been noticed many times on the preceding pages, platinum is very active as a catalytic agent, especially for reactions between gases. Advantage is taken of this on a large scale for the production of sulfuric acid by the contact process. The reactions take place on the surface of the metal and naturally go on all the more rapidly in the aggregate, the greater the surface exposed. For this reason the very finely divided black form of the metal which is obtained by the electrolysis of its chloride in solution, or by the reduction of the solution with a powerful reducing agent, is especially active and will cause the instantaneous explosion of a mixture of oxygen and hydrogen. The metal may be obtained in a spongy condition with large surface and high activity by gently heating ammonium chloroplatinate,  $(\text{NH}_4)_2\text{PtCl}_6$ , which decomposes and leaves spongy platinum. By heating this platinum sponge to whiteness and then hammering, it may be converted into compact metal, for at this temperature platinum welds very easily.

**Platinum Compounds.**—As may be seen from the table, platinum forms two series of compounds. In the platinous it is di- and in the platonic tetravalent. The platinous compounds are generally formed from the platonic by reduction.

**Platinous Hydroxide.**—Platinous hydroxide,  $\text{Pt}(\text{OH})_2$ , is a black precipitate which is soluble in acids but not in bases. With hydrochloric acid it forms chloroplatinous acid,  $\text{H}_2\text{PtCl}_4$ , whose potassium salt,  $\text{K}_2\text{PtCl}_4$ , potassium chloroplatinite is used in making platinum photographic prints. Similar compounds are well known in which chlorine is replaced by cyanogen. These are called platinocyanides. The barium platinocyanide,  $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ , is very fluorescent and shines under the influence of ultra-violet light and X-rays. Advantage is taken of this in making screens for X-ray work.

When platinum dissolves in aqua regia it forms **chloroplatinic acid**,  $\text{H}_2\text{PtCl}_6$ , which gives sparingly soluble chloroplatinates with potassium and ammonium salts,  $\text{K}_2\text{PtCl}_6$ , and  $(\text{NH}_4)_2\text{PtCl}_6$ . These form yellow precipitates which consist of small octahedrons and are very characteristic for platinum. When heated they decompose and leave spongy platinum and potassium chloride from  $\text{K}_2\text{PtCl}_6$ , or simply platinum from the ammonium salt. When silver salts are added to solutions of the chloroplatinates, precipitates of  $\text{Ag}_2\text{PtCl}_6$ , are formed and not  $\text{AgCl}$ , which shows that the chloroplatinate ion is a stable complex ion. By heating chloroplatinic acid in a stream of chlorine, platinum chloride,  $\text{PtCl}_4$ , is formed. When dissolved in water this gives  $\text{H}_2\text{PtCl}_4\text{O}$ .

**Platinic Hydroxide.**—Platinic hydroxide,  $\text{Pt}(\text{OH})_4$ , is formed by the addition of bases to chloroplatinate solutions. It is soluble both in acids and bases. Complex platinates are formed by the action of bases upon the hydroxide. The potassium salt may be represented by the formula,  $\text{K}_2\text{Pt}(\text{OH})_6$ , and is considered analogous to the chloroplatinates.

**Analytical Properties of Platinum.**— $\text{PtS}$ , and platinic sulfide,  $\text{PtS}_2$ , are precipitated by hydrogen sulfide from the respective salts. They are not soluble in dilute acids but dissolve in yellow ammonium sulfide, forming thioplatinates. Platinum compounds are slowly reduced to the metal by ferrous salts but not by oxalic acid. This latter property is a distinction from gold.

## CHAPTER XXXI

### RADIOACTIVITY

In discussing radium, thorium, and uranium, mention was made that these substances are radioactive; and by this is meant that they spontaneously give out heat and other forms of energy which are able to affect a photographic plate; to cause certain substances to fluoresce; and to render the air in their neighborhood a conductor of electricity. These other forms of energy, for lack of a better name, are called rays; and from this comes the term radioactivity. Three different kinds of these rays are distinguished; the alpha, beta, and gamma rays.

The alpha rays are responsible for most of the ionization of the air produced by radioactive substances; they can penetrate the air only a few centimeters and are easily stopped by paper. They are connected with the development of the greater part of the heat evolved by such substances. When uninfluenced by external forces they move in straight lines; but under the influence of an electrostatic or a magnetic field, they are slightly bent out of their path and act as though they consisted of a stream of rapidly moving small particles charged with positive electricity. Calculations based upon the bending of the path of the rays in these two fields indicate that 2 gm. of the rays would carry 96,500 coulombs and that they move with one-tenth the velocity of light. These rays are supposed by many to be atoms of helium carrying two positive charges of electricity.

The beta rays are more penetrating than the alpha rays and pass readily through paper and even through thin sheets of metal. They are especially active toward a photographic plate. Like the alpha rays they move in a straight line, unless influenced by a magnetic or electrostatic field when they are deflected in the opposite direction from that in which the alphas are turned and much more strongly. They act like negatively charged particles, and calculations based upon this assumption indicate that 1 gm. of beta rays would carry  $800 \times 96,500$  coulombs and move about

one-third as fast as light. These rays appear to be identical with the cathode rays of a high vacuum tube. The very small particles which are supposed to constitute these rays are called electrons, and it was formerly thought by some that the atoms of different elements were made up of about 800 times as many of these electrons as there were units in the atomic weight. This view seems now to have been generally abandoned.

The gamma rays are very penetrating and will pass readily through things which will stop the other forms of radiations. They are produced in much smaller amounts than the other rays. They are not deflected by magnetic or electrostatic fields and seem to be identical with X-rays. They are probably produced by the impact of the beta rays.

Certain experiments have been performed with the  $\alpha$ -rays which furnish the strongest evidence yet brought forward that particles of about the supposed size of the atoms exist. These experiments may be outlined as follows: A source of  $\alpha$ -rays is placed at some distance from and in line with a brass tube. In the axis of the tube and insulated from it is a wire connected with an electrometer. There is a high difference of potential between the tube and the wire. As the  $\alpha$ -rays enter the tube, they render the air within a conductor and the needle of the electrometer moves. If the radioactive substance is far enough from the tube, the movement of the electrometer is intermittent and the jumps come at intervals of a few seconds. This shows that the stream of  $\alpha$ -particles is not continuous, or the movement would have been steady. By counting the jumps it is possible to determine the number of particles entering the tube in unit time. If now an insulated plate of metal the size of the opening in the tube be placed at the mouth of the latter, it will absorb the  $\alpha$ -rays and take up the charge of electricity that they carry. By determining the charge acquired in unit time, the charge on one particle can be calculated, and from this, assuming that the  $\alpha$ -particles are helium atoms, since 4 gm. of  $\alpha$ -particles carry  $2 \times 96,500$  coulombs, the number of particles in a gram mole of helium and the mass of a single molecule may be calculated. The results are that a gram mole contains  $6.2 \times 10^{23}$  molecules, and a molecule or atom, for they are identical in helium, weighs  $6.4 \times 10^{-24}$  gm.

A great mass of hypothesis and theory has been woven around the facts of radioactivity until, at the present time, it is not always easy to tell what is fact and what is fancy. But the following facts seem to be established beyond a doubt. First, that the radioactive substances, uranium, thorium, and radium are as truly elements for all chemical purposes as any others of our elements. Second, that these elements are continually and spontaneously undergoing transformations with a decrease in energy which appears in the form of heat and the various rays. One gram of radium gives out 118 gm. calories of heat per hour. Third, that in the case of radium, one of the products of the transformation is a gaseous substance, called radium emanations or niton and that it is an element of the argon group of inert gases, since it is unattacked by any chemical treatment and has a characteristic spectrum similar to that of the other gases of the group. It has a molar weight of 222.4, which is probably also its combining weight. It is highly radioactive and changes in about a month into other things, one of which is the undoubted element helium. Fourth, that radium is present in every uranium ore in practically a constant ratio to the uranium content of the ore. These and other facts of a similar nature are interpreted to mean that radioactive elements decay and pass finally into other and more stable elements, and that they follow the law of successive reactions in going through a number of stages. Radium is supposed to be one of the decomposition products of uranium, and the radium emanation in turn comes from the radium and goes on into helium, etc.

Uranium salts which have been kept for some time give out all three kinds of rays. But when such a salt is dissolved in water and ammonium carbonate added until the precipitate which first forms is redissolved, a very small residue is left which gives no alpha rays but has all the beta and gamma activity of the original salt. The uranium carbonate which has redissolved has all the alpha activity of the original compound but gives rise to no beta or gamma rays. The undissolved precipitate is called uranium-X, and is chemically unlike uranium. If the uranium carbonate be reconverted into the nitrate and then reprecipitated and dissolved by ammonium carbonate, no farther precipitate of uranium-X will be formed. But let both the uranium-X and

the uranium preparation stand for some time, and it will be found that at the end of about 21 days the uranium-X will have lost half of its activity and the uranium will have regained half of the beta and gamma activity which it lost, and that these changes will go on until finally the uranium will recover its original activity. If now it be reprecipitated and redissolved by ammonium carbonate, a further residue of uranium-X will be obtained. This series of operations may be repeated as often as desired with the same sample of uranium, and it will always be found that when the repetition is made immediately that no further residue of uranium-X can be obtained, but after standing for some time it can always be secured. Therefore, uranium-X is something which grows in a uranium compound and which gives off beta and gamma rays and is half transformed into something else in 21 days, while uranium passes into uranium-X with the production of alpha rays. There is some evidence that this uranium-X passes into a substance called ionium which passes through a number of slow changes into radium and this into radium emanation and so on as shown in the table on page 605. In this table, helium does not appear specifically; it is formed in the greatest quantity during the transformation of the niton but is probably produced in every case where the change gives alpha rays.

Other radioactive elements go through similar series of changes; thorium gives thorium-X, and thorium-X an emanation which is much shorter lived than the radium emanation. Radium emanation or niton is a very interesting substance. It is a colorless gaseous substance which has a critical temperature of  $104.5^{\circ}$  and a critical pressure of 62.5 atmospheres. The liquid emanation is colorless and transparent and boils at  $-62^{\circ}$ . It freezes to an opaque solid at  $-71^{\circ}$ . At the temperature of liquid air, the solid emanation has practically no vapor pressure, and hence it is easily separated from hydrogen and helium which are not condensed at this temperature.

In the gaseous state niton follows the gas laws, and has its own peculiar spectrum which is distinct from that of any other substance.

The quantity of the emanation obtainable at any one time has



Active substance	Destruction period T.	Radiation	Path of rays	Various properties
Uranium.....	$6 \times 10^9$ yrs..	$\alpha$	3.5 cm.	At. wt. 238.5. Well-known chemical properties.
Radio-uranium.....				Partly carried down by barium sulfate.
Uranium-X.....	20.7 days....	$\beta\gamma$		Prep. from uranium with iron hydroxide and bone-black, more soluble in water than in ether.
Ionium.....	1500 yrs. (?)	$\alpha$	2.8 cm.	Properties much like those of thorium.
Radium.....	2000 yrs. ....	$\alpha$	3.5 cm.	At. wt. 226.4. Group of alkaline earths. Luminous salts. Evolves heat (1 grm. of radium in radioactive equilibrium evolves 118 calories. per hour.
Radium emanation (niton).	3.86 days....	$\alpha$	4.23 cm.	Inert gas. Prin. lines of the characteristic spectrum: 4349.8; 4166.6; 3981.6. The emanation in equilib. with 1 grm. of Ra occupies 0.60 cu. mm. under a pressure of 1 atmosphere.
Radium A.....	3.0 min.....	$\alpha$	4.83 cm.	The deposit of induced activity is volatile at 800-900°. Sol. in strong acids.
Radium B.....	26.7 min....	$\beta$		The deposit of induced activity is volatile at 600-700°. Precipitates together with BaSO <sub>4</sub> .
Radium C.....	19.5 min....	$\alpha, \beta, \gamma$		The deposit of induced activity is vol. at 1000-1300°. Is dep. on Ni and Cu. In acid sol. Ra B and Ra C can be sep. by electrolysis.
Radium D.....	12 yrs. (?)...	No rays...		Prop. similar to those of Pb. Volatile below 1000°.
Radium E <sub>1</sub> .....	6.3 days....	No rays...		Can be sep. from Ra D by bone-black and also by electrolysis.
Radium E <sub>2</sub> .....	4.8 days....	$\beta, \gamma$		
Radium F or polonium.	140 days....	$\alpha$	3.86 cm...	Is dep. on Bi, Cu, Sb, Ag, and even Pb. Sulfid insol. Carried down with basic salts of Bi. Precip. by SnCl <sub>2</sub> . Volatile toward 1000°.

Note.—By destruction period is meant the time during which one-half of the element will be transformed. The path of the rays give the distance which the  $\alpha$  rays will go in air at atmospheric pressure before they are absorbed.

always been very small but its molar weight has been determined by Ramsay (see p. 323) to be 222.4.

The emanation is intensely radioactive, and produces strong fluorescence in the glass of the vessels in which it is confined. The color of this fluorescence changes with the temperature and the kind of glass. It gives out heat in comparatively large quantities. In fact 75 of the 118 calories evolved per hour by a gram of radium are due to the emanation which the radium has produced and is retaining. Like all other radioactive substances the emanation spontaneously undergoes transformation, and one of the products, as has been mentioned before, is helium. The decrease in energy accompanying this and similar transformations is without much question the source of the energy which the radio-active substance gives out. The emanation decomposes at such a rate that one-half of it is transformed in 3.86 days and practically all in about a month.

Perhaps because of the large quantity of energy which it evolves in its transformation, radium emanation is able to bring about chemical changes in many of the substances with which it comes in contact. It decomposes water, changes oxygen to ozone, and does many similar things. At one time Ramsay claimed that it would change copper into lithium, but others have not been able to confirm this. In a recent article he asserts that when the emanation acts upon solutions of compounds of silicon, titanium, zirconium, thorium, and lead, all members of the carbon group, that carbon dioxide is produced in solutions which were previously free from carbon. If this be true, radioactive elements not only are transformed spontaneously into other elements but also are able to transmute inactive elements into other elements. The confirmation of these observations will naturally be awaited with interest. The transformation of niton into helium is significant as indicating a possible source of the helium which is present in natural gas since the latter also contains niton.

Actinium and thorium also give rise to emanations which while highly radioactive are inert chemically, and perhaps have higher molar weights than the radium emanation, but this has not been determined experimentally because the emanations decompose so very rapidly. Actinium's is half decomposed in

3.9 seconds while that from thorium is somewhat longer lived and requires 54 seconds for the transformation of one-half of itself. Because of their high rates of decay, only very small quantities of these emanations have been obtained; but in comparison with their mass, they are intensely radioactive. They may be easily distinguished from niton and from each other by the difference in their rates of decay.

The following is a list of the names of the persons who have been  
 named in the various reports of the Board of Directors of the  
 National Bank of Commerce, from the year 1910 to the present  
 time. The names are given in alphabetical order, and are  
 followed by the year in which they were first named.

- A. B. ... 1910
- C. D. ... 1911
- E. F. ... 1912
- G. H. ... 1913
- I. J. ... 1914
- K. L. ... 1915
- M. N. ... 1916
- O. P. ... 1917
- Q. R. ... 1918
- S. T. ... 1919
- U. V. ... 1920
- W. X. ... 1921
- Y. Z. ... 1922

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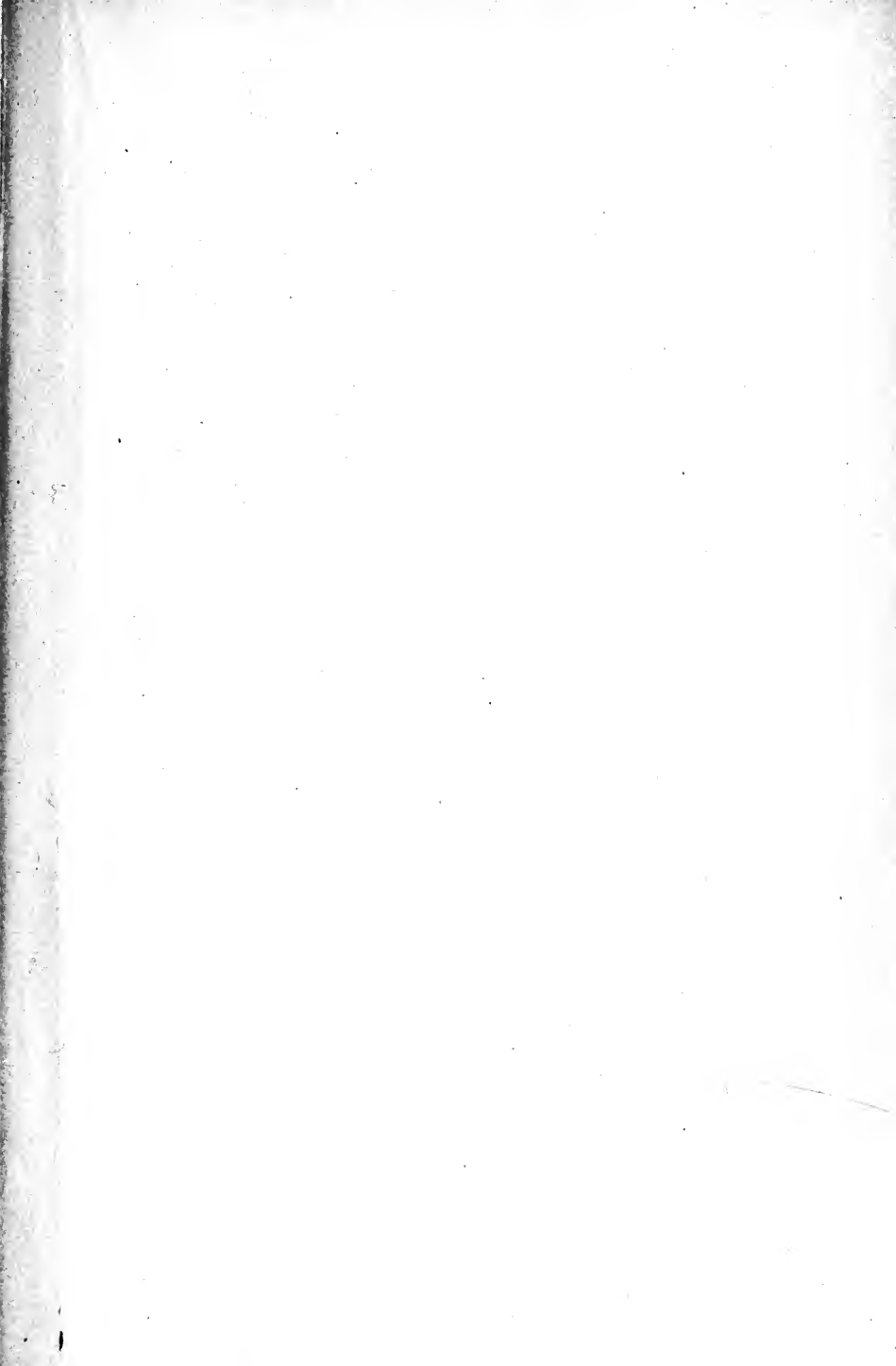
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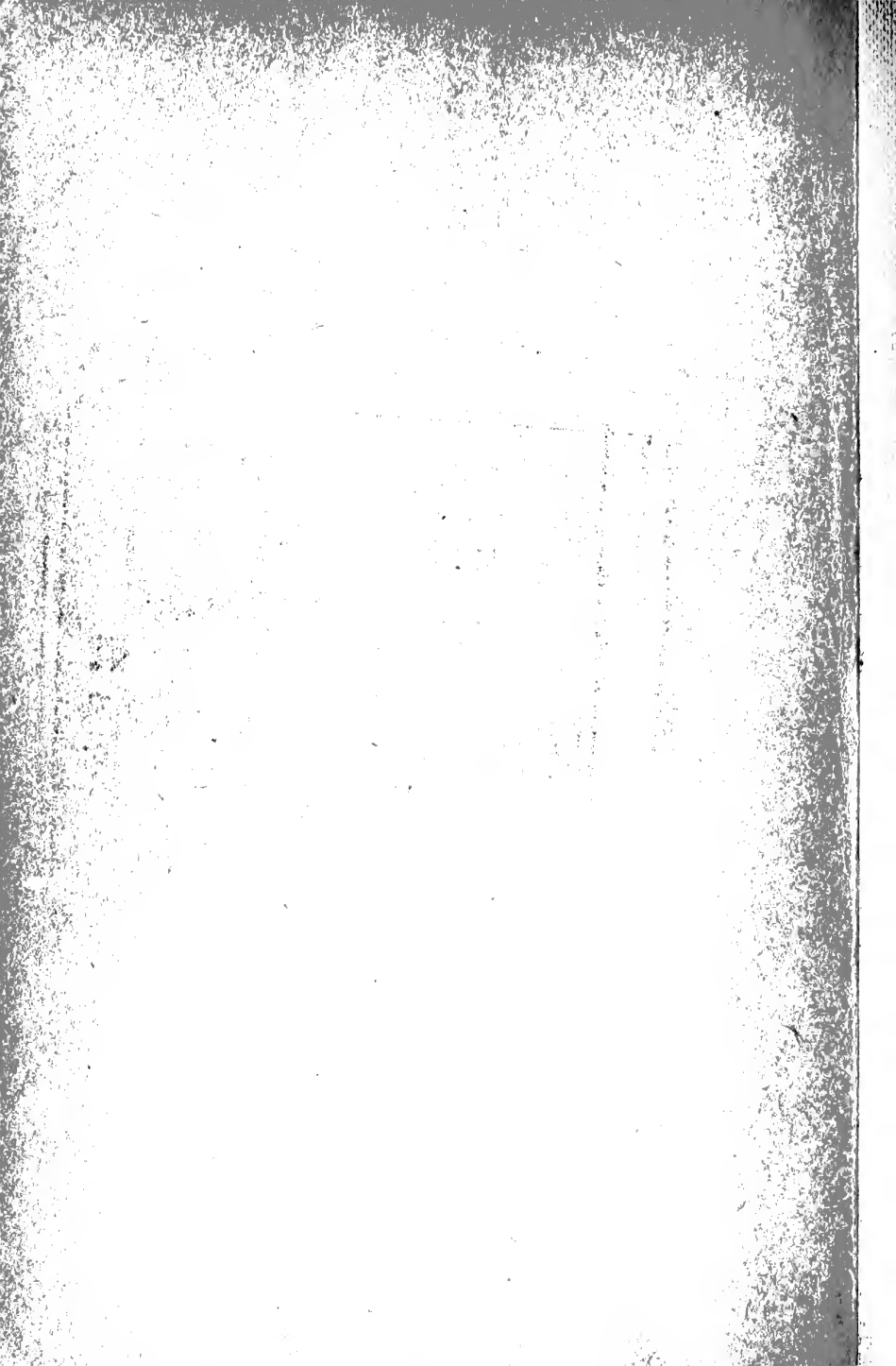












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