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OUTLINES OF CHEMISTRY

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OUTLINES OF CHEMISTRY

A TEXT-BOOK FOR COLLEGE STUDENTS

BY

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REVISED

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PREFACE TO THE FIRST EDITION

THIS book is intended to represent one year's work of chemistry in college. It should be used in connection with a course of experimental lectures and laboratory exercises. The matter has been selected so as to meet the needs of those that can devote but one year to the study of chemistry, and also to serve as a suitable basis for future work in the case of students who desire to pursue the subject further. In writing the book, the author has naturally had in mind the needs of his own students, over six hundred in number, who are preparing for careers in chemistry, pharmacy, medicine, engineering, or agriculture, or who desire a course in chemistry for work in other natural sciences or as a means of general culture.

In the first five chapters, experimental work has been placed in the foreground, and all reference to atomic and molecular theories has been purposely avoided in order that the student may properly be impressed with the fundamental facts and laws, which are independent of the theories, though they serve as a foundation for the latter. In the sixth chapter, these fundamental laws are then reviewed, and the atomic and molecular theories are presented as views growing out of the experimental facts. The nomenclature is then also introduced, and the reactions which so far have been written in words are expressed by means of chemical symbols. This offers an excellent opportunity for reviewing the experimental work of the foregoing chapters. While the teacher is somewhat inconvenienced by thus postponing the introduction of the atomic theory and the use of formulation till the student has at least a fair stock of carefully selected facts upon which to found the theory, it really pays to make the exertion, for thus greater interest is created and the student sees the facts and theoretical views

in their proper relations. He becomes a clear, logical thinker, and does not look upon the atomic and molecular theories as something arbitrary, metaphysical, and well-nigh incomprehensible. The method here adopted is not new. It is essentially the same in principle as that followed by Bunsen and many other successful teachers of chemistry.

Throughout the book, the endeavor has been to convey the salient facts in as simple and direct a manner as possible, developing cardinal principles, and carefully keeping the distinction between facts and theories in mind. The aim has been to enlist the interest of the student in the study of chemistry, and to this end the historical development of certain aspects of the subject has been presented as far as space would permit.

The most important technical applications and processes have constantly been emphasized, though they have been introduced in connection with the description of the various elements and compounds rather than as special chapters. On the other hand, it has been thought best to treat the subjects of thermochemistry and solutions and electrolysis in special chapters, after a sufficient number of fundamental facts have been acquired by the student, so that he is in a position to comprehend the more difficult relationships which these topics involve.

Only the essential parts of chemical theory which can be comprehended by college students who are beginning the study of chemistry have been presented. My own experience would indicate that fully as much has been given as they can well digest at this stage of their work. In touching upon controverted points, the aim has been to present both sides of the question involved. I have felt that the teacher should not entirely avoid mooted questions even during the first year of work in chemistry, for by so doing the impression is conveyed that all matters are in a settled state, and thus a powerful stimulus toward further study and inquiry is lost. On the whole, however, the presentation of the subject has been along rather well established, conservative lines. The dominant idea has been to select with care what the student needs, what he can reasonably be asked to comprehend, at his stage of advancement, and to present this in a clear, simple, and direct manner,

taking the trouble to repeat and to emphasize here and there in order to secure the desired end.

My best thanks are due to Dr. J. H. Walton for suggestions and reading of proof, also to Messrs. C. W. Hill, D. Klein, F. C. Krauskopf, and W. G. Wilcox for reading proof sheets of some of the chapters. Additional suggestions or corrections to be used in preparing further editions will be welcomed from others.

LOUIS KAHLENBERG.

MADISON, WISCONSIN,
June 8, 1909.

PREFACE TO THE SECOND EDITION

In preparing this new edition, the entire book has been gone over with special care so as to bring the subject matter up to date and improve the presentation wherever possible. As a special aid to the student, a set of review questions has been added to each chapter. These questions are intended to cover the matter presented in the respective chapters, but they by no means exhaust the subject. On the contrary, the questions will doubtless serve to suggest many others to the teacher.

The wide popularity which the first edition of this book has enjoyed among students and teachers has been gratifying to the publishers and the author, and it is hoped that the new edition will similarly commend itself to a still larger circle. The aim has been to keep the presentation as simple, clear, and direct as possible, giving as much theory as is necessary for a thorough comprehension of the important facts to be inculcated, yet always bearing in mind that the book is essentially for first year college students whose interest must be awakened, and who must not be overwhelmed with too much detailed and abstruse matter. To the many kind friends who have so generously aided by means of helpful suggestions the author desires to express his best thanks.

LOUIS KAHLENBERG.

Madison, Wisconsin,
February, 1915.

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OUTLINES OF CHEMISTRY

CHAPTER I

THE SCOPE OF CHEMISTRY AND ITS RELATIONS TO OTHER SCIENCES

Chemical Change, Elements, and Compounds

Our own bodies, and the various objects that surround us, constitute the subject of study of the natural sciences. The investigation of the things that make up the universe as we know it, is conducted by means of our senses, either aided or unaided. For the sake of classifying our knowledge, we are wont to distinguish between the biological sciences, which deal with living things, and the so-called physical sciences of astronomy, geology, physics, and chemistry. Astronomy, which deals with the heavenly bodies, is nevertheless closely related to the sciences of physics and chemistry, though obviously not to biology. But the study of living things and the life history of the earth and the processes that are continually going on on its surface is inseparably linked with the subjects of physics and chemistry. The latter sciences may indeed be regarded as basal in character. The study of **matter** — that is, anything which occupies space — comes within the scope of these two sciences. Viewed in this light, biology, astronomy, and geology merely present special complex phases and combinations of physics and chemistry.

Physical and Chemical Changes. — The changes which any object may undergo are either superficial or deep-seated in character. Thus, if a stick of sulphur be thrown or whirled through the air, the character of the sulphur is not altered, though the sulphur has undergone change of position through expenditure of mechanical energy upon it. **Energy** is anything which does work or is capable of doing work. Energy itself is measured by the amount of work it has done or is

capable of doing. Indeed, as energy is always measured in terms of work, the two are often regarded as synonymous. **Work** is equal to the force multiplied by the distance through which the force acts, **a force** being defined as that which causes or modifies motion, the latter being a change of place. The motion might have been imparted to the sulphur by means of the muscles or by a contrivance in which the energy was furnished by gravity, heat, light, electricity, magnetism, etc. These agencies are consequently capable of doing work; that is, they represent **forms of energy.** As long as the sulphur remains sulphur, no matter through what motions or other alterations, like contraction, expansion, electrification, change of temperature, pulverization, liquefaction, or vaporization, it may go, the change in question is called a **physical change**, and the study of such changes in all their various phases belongs to the subject of physics. But if, for example, we burn the sulphur in the air we obtain a gas of a pungent odor which may be condensed with the aid of pressure and lowering of the temperature to a colorless, mobile liquid. This is quite unlike sulphur in all its various properties, and we consequently say that a new substance has been formed. The process of forming a new substance is called a **chemical change.**

Any process in which given substances disappear and new ones are formed is chemical, and the study of such deep-seated processes in all their various phases is the subject with which the science of chemistry is concerned. It would thus seem fairly easy to distinguish between chemical and physical processes. Indeed, in general, such a distinction can readily be made on the basis of what has just been said. But whether new substances have been formed must be decided from the properties of the material; and there must consequently be some definite way of telling whether an alteration of substance has occurred or not. It is evident at once that the term *substance* must be clearly defined. For our present purpose, it will suffice to say that a **substance** is matter which is perfectly homogeneous throughout, considered without respect to shape or amount. Thus sulphur, iron, and water are substances. Many things which are apparently homogeneous in character are not so in reality. Thus, the atmosphere on closer study is found to be a mixture of nitrogen, oxygen, carbon dioxide, and other gases; sea water is found to

consist of water together with various saline substances; brass is made up of copper and zinc in proportions that may vary to a considerable extent in different samples.

If we pulverize a piece of roll sulphur and grind it together with iron filings in a mortar as intimately as possible, a fine grayish powder results which has the outward appearance of homogeneity. On closer inspection, however, with the aid of a microscope perchance, this powder appears heterogeneous; in other words, it is merely a **physical mixture.** Indeed, it is very easy to separate the iron from the sulphur, for by passing a magnet through the mixture the iron will adhere to the magnet, and the sulphur will be left behind. We could also separate the iron from the sulphur in the mixture by treating the latter with carbon disulphide, which liquid dissolves the sulphur and leaves the iron unaltered. The mixture of iron filings and sulphur represents a typical physical mixture. It is obviously heterogeneous in character, the proportion of iron and sulphur in the mixture may be varied at will, and the iron and sulphur may readily be separated from each other by simple means.

If now we heat some of the mixture of pulverized sulphur and iron filings in a test tube, we observe that at a certain temperature the contents of the tube begin to glow. As we take it out of the flame the glowing nevertheless increases, and the contents of the tube become hotter. After a time the glowing becomes weaker, and gradually ceases as the material cools. It is evident that by raising the temperature of the mixture of iron filings and sulphur to a certain point, a change was inaugurated, which on taking away the source of heat nevertheless continued, giving off additional heat and light. On examining the contents of the tube after it has cooled to room temperature, we find a black mass, quite unlike either the sulphur or iron in appearance. We can no longer detect heterogeneity in it even with the aid of the microscope. The magnet is unable to extract iron from this material, and carbon disulphide will not alter it in any way. A few drops of hydrochloric acid poured upon it evolve a malodorous gas called hydrogen sulphide, which is not formed when a simple mixture of iron filings and sulphur is moistened with that acid. We clearly have formed a new substance by heating the sulphur and iron together. It is called ferrous sulphide, and results from simple union of sulphur and

iron at elevated temperatures. It has been found that ferrous sulphide contains 63.52 per cent of iron and 36.48 per cent of sulphur, and that it always has exactly this composition no matter by what methods it has been formed. This is in fact a characteristic of all chemical compounds. We may express this fact by saying that *every definite chemical compound always contains the same ingredients in the same proportion by weight.* This is the **law of definite proportions.** *A law, as the word is used in science, is a general statement summarizing what has actually been found to be true in a large number of individual cases that have been carefully investigated.*

Other typical examples of chemical change are the rusting of iron, the combustion of coal or wood, the decomposition of water by electrolysis, the formation of quicklime from limestone by the agency of heat, the change of carbon dioxide and water into starch by sunlight in the green leaf of the plant, and the darkening of a photographic plate when exposed to light. In all these cases new substances are formed, and the actions are accompanied by changes in temperature, volume, outward appearance, and other specific properties which characterized the original substances before the change occurred. It is the province of chemistry to study such changes in all their various aspects. This involves a close study of the composition and specific properties of the substances before and after the chemical change, which is commonly termed the chemical reaction, has taken place. But, in addition, a study of the conditions that must obtain in order that the reaction may begin and proceed, and an investigation of the various energy changes that accompany the reaction, also fall within the field of chemistry. Thus we have various branches of chemistry. So *analytical chemistry* seeks to determine the qualitative and quantitative composition of substances by tearing them apart or analyzing them; *synthetic chemistry* seeks to build up more complex substances from simpler ones; *thermochemistry* concerns itself with the thermal changes accompanying chemical reactions; *electrochemistry* is concerned with electricity as an agent in producing chemical changes, or as an accompaniment of chemical phenomena; *photochemistry* treats of the relations of light to chemical changes. In the crust of the earth, in the atmosphere, in natural waters, in the bodies of plants and ani-

mals, chemical changes are continually going on. Upon these all life on the globe depends. Every breath we breathe, every move we make, every thought we think, is accompanied by chemical changes and their concomitant physical phenomena as above briefly mentioned. The importance of the study of chemistry, therefore, is clearly apparent, and it is also evident why there must needs be many special and applied lines of this subject, which seek to investigate certain special fields. Thus we have agricultural chemistry, pharmaceutical chemistry, physiological chemistry, food chemistry, industrial chemistry, etc., the province of each of which is indicated sufficiently by the name itself.

From what has been stated, it would seem a fairly simple matter to distinguish a chemical change from a purely physical one, but this is by no means always easy. Suppose a block of ice and one of common salt be placed in contact with each other; we note that the salt and ice gradually disappear, forming a brine. Evidently the brine has quite different properties from those of either the salt or the ice. Moreover, there was a marked change of temperature, in this case a cooling effect, as the salt and ice acted on each other. Furthermore, a contraction ensued, for the volume of the brine is less than the sum of the volumes of the blocks of ice and salt. Again, as a block of ice and one of paraffine, or one of salt and one of paraffine, for example, do not act on each other at all when brought into contact, it is clear that the action between ice and salt takes place because of the specific nature of the substances. Furthermore, it has been found that below $-22°$ C. ice and common salt no longer act on each other, just as iron and sulphur do not act on each other at ordinary temperatures. Raise the temperature sufficiently in each case, and at a certain definite point action begins. Thus, the interaction of ice and common salt apparently bears all the earmarks of a genuine chemical change. This is indeed true except in one particular which has not yet been mentioned, namely, it is possible to vary the composition of the brine gradually, by adding common salt to it till a point of saturation is reached. Even then the brine will still take up somewhat more salt gradually if the temperature of the whole is slowly raised. The brine is termed a solution of common salt in water. It results from the action of salt and water on each other. The

water used may be liquid, or in form of ice above $-22°$ C. A distinction is commonly made between **solutions and chemical compounds.** *In a solution, the relative amounts of the ingredients that it contains may be varied gradually within certain limits,* as we have seen in the case of the brine. *In a chemical compound, the constituents cannot thus be varied in amount.* Not many years ago, chemists spoke of solutions as chemical combinations according to variable proportions, and this term is indeed indicative of the real relation that they bear to definite chemical compounds which follow the law of definite proportions.

Brine, then, is not a mere physical mixture, and it is consequently not to be classed with such mixtures as that of sulphur and iron filings rubbed together in a mortar, which represents a typical physical mixture. In chemistry we frequently have to deal with (1) physical mixtures, (2) solutions (*i.e.* compounds according to variable proportions), and (3) definite chemical compounds.

As further typical examples of solutions may be mentioned, solution of sugar in water, of camphor in petroleum oil, of ether in alcohol, of carbon disulphide in olive oil. The subject of solutions clearly forms an important part of chemistry, and it will consequently be considered more fully later.

Chemical Elements. — A careful study of all substances known has revealed the fact that there are about eighty which it has been impossible to decompose into simpler substances thus far. These substances are regarded as elementary in character. They are termed the **chemical elements.** Whether a substance is an element or not is thus determined by experiment. As new methods of experimental attack are discovered, substances that are now regarded as elements may prove to be complex and consequently capable of synthesis. Thus at one time lime and caustic potash were regarded as elements, whereas now we know that lime contains calcium and oxygen, and caustic potash consists of potassium, hydrogen, and oxygen. Sir William Ramsay found that the emanations from radium show the spectra of helium, argon, and neon, and this is by many regarded as a case of synthesis of the latter gases from the products of the decay of radium. Again, Ramsay claims to have obtained spectroscopic traces of lithium by the action of radium emanation upon copper sulphate solutions, though

Mme. Curie's investigations do not substantiate his results. Thus it is evident that some of the substances we now term elements may prove to be composite. It is also obviously impossible to state just how many elements there are, for it is uncertain whether some substances are elementary or complex in character. The following is an alphabetical list of the chemical elements as commonly recognized at present.

CHEMICAL ELEMENTS

Aluminum	Europium	Mercury	Silicon
Antimony	Fluorine	Molybdenum	Silver
Argon	Gadolinium	Neodymium	Sodium
Arsenic	Gallium	Neon	Strontium
Barium	Germanium	Nickel	Sulphur
Bismuth	Glucinum	Nitrogen	Tantalum
Boron	Gold	Osmium	Tellurium
Bromine	Helium	Oxygen	Terbium
Cadmium	Hydrogen	Palladium	Thallium
Cæsium	Indium	Phosphorus	Thorium
Calcium	Iodine	Platinum	Thulium
Carbon	Iridium	Potassium	Tin
Cerium	Iron	Praseodymium	Titanium
Chlorine	Krypton	Radium	Tungsten
Chromium	Lanthanum	Rhodium	Vanadium
Cobalt	Lead	Rubidium	Xenon
Columbium	Lithium	Ruthenium	Ytterbium
Copper	Lutecium	Samarium	Yttrium
Dysprosium	Magnesium	Scandium	Zinc
Erbium	Manganese	Selenium	Zirconium

It will be observed that the list contains a goodly number of common, well-known substances. Notably, it appears that all the metals are elements. Again, there are substances in the list which are not metals, like sulphur, chlorine, bromine, iodine, oxygen, hydrogen, phosphorus, etc. *The elements may be divided into two groups; namely, the metals and non-metals.* It is difficult to draw a sharp line between these groups, however, for elements like arsenic, antimony, and tellurium clearly represent transitions between the metals and non-metals. Such transition elements are sometimes called **metalloids.**

Some of the elements are gases, others are liquids, and still others are solids, under ordinary conditions of temperature and pressure. Whether an element is a solid, liquid, or gas

is determined entirely by the conditions of temperature and pressure to which it is subjected.

Less than half of the elements mentioned in the table enter into the composition of ordinary objects. The solid crust of the earth, also called the lithosphere, makes up about 93 per cent of all known terrestrial matter, while the ocean represents about 7 per cent, and the atmosphere only 0.03 per cent, of the total. The following table, by F. W. Clarke, gives an estimate of the relative amounts of the elements contained in the lithosphere and the ocean. The third column of the table gives a total average including the atmosphere.

AVERAGE COMPOSITION OF LITHOSPHERE, OCEAN, AND ATMOSPHERE

	Lithosphere (93 Per Cent)	Ocean (7 Per Cent)	Average Including the Atmosphere
Oxygen	47.07	85.79	49.78
Silicon	28.06	—	26.08
Aluminum	7.90	—	7.34
Iron	4.43	—	4.11
Calcium	3.44	0.05	3.19
Magnesium	2.40	0.14	2.24
Sodium	2.43	1.14	2.33
Potassium	2.45	0.04	2.28
Hydrogen	0.22	10.67	0.95
Titanium	0.40	—	0.37
Carbon	0.20	0.002	0.19
Chlorine	0.07	2.07	0.21
Bromine	—	0.008	—
Phosphorus	0.11	—	0.11
Sulphur	0.11	0.09	0.11
Barium	0.09	—	0.09
Manganese	0.07	—	0.07
Strontium	0.03	—	0.03
Nitrogen	—	—	0.02
Fluorine	0.02	—	0.02
All other elements	0.50	—	0.48
	100.00	100.00	100.00

The following table gives the approximate amounts of the elements found in the human body: —

AVERAGE ELEMENTARY COMPOSITION OF THE HUMAN BODY

Oxygen	66.0	per cent
Carbon	17.6	per cent
Hydrogen	10.1	per cent
Nitrogen	2.5	per cent
Calcium	1.5	per cent
Phosphorus	1.0	per cent
Potassium	0.4	per cent
Sodium	0.3	per cent
Chlorine	0.3	per cent
Sulphur	0.25	per cent
Magnesium	0.04	per cent
Iron	0.004	per cent

Silicon, Fluorine, Iodine, etc., in traces.

Compounds. — Most substances are non-elementary in character; that is, they are combinations of two or more elements. Such substances are consequently termed **compounds.** They may be formed by direct union of the elements with one another under proper conditions; as, for instance, sulphur may unite with iron to form ferrous sulphide. Again, limestone, which is carbonate of calcium, decomposes at a high temperature, forming two simple substances, lime and carbon dioxide, the latter being a gas. Further, by action of two compounds on each other, two other compounds may result. As an example, when common salt and nitrate of silver are brought together in aqueous solution, silver chloride, a substance insoluble in water, and sodium nitrate, a soluble substance, are formed. This latter change is termed **double decomposition** or **metathesis.**

In the three cases cited we have, indeed, *the three types of chemical changes; namely,* (1) *the direct union of two or more substances to form a single compound,* (2) *the breaking up of a compound into simpler ones, and* (3) *the interaction of substances with one another to form new substances.*

Like elements, compounds may also assume the solid, liquid, or gaseous state, according to the conditions of temperature and pressure that obtain. However, by no means all compounds are capable of assuming these three states, for many readily decompose when an attempt is made to liquefy them or volatilize them by means of heat.

Compounds which contain different elements are, of course, different in character. The same is true of compounds that contain the same elements, though in different proportions by weight. For a long time it was thought that one compound could differ from another only because it contained either different elements, or the same elements in different proportions. However, we now have knowledge of a large number of compounds that are quite different substances, and yet they contain the same elements in exactly the same proportion by weight. Such compounds are called **isomers**, and the difference between them is explained by the different manner in which the elements are combined in these substances, in other words, by the difference in inner structure or constitution of the compounds.

Conservation of Mass. — Investigations have shown that when chemical changes take place, the weight of all the substances before the reaction is equal to the weight of all the substances after the reaction has taken place. In other words, *in any chemical change the total weight remains the same.* As at any place on the surface of the earth weight and mass are proportional to each other, we may say that *during chemical changes, the total mass of the reacting substances remains constant.* This is simply the **law of conservation of mass**, which applies to chemical as well as to physical changes. It is sometimes called the law of conservation of matter. It is the outcome of experimental investigations, the most careful of which were conducted by having chemical changes go on in sealed glass vessels, which, together with their contents, were weighed before and after the substances they contained had reacted chemically on one another.

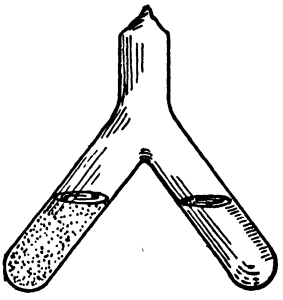


FIG. 1.

Figure 1 shows a common type of such sealed glass tubes. The substances are introduced into each limb, and the tube is then sealed by drawing off the end as shown. After the whole has been very accurately weighed, the contents are allowed to act on each other by inclining or shaking the tube. After the action has ceased and the whole has cooled to room temperature, the tube is carefully weighed again. H. Landolt has performed

many careful experiments of this nature in recent years. His results show that if there is any change of weight, it lies very near the limit of experimental error. That is, it is so slight as to be quite negligible for all ordinary purposes.

Conservation of Energy. — Like mass, *energy also cannot be created or destroyed. It can simply be transformed.* Thus, for example, electricity may be converted into heat, mechanical energy, or chemical energy; and again, each of these latter may be converted back into electricity.

When coal burns, to be sure, new substances are being formed, but in addition chemical energy is being converted into heat and light. When water is decomposed by means of the electric current, electrical energy is being converted into chemical energy. When lime is produced at the high temperature of the limekiln, heat is transformed into chemical energy. When starch is formed in the sunlight in the green leaf of the plant, light is converted into chemical energy.

The Cause of Chemical Change. — As to the cause why certain substances act on each other to form new substances under given conditions and other substances do not, we are quite ignorant. Thus, we cannot tell why a piece of sulphur will burn when heated in the air and a piece of platinum or gold will not. We know that, in the act of burning, the sulphur unites with the oxygen of the air, and therefore we explain this by saying that sulphur and oxygen have a specific attraction for each other. This specific attraction, which is regarded as the cause of chemical union, is commonly called **chemical affinity.** Thus, the fact that platinum and gold do not burn when heated in the air is explained by saying that these elements have too slight a chemical affinity for oxygen.

The word *affinity* means relationship. It was adopted at a time when it was thought that substances that are similar are more prone to unite chemically with one another than those which are dissimilar. While it is true, as we shall see, that substances of similar characteristics do frequently unite chemically, nevertheless, as a rule, substances that are unlike in character react more energetically with one another. So, for instance, while metals do form chemical compounds with metals, yet they react much more energetically with non-metals and thus form stabler compounds.

Factors affecting Chemical Change. — In order that a chemical change may take place, it is first of all necessary that the substances that are brought together be of the right kind; that is, they must be of such a specific nature that they will react. According to the preceding paragraph, we should say, the substances must have chemical affinity for one another. When we study any substance as to its power to react with other bodies to form new substances, we are investigating the **chemical properties** of the substances. *Intimate contact of the substances that are to react is always necessary.* From this fact we conclude that *chemical affinity acts at insensible distances.* Again, *temperature is a great factor in promoting chemical change;* indeed, in most of the changes studied in the laboratory, temperature is second only to chemical affinity itself in determining whether chemical action will take place or not. *Electricity, light, pressure, concussion, various forms of vibration, contact with other substances which often need to be present only in relatively minute quantity, are also frequently important factors in determining whether a chemical change will proceed or not.* Furthermore, *the relative amounts of the reacting substances brought into contact also affect the rate of a chemical change and the extent or degree of completion to which it will proceed.*

REVIEW QUESTIONS

1. What is a science?
2. Name five of the more fundamental natural sciences and state of what each treats.
3. Distinguish between chemical change and physical change, and give six examples of each.
4. What is a *substance,* as that term is used in chemistry?
5. Distinguish between a physical mixture, a solution, and a chemical compound, giving three examples of each. What is a chemical element?
6. Name the important phenomena that may accompany chemical change.
7. Make a list of the most important metallic elements that occur in the earth's crust. Make a similar list of the nonmetallic elements.
8. What elements occur in the human body to the extent of 1 per cent or more?
9. Mention the three types of chemical change, giving illustrations.
10. State the law of conservation of mass; also the law of conservation of energy. Illustrate by an example in each case.
11. What is meant by the term "chemical affinity"?
12. Prepare a list of the more important factors or agencies that may inaugurate chemical change or affect its rate of progress.

CHAPTER II

HYDROGEN

History. — It was known to Paracelsus (1493–1541) that an inflammable gas is produced when dilute acids act on certain metals; but the English physicist Cavendish (1731–1810) was the first to isolate hydrogen and recognize it as a special gas. In 1766 he prepared hydrogen by the action of either hydrochloric or sulphuric acid on zinc, iron, or tin, and described the characteristic properties of the gas. Hydrogen is an essential constituent of water, and derives its name from the Greek words meaning water and to generate.

Occurrence. — Hydrogen is perhaps the most widely distributed element in the universe. It occurs in very large quantities in the sun, where it is heated to incandescence owing to the high temperature that obtains. It is found in all fixed stars and nebulæ that have been examined by means of the spectroscope. On the earth it occurs only in small amounts in the free state. The atmosphere contains only about 0.005 per cent of uncombined hydrogen by volume. In the gases emitted from volcanoes, oil wells, and some natural salt deposits, notably those at Stassfurt, hydrogen is found in the free state. It occurs further in the gases resulting from certain forms of fermentation, in the gases emitted from living plants, and in the intestinal gases of human beings and animals. In meteoric iron, and in various minerals, hydrogen has also at times been found as an occlusion.

While hydrogen exists only in small quantities in the free state on the earth, in combination with other elements it is found in very large quantities. Thus, 11.19 per cent of the weight of water consists of hydrogen. It forms an essential part of all plants and animals, in which it occurs chiefly in combination with the elements oxygen, carbon, and nitrogen. In petroleum, natural gas, and marsh gas it occurs combined with carbon. It is an essential constituent of all acids.

Preparation. — When an electric current is passed through water acidulated with sulphuric acid (Fig. 2), both hydrogen and oxygen are produced, two volumes of the former and one volume of the latter appearing at the opposite plates used as electrodes. This method is an excellent one for preparing very pure hydrogen. The process itself is, however, somewhat complex in nature and will receive special attention later (see Electrolysis).

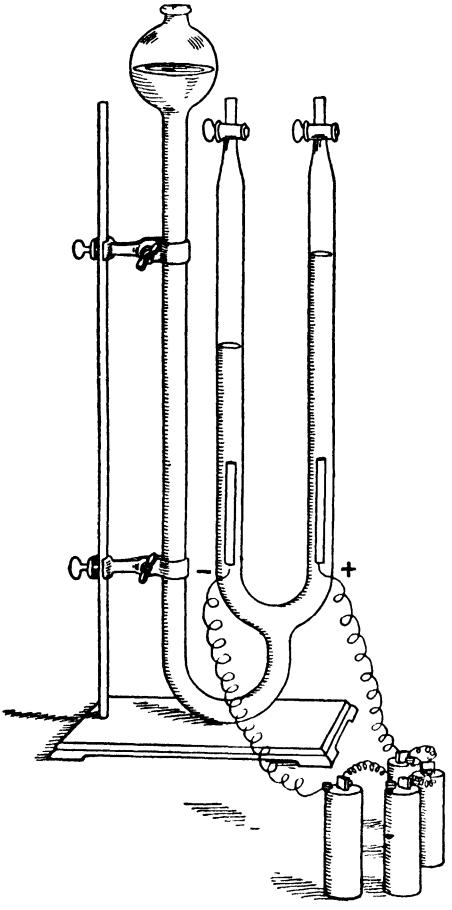


FIG. 2.

When metallic sodium acts on water, hydrogen and caustic soda are formed. The sodium may be introduced into a test tube which has been filled with water and inverted in a basin as shown in Fig. 3. The metal, being lighter than water, rises in the tube, and as the hydrogen is generated it forces the water out of the tube. The metal melts owing to the heat generated during the reaction and floats in form of a globule on top of the water. We may express what takes place by writing:—

$$\text{Water} + \text{Sodium} = \text{Hydrogen} + \text{Caustic Soda.}$$

The latter substance is dissolved in the water after the change has taken place. It may be obtained as a white solid by boiling the solution till all the water has evaporated. The caustic soda solution turns red litmus blue, has an "alkaline"

taste, and feels slippery to the touch. Caustic soda consists of three elements, sodium, oxygen, and hydrogen. It is also called sodium hydroxide. It is a strong alkali, that is, a substance which is able to neutralize acids and thus form salts.

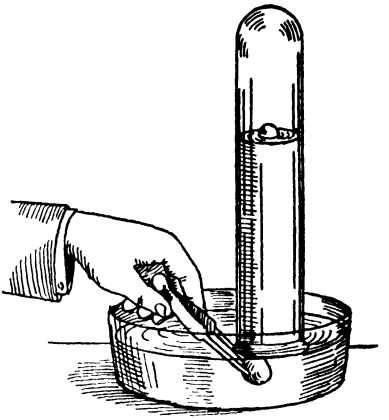


FIG. 3.

Potassium acts on water like sodium, only much more vigorously. The metal in this case catches fire and burns with a brilliant flame. Frequently the action is so violent as to result in explosions. Lithium, rubidium, cæsium, barium, strontium, and calcium also act on water at room temperature, forming hydrogen and the hydroxide of the metal employed. It is therefore evident that all of these metals cannot be kept in contact with the air, which always contains some moisture. They are kept under hydrocarbon oils, like kerosene, with which they do not react.

Magnesium decomposes water at room temperatures, but very slowly indeed. If, however, a magnesium salt is dissolved in the water, the action goes on much more rapidly. Magnesium salts aid the action by dissolving the magnesium hydroxide formed, which would inclose the metal in a pro-

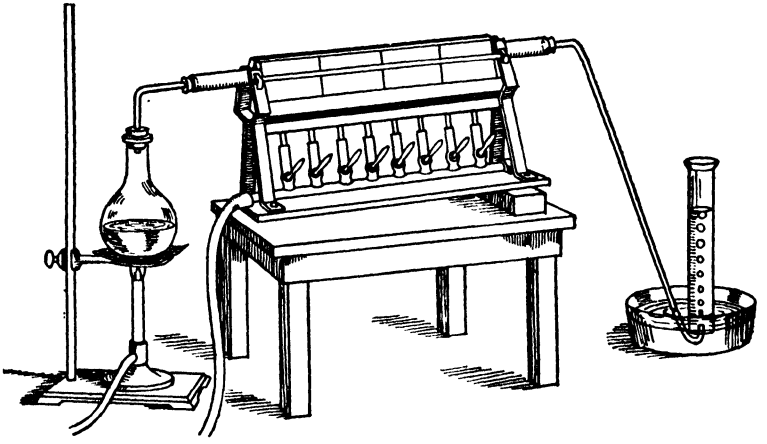


FIG. 4.

tecting film. On boiling water magnesium acts quite readily, forming hydrogen and the hydroxide of the metal. Zinc or iron when heated to redness in a tube will decompose steam, yielding hydrogen and an oxide of the metal employed (Fig. 4). Furthermore, by similarly passing steam over red-hot carbon, hydrogen and carbon monoxide are formed. This latter process is used in making water gas (which see).

By boiling zinc in aqueous caustic potash solution, hydrogen and potassium zincate result. The latter is a salt which remains in solution; thus: —

Caustic Potash + Zinc = Potassium Zincate + Hydrogen.

Caustic soda acts like caustic potash. Aluminum acts in a manner similar to zinc. In this case an aluminate instead of a zincate is formed and remains in solution. By heating zinc dust or scrap iron with slaked lime, hydrogen is liberated, and an oxide of the metal used is simultaneously formed. This method is frequently used for preparing hydrogen in large quantities for industrial purposes.

By far the commonest way of preparing hydrogen in the laboratory is by treating zinc with dilute sulphuric acid. The apparatus used for this purpose is shown in Fig. 5. In this reaction there is formed, besides hydrogen, a white salt

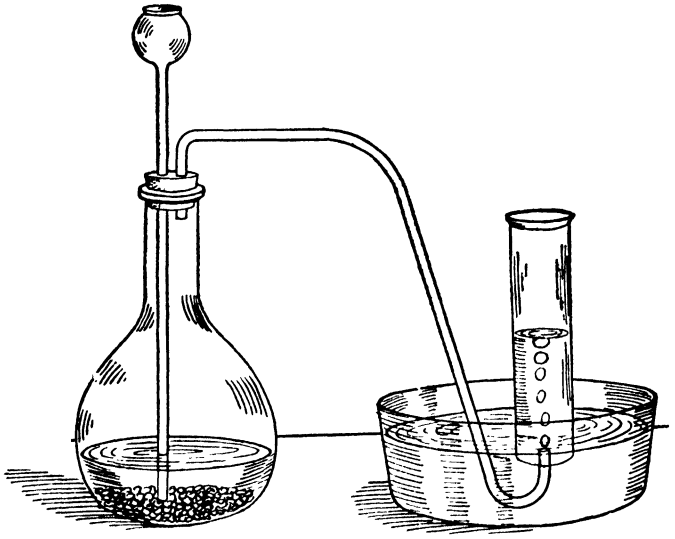


FIG. 5.

called zinc sulphate. It remains in solution, and may be obtained in form of crystals by evaporating the solution to a small bulk and allowing it to cool. We may express the change thus : —

Sulphuric Acid + Zinc = Hydrogen + Zinc Sulphate.

Instead of sulphuric acid, dilute hydrochloric acid or acetic acid may be used. Furthermore, iron may be substituted for the zinc, in which case hydrogen and corresponding salts of iron are formed. Hydrogen thus obtained is never quite pure. The impurities present in ordinary zinc and iron, such as carbon, arsenic, sulphur, and phosphorus, combine with some of the hydrogen, and the relatively small amounts of the resulting gases contaminate the larger portion of hydrogen which remains. These impurities may be removed by passing the gas through appropriate absorbents. Ordinary cast iron usually contains so much of the impurities mentioned, notably of carbon, that, when treated with an acid, the hydrogen liberated is contaminated sufficiently to have a very disagreeable odor.

Properties. — Hydrogen is the lightest of all known substances. It is a colorless, odorless, tasteless gas. At 0° and 760 mm. barometric pressure, namely, under standard conditions, one liter weighs 0.08987 gram. It is 14.388 times lighter than the air; in other words, its specific gravity with respect to air is 0.0695. Because of the lightness of hydrogen, jars containing the gas are held bottom upward.

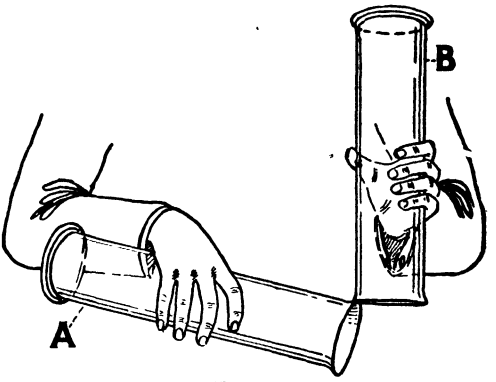


FIG. 6.

Figure 6 shows how hydrogen may be transferred from one jar *A* into another jar *B*. At and below − 241°, its critical temperature, hydrogen may be liquefied by subjecting it to pressure. At − 241° a pressure of 20 atmospheres will liquefy the gas; but at − 252.5° the vapor tension of liquid hydrogen is practically one atmosphere; that is to say, the liquid boils at

the last-named temperature. Liquid hydrogen is clear and colorless, like water, and has a specific gravity of about 0.07. Solid hydrogen may be obtained by evaporating liquid hydrogen in a partial vacuum. The melting point of the solid, which consists of white crystals, is $-259°$. Its power to refract light is 6.5 times greater than that of air.

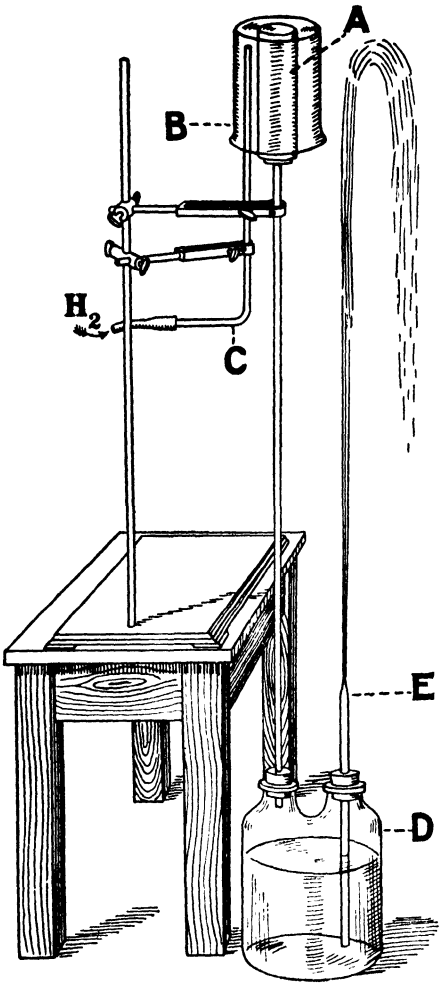


FIG. 7.

On account of its lightness, hydrogen diffuses very rapidly, and readily passes through porous substances like unglazed porcelain, brick, mortar, and paper. The rate of diffusion of gases is inversely proportional to the square roots of their densities; hence, air diffuses only $\sqrt{0.0695}$ or 0.2636 time as fast as hydrogen. The rapid diffusion of hydrogen may be demonstrated by means of the apparatus shown in Fig. 7. When the unglazed porcelain cup *A*, which contains air, is surrounded with hydrogen gas, which is passed into the inverted vessel *B* by means of the tube *C*, the hydrogen diffuses into the porous cup *A* much faster than the air diffuses out. A pressure is consequently produced in *A* which is connected with the Wolf bottle *D* containing water; and this pressure forces the water out of the tube *E* in form of a fountain.

Hydrogen is but slightly soluble in water, for only 19 volumes are absorbed by 1000 volumes of water at 15°. Certain

solids absorb hydrogen in notable quantities. Freshly ignited charcoal absorbs about twice its volume of hydrogen. Palladium absorbs 500 volumes, platinum 49 volumes, iron 19 volumes, gold 46 volumes, copper 4.5 volumes, nickel 17 volumes, aluminum 2.7 volumes, lead 0.15 volume. At red heat, palladium may even absorb as much as 900 volumes, according to Graham. This power of solids to absorb gases is sometimes termed *adsorption*, or *occlusion*. The amount absorbed depends upon the specific nature of the solid and also of the gas; and as the absorption is accompanied with changes of temperature and of volume, it is clear that the phenomenon is akin to the process of solution. Furthermore, hydrogen passes through iron and platinum tubes when these are hot. This is readily explained by the fact that these metals absorb the gas.

The most notable characteristic of hydrogen is its inflammability. It burns readily in the air or in oxygen, and the product formed is water. This can easily be shown by holding a cold bell jar over a burning jet of hydrogen (Fig. 8). The water

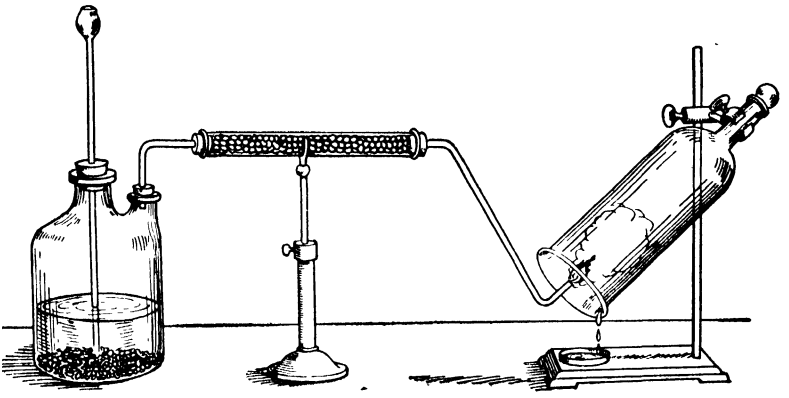


FIG. 8.

formed condenses in drops on the sides of the jar. At ordinary temperatures, hydrogen and oxygen do not act on each other appreciably, but the action takes place when the gases are heated to the kindling temperature, which is about 615°, according to V. Meyer. The hydrogen flame is colorless. To show this the gas must be burnt from a platinum jet, which is not affected during the process, so that particles of foreign matter do not get into the flame and color it. When a glass

tube is held over a hydrogen flame, as shown in Fig. 9, the column of air in the tube is set in vibration, thus producing the phenomenon known as the singing flame.

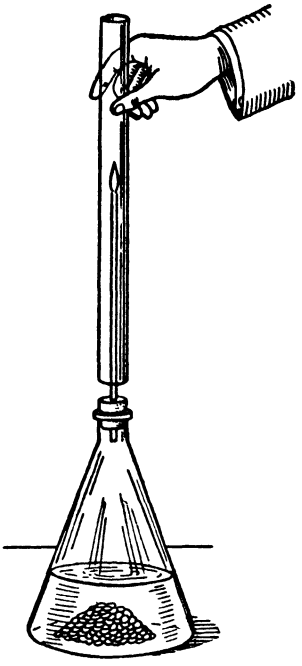


FIG. 9.

The hydrogen flame is very hot, which is evident from the fact that platinum, which fuses above 1700°, will melt in it. The burning of one gram of hydrogen develops about 34.5 large calories of heat, which is enough heat to raise the temperature of 345 grams of water from 0° to the boiling point or to melt 431 grams of ice.

Hydrogen is not poisonous, but animals would suffocate in the gas for lack of oxygen, without which they cannot live. Hydrogen will also not support ordinary combustion. Thus, when a lighted candle is thrust into a jar of hydrogen (Fig. 10), the gas at the mouth of the jar is set on fire, but the flame of the candle is extinguished.

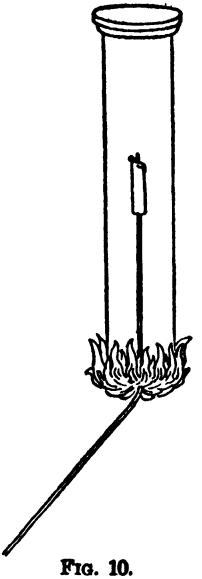


FIG. 10.

At room temperatures and atmospheric pressure hydrogen is rather inert chemically, combining with vigor with but one element; namely, fluorine. But in the sunlight, hydrogen becomes more active, notably toward chlorine, with which it combines readily, forming hydrochloric acid. With nitrogen, hydrogen forms ammonia; with sulphur, hydrogen sulphide; with carbon, marsh gas and other hydrocarbons. A compound of hydrogen with another element is called a *hydride*. Thus, water may be termed a hydride of oxygen; it may also be called an oxide of hydrogen.

Since hydrogen readily unites with oxygen at elevated temperatures, it may be used to deprive some compounds of their

oxygen content. So when copper is heated in the air it turns black because of union of the surface layers with oxygen of the air, and when this hot, black copper oxide is now brought into an atmosphere of hydrogen, the latter gas unites with the oxygen, forming water and bright, metallic copper. The process of union of the copper with oxygen is termed *oxidation*, whereas the process of depriving the copper oxide of its oxygen content is called *reduction. Oxidation and reduction are thus opposite processes.* At higher temperatures, hydrogen is similarly able to reduce quite a number of oxides, such as the oxides of lead, iron, mercury, zinc, and nickel. On account of its power to abstract oxygen from compounds, hydrogen is called a *reducing agent.* The process of oxidation and reduction of copper is readily illustrated by means of the apparatus shown in Figs. 11 and 12. The bright copper

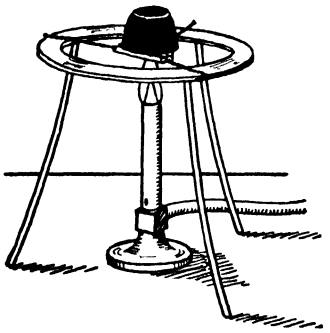


FIG. 11.

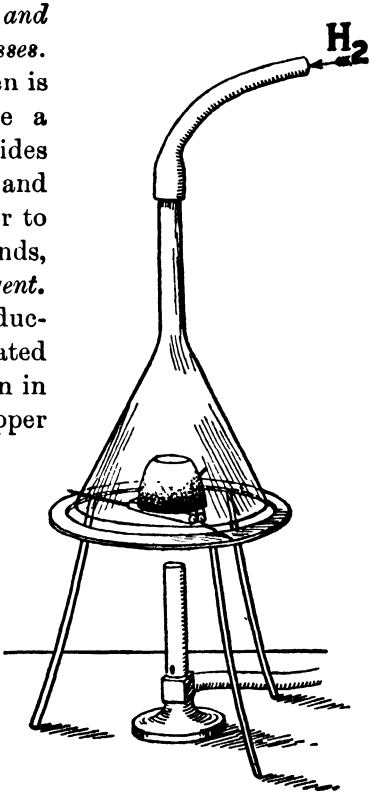


FIG. 12.

crucible is heated by means of the burner as shown in Fig. 11. The black oxide of copper is thus formed on the surface of the crucible. The flame is now extinguished, and while the crucible is still quite hot it is brought into an atmosphere of hydrogen. This is accomplished by holding the large funnel, through which a strong current of hydrogen is being passed, down over the crucible so as to envelop it (Fig. 12); the black crucible thus quickly assumes a bright copper color.

Uses. — Besides being employed as a reducing agent in various chemical operations in the laboratory and the industries, hydrogen finds use on account of its lightness and combustibility. Its lightness makes it specially suitable for filling balloons. Hydrogen prepared by electrolysis and placed, under pressures of 100 to 150 atmospheres, in steel cylinders (Fig. 13), is now an article of commerce. Mixed with carbon monoxide, hydrogen forms an important part of water gas, which is used for heating purposes. Hydrogen is too expensive for use in ordinary heating. It is at times employed as fuel in operations where very high temperatures are required, as in working platinum and other metals having a high melting point.

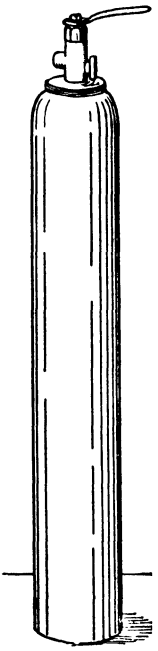


FIG. 13.

Hydrogen Equivalents of Metals. — Whether a metal liberates hydrogen from water itself or from various dilute acids, the amount of hydrogen which a given weight of a certain metal will set free is the same. The amount of hydrogen which a definite weight of a given metal is able to liberate may be ascertained by means of the apparatus shown in Fig. 14. Water is first placed in the beaker *B*. The graduated tube *A* is placed into the water as shown, and by means of suction at the upper end of *A*, while the cock *C* is open, the water is drawn up the tube till it is filled to a little above the cock, which is then closed. The tube *A* is then raised slightly and its lower end placed into the little crucible *D*, which contains a weighed quantity of a metal, say magnesium. The upper end of *A* is then filled with dilute acid, which by carefully opening the cock *C* is allowed to flow down upon the metal. The cock *C* is closed before all the acid has passed the cock so as to avoid admitting air into the graduated tube. After the acid has dissolved the

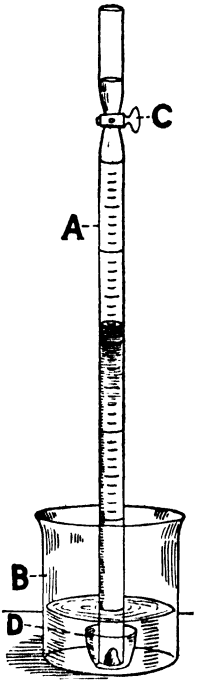


FIG. 14.

metal completely, the level of the liquid in the tube *A* is adjusted so that it is the same as that in the beaker. The volume of the hydrogen is noted, the temperature and barometric pressure are taken, and from these data the volume of the hydrogen under standard conditions is computed. Knowing this and the weight of one liter of hydrogen, the weight of the hydrogen liberated may readily be calculated. The result would be the weight of hydrogen displaced from the acid by the given weight of magnesium, and from this the amount of magnesium required to liberate 1 gram of hydrogen can easily be found. An experiment of this kind yields the result that it requires 12.16 grams of magnesium to liberate 1 gram of hydrogen. Similarly, it has been found that 23.00 grams of sodium, or 39.10 grams of potassium, or 9.03 grams of aluminum, or 27.9 grams of iron, or 59.5 grams of tin, or 32.7 grams of zinc are required to set free 1 gram of hydrogen. The quantities mentioned are called the *hydrogen equivalents* of the respective metals; or sometimes they are simply spoken of as the *chemical equivalents*. It is evident that the amounts of the various metals that are chemically equivalent to 1 gram of hydrogen are very different. The chemical equivalents of the elements are of great importance, and they will be referred to again later.

When each of the metals above mentioned acts upon dilute hydrochloric acid, it is evident, from even a rough observation, that the rate with which the different metals liberate hydrogen varies greatly. Arranging these metals in the order of rapidity with which they react with dilute acid, we have: potassium, sodium, magnesium, aluminum, zinc, iron, and tin, the action being strongest in the case of potassium, and weakest in the case of tin. This gives us an idea of the relative affinity or chemical attraction that exists between these metals and the dilute aqueous solution of the acid used, or rather between the metals and that part of the aqueous acids with which the displaced hydrogen was combined. By measuring accurately, at constant temperature, the rate of the liberation of hydrogen per minute when one and the same area of the different metals acts on samples of the same dilute acid solution, the relative affinities of the metals for the acid may be determined; for, other factors being constant, *the rate with which a chemical reaction proceeds is proportional to the chemical affinity that comes into play.*

REVIEW QUESTIONS

1. Where is hydrogen found in nature?
2. Name six compounds that contain hydrogen.
3. Give four *general* methods for preparing hydrogen in the laboratory.
4. What are the most important properties of hydrogen, and what practical use is made of hydrogen gas?
5. Give two illustrations of the adsorption of hydrogen by solids.
6. What is formed when hydrogen burns in the air? What are the characteristics of the hydrogen flame?
7. What is a hydride? Give three illustrations.
8. Give an illustration of the process of reduction; also one of the process of oxidation.
9. What are the products formed when dilute sulphuric acid acts on zinc? What becomes of these products? Similarly, what are the products formed when aluminum acts on sodium hydroxide and what becomes of them in the experiment?
10. How test a hydrogen generator to ascertain if it is free from air? Why is it necessary to do this?
11. Define the term "hydrogen equivalent," and illustrate by two examples.
12. If the metal used in determining the hydrogen equivalent contained two per cent of insoluble material, would the hydrogen equivalent found by the method shown in Fig. 14 be too high or too low?
13. How many grams of hydrogen could be obtained by the action of 200 grams of iron on an acid? What volume would this gas occupy at 0° C. and 760 mm. pressure? What volume would it occupy at 20° C. and 744 mm. pressure?
14. How many grams of sodium would be required to liberate five liters of hydrogen measured over water at 22° C. and 750 mm. pressure?
15. What volumes of hydrogen and oxygen form the most explosive mixtures of these two gases?
16. How do you account for the disagreeable odor of the gas that is liberated when hydrochloric acid acts upon cast iron? How could you demonstrate that hydrogen gas is quite odorless?
17. When and by whom was hydrogen gas first isolated? How was this gas prepared by its discoverer?
18. What explanation can you give of the following facts: sodium liberates hydrogen from water at room temperatures; magnesium liberates that gas from boiling water; red hot iron liberates it from steam; and gold does not decompose water at all.
19. What peculiar property does metallic palladium manifest toward hydrogen gas, especially when red hot?
20. How do you explain the fact that a candle will not burn in an atmosphere of hydrogen?
21. If materials like fats, oils, and wood will not burn in an atmosphere

of hydrogen, why is it nevertheless not feasible to use the latter gas as a fire extinguisher?

22. Though animals die when left in an atmosphere of hydrogen gas, how could you prove that the latter is not poisonous?

23. Explain how the density of hydrogen may be found by ascertaining how fast the gas flows from a very small orifice.

24. What causes the loud report when a mixture of oxygen and hydrogen gases is brought in contact with a flame or a spark? Give a detailed explanation of each step in the process.

CHAPTER III

OXYGEN

History.— Oxygen was discovered in 1774 by Joseph Priestley, who liberated the gas by heating the red oxide of mercury. It was independently discovered in 1773 by Scheele, but he did not publish his work till 1775. Lavoisier, who found the discovery of the gas of particular interest in connection with his studies of the process of combustion, named the element *oxygen*, from the Greek words meaning acid and to generate. He found that the union of oxygen with such elements as sulphur, nitrogen, and arsenic produced substances that were sour to the taste, and in general behaved like other well-known acids. His conclusion was that oxygen is an essential constituent of all acids, but later work has shown this to be erroneous.

Occurrence.— Oxygen is the most abundant element on the earth. The atmosphere contains about 21 per cent of free oxygen by volume. Water contains 88.88 per cent of oxygen by weight, and the rocks of the earth's crust contain from 44 to 48 per cent. It is present in all animals and plants, in which it occurs in combination with hydrogen and carbon, and also with hydrogen, carbon, and nitrogen.

Preparation.— (1) When liquid air is allowed to evaporate, the nitrogen, which is more volatile than the oxygen, passes off first, and thus a considerable portion of the oxygen is left in the container, approximately free from nitrogen. (2) By electrolysis of water, acidified with sulphuric acid, two volumes of hydrogen and one volume of oxygen are produced. (3) By heating red oxide of mercury, this compound is decomposed, yielding oxygen and mercury; similarly, the oxide of silver may be decomposed by heat. Again, the peroxides of manganese, lead, and barium give off a portion of their oxygen on heating them. The peroxides of these metals also evolve oxygen when heated with sulphuric acid. (4) Certain salts rich in oxygen give off their oxygen content either in part or entirely upon being heated.

Thus, saltpeter yields oxygen and potassium nitrite on ignition, and *potassium chlorate when heated yields oxygen and potassium chloride. The latter method is very commonly used for preparing oxygen for laboratory purposes.* One hundred grams of potassium chlorate yield about 39 grams of oxygen. In the process of heating potassium chlorate, potassium perchlorate first forms, and this upon further heating breaks down into oxygen and potassium chloride. (5) By treating a solution of hydrogen peroxide, acidified with sulphuric acid, with potassium permanganate or potassium bichromate, oxygen is evolved. This method is very convenient for laboratory purposes. (6) When bleaching powder acts on peroxide of hydrogen, oxygen is evolved. (7) Barium oxide when heated in the air to about 500° takes on oxygen, forming barium peroxide. The latter on being heated up to 1000° parts with half of its oxygen, forming the original barium oxide, and the process can then be repeated. This is known as Brin's process. It will be seen that it is a convenient method of preparing oxygen from the air. It is used for preparing oxygen for commercial purposes. (8) The green leaves of plants in the sunlight decompose carbon dioxide and water, forming starch and oxygen. Large quantities of oxygen are thus supplied to the atmosphere.

Properties. — Oxygen is a colorless, odorless, tasteless gas. It is 1.10 times as heavy as air. One liter under standard conditions (0° and 760 mm.) weighs 1.4290 grams. Its power to refract light is only 0.8616 time that of air. The gas may be liquefied at and below −119°, its critical temperature. At −119° a pressure of fifty atmospheres is required to liquefy oxygen. This pressure is consequently the critical pressure. Liquid oxygen is a light blue, mobile liquid which boils at −182.5° under atmospheric pressure. It is attracted by a magnet. At −182.5° the specific gravity of the liquid is 1.1315. By means of liquid hydrogen, Dewar froze oxygen to a pale blue, snowlike solid, whose melting point is − 227°.

Oxygen is slightly soluble in water. At 0° and atmospheric pressure 100 volumes of water dissolve four volumes of oxygen, while at 15°, 3.4 volumes of the gas are absorbed. Oxygen may consequently be collected over water.

Chemically, oxygen is a very active substance combining directly with all known elements, the only exceptions being

fluorine and the gases of the argon group, namely, helium, neon, argon, krypton, and xenon. The compounds of the elements with oxygen are called oxides. At ordinary temperatures, oxygen unites but slowly with most substances. Thus, the rusting of iron consists of a slow union with oxygen of the air. Sodium is oxidized quite rapidly on exposure to air or oxygen at room temperature, while in the case of wood, charcoal, or sulphur, the union with oxygen at ordinary temperatures proceeds very slowly indeed. However, at elevated temperatures all of these substances combine readily and vigorously with oxygen, with concomitant evolution of heat and light. This process is termed **combustion**. All chemical processes which proceed with the evolution of light and heat may, in general, be called cases of combustion; ordinarily, however, the term is applied to union with oxygen. In an atmosphere of the latter gas, iron will burn with brilliant scintillations (Fig. 15) and evolution of much heat. The product formed is an oxide of iron of a reddish brown color.

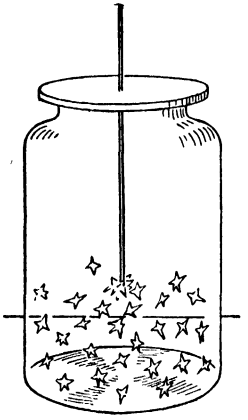


FIG. 15.

Phosphorus burns brilliantly in oxygen, forming phosphoric oxide, consisting of white fumes which condense on the sides of the container. On moistening this white solid with water, a solution of phosphoric acid is formed. This solution is sour and turns blue litmus red. Carbon burns in oxygen to carbon dioxide; sulphur burns to sulphur dioxide (Fig. 16). These gases, too, form acids when treated with water. The oxides of phosphorus, carbon, and sulphur are consequently acid-forming oxides. They are also spoken of as acid anhydrides; that is, the acids minus water.

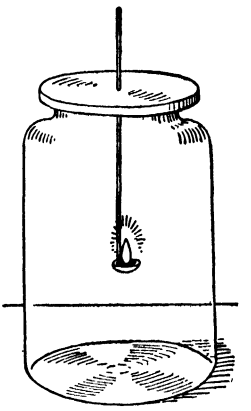


FIG. 16.

Sodium when burned in oxygen forms a white powder, called sodium oxide, which readily dissolves in water, yielding a solution which is alkaline to the taste, turns red litmus blue, and

feels slippery to the fingers. It is an alkali or base, and is capable of reacting with acids, forming salts whose aqueous solutions have no effect on litmus, *i.e.* they are neutral. Potassium and calcium also burn readily in oxygen, forming the oxides of potassium and calcium. These are white caustic substances which resemble the oxide of sodium. The oxide of calcium is ordinary lime. The oxides of potassium and calcium are caustic alkalies. Other oxides, like those of zinc, iron, and lead, are insoluble in water. They are consequently tasteless and do not affect litmus. The oxides of most metals can be formed by direct union with oxygen. Some metals, like gold and platinum, do not burn in oxygen, but their oxides may be formed indirectly by double decomposition. On heating such oxides, they yield the metal and oxygen.

Combustion in the Air. — The combustion of substances in the air yields precisely the same products as combustion in oxygen. Indeed, the process of burning substances in the air is in all respects, except in brilliancy, rapidity, and vigor, like that of burning them in oxygen. As the oxygen of the air is diluted with four times its volume of nitrogen, which latter gas is rather inert in character, it is quite natural that combustion in the air should go on less vigorously than in oxygen. The total energy liberated as heat is the same, however, whether the oxidation of a substance takes place rapidly in pure oxygen, or less rapidly in the air, or extremely slowly at ordinary temperatures in the air.

Kindling Temperature and Temperature of Combustion. — In order to burn a substance in oxygen, it must be heated to a certain minimum temperature at which it will burst into flame. This temperature, which is very different for different substances, is called the kindling temperature. Thus, phosphorus catches fire at a much lower temperature than sulphur, and the latter ignites at a lower temperature than wood.

The highest temperature attainable during the process of combustion of a substance is sometimes called the temperature of combustion. It varies greatly with the nature of the substance. It is higher in pure oxygen than in air, and higher in compressed oxygen than in that gas at atmospheric pressure. The temperature of combustion is generally very much higher than the kindling temperature.

Heat of Combustion. — The heat evolved during the combustion of a substance is called its heat of combustion. As above stated, it is the same whether the combustion goes on rapidly or slowly, though the maximum temperature reached during the process of combustion varies greatly under different conditions.

The unit of heat is the calorie. The small calorie is the amount of heat required to raise 1 gram of water 1 degree; the large calorie is 1000 times as large, *i.e.* it is the amount of heat required to raise 1000 grams of water 1 degree in temperature. It is very important to ascertain the heat of combustion of various substances, not only for purely scientific purposes, but also for the determination of the relative value of fuels and certain classes of food. Heats of combustion will consequently receive special consideration in the chapter on thermochemistry.

Different Stages of Oxidation. — While it is true that combustion in the air or in oxygen is essentially the same process, except as to rapidity, it not infrequently happens that when a substance is burnt in an excess of oxygen, more of the latter enters into the oxides formed than when the burning proceeds in the air. Thus, when iron is oxidized by heating it in the air, a black oxide is formed which is magnetic in character, and which consists of 72.38 per cent iron and 27.62 per cent oxygen; whereas when iron is burned in oxygen, there is formed mainly a reddish brown oxide of iron which is practically non-magnetic, and which contains 69.96 per cent iron and 30.04 per cent oxygen. By carefully heating the latter oxide in a current of hydrogen at 500° a black oxide may be obtained which consists of 77.75 per cent iron and 22.25 per cent oxygen. Writing the composition of these oxides of iron, the only ones known, in form of a table, we have as follows: —

Per Cent Iron	Per Cent Oxygen	Parts Oxygen to 77.75 Parts Iron
(1) 72.38	27.62	29.67
(2) 69.96	30.04	33.38
(3) 77.75	22.25	22.25

In the third column are placed the amounts of oxygen by weight combined with one and the same amount of iron; namely,

77.75 parts. The latter figure was chosen simply for convenience, as it represents the percentage of iron in the oxide poorest in oxygen. Now, inspecting the table, we see that

$$29.67 : 22.25 = 4 : 3,$$

and that

$$33.38 : 22.25 = 3 : 2.$$

This means that in these three different oxides of iron the amounts of oxygen that are combined with one and the same amount of iron are simple, rational multiples of one another This being the case, had we calculated the amounts of iron combined in these oxides with one and the same amount of oxygen, we should have found that these amounts of iron are also simple, rational multiples of one another.

Again, there are five different oxides of lead known. These are as follows: (1) lead suboxide, a black substance formed when lead is heated at its melting point in the air; (2) litharge, a yellow powder formed when lead is very strongly heated in air; (3) lead sesquioxide, an orange-yellow powder formed when bleaching powder acts on litharge dissolved in caustic potash; (4) red lead or minium, a bright red powder, which may be obtained by heating litharge in the air at a temperature not above 450°; and (5) lead peroxide, a brown powder, which may be prepared by treating red lead with dilute nitric acid. The percentage composition of these oxides is as follows: —

Name	Per Cent Lead	Per Cent Oxygen	Parts Lead to 3.72 Parts Oxygen
(1) Lead suboxide . . .	96.28	3.72	96.28
(2) Litharge	92.82	7.18	48.14
(3) Lead sesquioxide . .	89.61	10.39	32.09
(4) Red lead	90.65	9.35	36.11
(5) Lead peroxide . . .	86.60	13.40	24.07

In the last column we have the amount of lead combined with 3.72 parts of oxygen in each of the oxides. Comparing the figures in the last column we note as follows: —

(1) and (2) $96.28 : 48.14 = 2 : 1,$
(1) and (3) $96.28 : 32.09 = 3 : 1,$
(1) and (4) $96.28 : 36.11 = 8 : 3,$
(1) and (5) $96.28 : 24.07 = 4 : 1.$

Thus we see that in the five oxides of lead, the amounts of lead combined with one and the same amount of oxygen are simple multiples of one another. Obviously the amounts of oxygen which in these oxides are combined with one and the same amount of lead are also simple multiples of one another.

Law of Multiple Proportions. — These results of the quantitative study of the composition of the oxides of iron and lead are typical of a large number of similar cases. It has been found to be general, that *whenever two elements form more than one compound with each other, the amounts by weight of the one that are united with one and the same weight of the other are simple rational multiples of one another.* This is the law of multiple proportions. It was discovered by John Dalton about 1806. Many careful analyses of various compounds have since yielded results confirming this law, which is of fundamental importance in chemistry. As we proceed, we shall meet numerous additional instances illustrating the law of multiple proportions.

Rôle of Oxygen in Respiration. — Oxygen is necessary for all animal life. If the oxygen supply is cut off from an animal, it soon dies from suffocation. Pure oxygen may be inhaled without evil effects for a while. An animal placed in oxygen shows invigoration by its more lively movements; but after a while febrile symptoms appear, and a reaction sets in which may cause death. The air as it enters the lungs is virtually oxygen diluted with four times its volume of nitrogen. It is the oxygen only that is absorbed by the membranes of the lungs. Furthermore, only 4 to 5 per cent of the oxygen contained in the air is thus absorbed in the process of respiration. The exhaled air contains water and also about 3 to 4 per cent of carbon dioxide, gained from the body.

The oxygen from the air passes through the membranes of the lungs, into the blood, where it is taken up by the blood corpuscles. The latter contain hemoglobin, a crystalline substance which unites with oxygen, forming oxyhemoglobin, which has a red color, giving a bright appearance to arterial blood. As oxyhemoglobin attached to the blood corpuscles, the circulation carries the oxygen to all parts of the body, where it is given off, entering into various combinations with the tissues. As the blood is thus deprived of oxygen, carbon dioxide, which is formed during the oxidation of the tissues, is

taken up and carried to the lungs, where it is exhaled and exchanged for oxygen. The blood deprived of a portion of its oxygen and laden with carbon dioxide is so-called venous blood. It is dark in color instead of bright red. On discharging its carbon dioxide and taking on oxygen, it is converted into so-called arterial blood, which is bright red. All of these processes go on much more rapidly and vigorously in an atmosphere of pure oxygen than in air. It is for this reason that animals succumb in oxygen; they are destroyed by the too rapid changes. On the other hand, if the supply of oxygen is unduly diminished, the transformations described, which are necessary for life, cannot go on and the animal dies of suffocation. As stated above, pure oxygen may be breathed for a time; it is frequently administered to patients who are suffering depression because of difficulty experienced in breathing.

Fishes derive their supply of oxygen by means of their gills from the oxygen dissolved in the water.

In the respiration of plants, carbon dioxide is taken up by the green leaves in the sunlight, and oxygen is exhaled. In the leaf, starch is simultaneously formed, as carbon dioxide and water act on each other with elimination of oxygen. Thus, while animals are using up oxygen in breathing and are giving off carbon dioxide, plants are taking up the latter gas and returning oxygen to the air.

Oxyhydrogen Blowpipe. — When a jet of hydrogen is burned in the air, a high temperature is developed; this may be

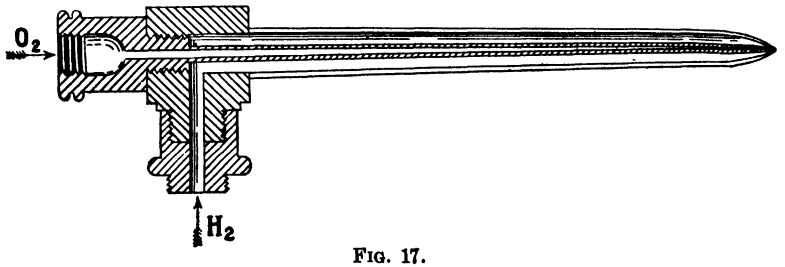


FIG. 17.

further increased by burning the jet in oxygen, or by supplying oxygen to the jet of hydrogen as it burns. The oxyhydrogen blowpipe (Fig. 17) is an arrangement for securing very high temperatures. As a rule the burner is made of brass. Hydrogen passes in as shown and issues at the tip, where the jet is

lighted. Oxygen is then passed in as indicated, and thus the gases do not mix except in the jet itself. In this way explosions are avoided. The oxyhydrogen flame readily fuses platinum or silica, and is used in working such refractory materials. When the jet is directed against a piece of lime, the latter is heated to incandescence, producing a very intense white light, known as Drummond's lime light. This is used at times in projection lanterns, and for signaling purposes where a very intense light is required.

Detonating Gas. — We have seen that when water is decomposed by electrolysis, two volumes of hydrogen and one volume of oxygen are produced. A mixture of these two gases in the proportions mentioned is highly explosive when ignited, for water is formed which, by the intense heat generated, is at once converted into steam, thus producing the explosion. The explosive character of oxyhydrogen gas may be demonstrated in a harmless way by making soap bubbles filled with the gas and then igniting them. Not too large a quantity of the gas should be exploded at once in a room, for the report is very loud and may rupture the eardrum.

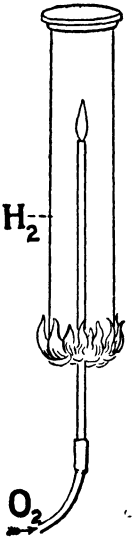


FIG. 18.

Combustion of Oxygen in Hydrogen. — It has been mentioned that a jet of hydrogen will burn in an atmosphere of oxygen, developing intense heat. It is equally possible to burn a jet of oxygen in an atmosphere of hydrogen (Fig. 18). The hydrogen is first lighted at the mouth of the cylinder, and a jet of oxygen is then introduced. It ignites and continues to burn in the atmosphere of hydrogen as shown. The fact that either of these two gases may be burned in an atmosphere of the other shows the real nature of combustion, which consists of a chemical union of the two gases. The product formed is, of course, water in either case.

Earlier Views of Combustion. — That the combustion of substances in the air is a process of oxidation was not recognized till Lavoisier showed it to be true by experiment. Before Lavoisier, the view prevailed that when a substance is burned a subtile principle flies out of it. This notion dates back to antiquity. It was probably suggested by

the rising of the smoke of ordinary fires. It was Georg Ernst Stahl (1660–1734), professor of medicine at the University of Halle, who first formulated a definite theory of combustion. He called the subtile principle, which he assumed flies out of bodies on burning them, **phlogiston**, which means that which is combustible. So, for instance, when mercury is heated in the air to 500° a red powder results, which, according to Stahl's view, would be dephlogisticated mercury. Similarly he looked upon other oxides as bodies that had been deprived of phlogiston. Anything that was combustible contained phlogiston. Thus carbon was considered very rich in phlogiston. By heating, for example, dephlogisticated lead (yellow oxide of lead) with carbon, the latter would give off phlogiston to the yellow powder and thus change it back to lead. In general, what we now term oxidation was regarded as dephlogistication, and what we call reduction was regarded as a process of taking on phlogiston. The phlogistic theory dominated chemistry in the eighteenth century; and, indeed, many chemical changes, and among them rather complicated ones, could in a way be explained by means of the theory. In fact, Cavendish, Priestley, and Scheele adhered to the phlogistic theory.

It was known to the adherents of the phlogistic view that when metals are calcined by heating them in the air, the resulting powder is heavier than the original metal. In fact, this was known even a hundred years before the phlogistic theory was promulgated; but it was not regarded as an especially vital fact in forming a correct view of combustion. It was not an age of careful quantitative experimentation, and the value of facts established by accurate measurements was frequently not seriously considered. And so it was that when Lavoisier pointed out that metals grow heavier when burned in the air, and argued that this means that something is added to the metal rather than subtracted from it during the process, his argument did not meet with favor, even on the part of the discoverers of oxygen themselves. The adherents of the phlogistic view argued that the fact that substances increase in weight when burned could not serve to prove that something, namely phlogiston, might not also fly out of the substances during the process of combustion. In order to explain the fact that substances grow heavier when burned, some of the followers of Stahl even

suggested that phlogiston might be a substance of negative weight.

Antoine Laurent Lavoisier (1743–1794), the founder of modern chemistry, laid great stress upon the increase in weight of substances during combustion, and when oxygen was discovered by Scheele and Priestley he actually demonstrated that it is this gas which unites with bodies when they are burned in the air. Thus, he heated a quantity of mercury in a retort (Fig. 19) in contact with air for twelve days. The end of the

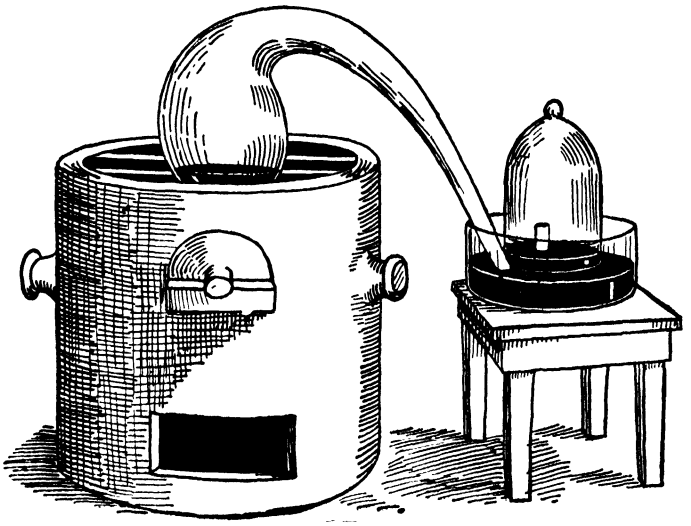


FIG. 19.

retort opened into a bell jar, the opening of which was shut off from the outer air by means of mercury, as shown. The total volume of the air in the retort and bell jar was about one liter. After the apparatus had cooled, it was found that a diminution of volume of the air in the apparatus amounting to about 170 cc. had taken place. From the calcined mercury, which he collected, he obtained 160 cc. oxygen by heating; and thus he showed by synthesis and analysis the real nature of calcined mercury. He further demonstrated that carbon unites with the oxygen of certain metallic oxides when heated, and that thus the metal itself is prepared by subtraction of oxygen from the calcined metal rather than by the addition of phlogiston to it. The views of Lavoisier were stoutly opposed by the follow-

ers of the phlogistic theory. However, facts began to increase in favor of Lavoisier's explanations, and when Cavendish showed that water is formed when hydrogen and oxygen unite chemically, the former's views soon triumphed. Whereas the followers of phlogiston regarded the metals and other combustible elements as compound bodies containing phlogiston, we now look upon them as simple bodies capable of uniting with oxygen under proper conditions.

REVIEW QUESTIONS

1. State how oxygen occurs in nature.
2. Make a list of five different methods of preparing oxygen in the laboratory, stating which of these methods is most commonly employed.
3. What are the important properties of oxygen?
4. What is combustion? What phenomena accompany this process? Give an illustration.
5. Define: kindling temperature, oxide, phlogiston, heat of combustion.
6. How does combustion in the air differ from combustion in oxygen? Illustrate.
7. State the law of multiple proportions and illustrate it by means of an example.
8. What is the relation of oxygen to animal life? To plant life?
9. What led to the overthrow of the phlogiston theory?
10. Why does painting an iron bridge or polishing a stove prevent rusting?
11. How many tons of oxygen are there in ten tons of water?
12. Compare the chemical and physical properties of hydrogen and oxygen; also the methods of preparing these gases.
13. What important views did Lavoisier introduce into chemistry, and upon what experiments were these views founded?
14. Who discovered oxygen? How did he prepare this gas?

CHAPTER IV

WATER

Occurrence.— Water is found in oceans, lakes, and rivers, in the soil and in the atmosphere. It occurs in the solid, liquid, and vapor states. As snow and ice it covers the vast fields of the polar regions, the highest mountain peaks, and, during the winter, large areas of the temperate zones. Falling in form of rain, snow, and hail, water permeates the soil and forms springs, lakes, and rivers that carry it to the sea. In the atmosphere, it exists as vapor which by condensation may form fogs and clouds. The amount of aqueous vapor that the air may hold varies with the temperature. One million liters of air saturated with water vapor at 0° contain 4800 grams of water, while at 20° and at 30° this amount of air will take up 17,000 and 29,840 grams of water, respectively. Ordinarily, air is saturated with water vapor to but two thirds of its capacity. When the moisture content of the air reaches but four tenths of its capacity, the air feels dry, whereas it requires nearly double this amount of humidity to cause the sensation of dampness. In all plants and animals, water is found in relatively large quantities. Usually organisms are made up of over fifty per cent of water. Many minerals, salts, and manufactured products contain water more or less loosely bound.

Preparation. — Water is formed not only when hydrogen and oxygen gases unite, but also when hydrogen acts on various oxides at high temperatures, and when compounds containing hydrogen are oxidized. It forms during the process of the oxidation of the tissues of organic beings, and together with carbon dioxide is exhaled by animals. All natural waters are, chemically speaking, impure. Rain water is the purest of natural waters, but even this contains air, dust, and not infrequently estimable amounts of nitrites and nitrates of ammonium. All water that has been in contact with the soil contains some of the ingredients of the latter in solution. On evaporating

off the water, these dissolved ingredients, which are in the main salts of various kinds, are left behind as a residue. The amount of material taken up from the soil by water varies very greatly with the nature of the soil. Thus from soil formed mainly from the disintegration of granite rocks, relatively small amounts of material are dissolved, whereas, from limestone soils large quantities enter into solution. By distilling natural waters, they may be freed from the dissolved, non-volatile ingredients. In this way pure water may be obtained. The process consists of boiling the water in a retort and condensing the steam formed (Fig. 20). In this process the condenser is,

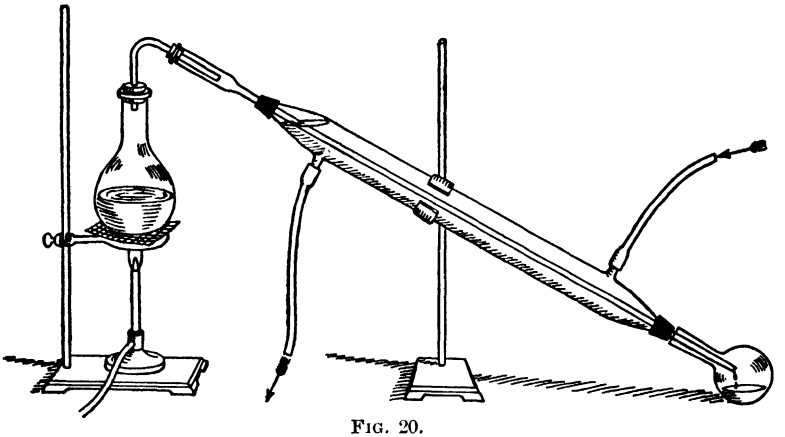


FIG. 20.

of course, always dissolved to a slight extent. The material of which it is constructed is somewhat soluble in water. Thus glass condensers are always somewhat attacked by water, though not sufficiently so to make the distilled water unfit for ordinary purposes. When a very pure water is desired, a block tin, or, still better, a platinum condenser, is used. On boiling water, the dissolved gases it contains are almost completely expelled. Distilled water tastes flat; whereas natural waters, which contain air, have a refreshing taste.

Natural Waters. — The solid ingredients in natural waters vary greatly in character and amount. In oceanic waters there is about 3.5 per cent of solid material, of which 2.7 per cent consists of common salt, and the remainder mainly of chlorides and sulphates of magnesium, calcium, and potassium, together with smaller amounts of the bromides and carbonates of these

metals. Some thirty elements occur in oceanic waters, most of them in very minute amounts. The water of the Dead Sea contains 22.8 per cent of saline matter and that of Great Salt Lake in Utah 23.04 per cent. Fresh water as we find it in rivers and many lakes usually contains from 0.005 to 0.15 per cent of solid material, and deep well water averages from 0.01 to 0.4 per cent. The amount of salts contained in the waters of springs and wells varies greatly with the character of the strata of the earth's crust with which the water has been in contact. Sandstone and granitic material is less attacked by water than soils rich in the carbonates of lime and magnesia; consequently, springs and wells in limestone regions contain much more solid material in solution than those where sandstone and granitic rocks abound. Rain water is really distilled water; though as it falls through the atmosphere it gathers dust and dissolves the atmospheric gases. If water is gathered during a shower, that which falls after a time is much purer than that which first falls to earth. This is due to the fact that the air is fairly well washed during the earlier part of a copious rainfall. Waters containing a large amount of calcium salts are called hard waters. They do not form a lather with soap, and do not soften vegetables properly when these are boiled in such water. Furthermore, these waters produce a hard sediment consisting mainly of carbonate of lime which clogs up cooking utensils, boilers, and pipes. The purification of hard waters will be considered in connection with the salts of calcium.

Potable Water. — For ordinary drinking purposes, water should be colorless, odorless, tasteless, and free from materials that may prove to be deleterious to health. The mineral ingredients commonly found in waters from springs, wells, brooks, rivers, and lakes are not injurious to the system. It is when these sources are contaminated by sewage, which very frequently gets into them, that the waters become dangerous to health; for the organic animal and vegetable material in decomposing develops products which may be injurious, and often affords a place for the growth of bacteria that cause disease. For this reason, any water that clearly shows that it has been contaminated by sewage is pronounced dangerous to health.

It is clear that a bacteriological examination ought to accom-

pany a chemical examination of a drinking water, for injurious organisms may be present in water even though the sewage contamination be so slight that a chemist would pronounce the water fit to drink. As common salt and organic matter and its decomposition products, especially nitrites and nitrates of ammonium, characterize sewage, the determination of the amounts of these ingredients forms the chief task of the chemist in analyzing a potable water. The air dissolved in natural waters renders it refreshing. As boiling kills the disease germs in water, it is frequently resorted to, especially in large cities, in cases of epidemics caused by contaminated water. The process of boiling expels the gases dissolved in the water and renders it insipid to the taste. Thus wholesome drinking water is not at all chemically pure water. The latter is not even common in chemical laboratories, for ordinary distilled water, though free from non-volatile ingredients, still contains carbon dioxide, air, and not infrequently ammonium salts in solution. These impurities are not of consequence, however, for ordinary purposes.

Very frequently, river and lake water must be used for drinking purposes, even though it is somewhat contaminated by sewage. These waters must then be subjected to purification, which commonly consists of filtration through beds of sand and exposure to the air, the oxygen of which being absorbed by the water, oxidizes the organic material to simpler products that are comparatively harmless to the human system. The filters, of course, must be renewed from time to time, for the organic material collects in them and thus they may after a while themselves become a source of contamination. On a small scale, the Pasteur-Chamberland water filter is entirely efficient in freeing water from suspended matter and bacteria. This filter consists of unglazed porcelain, generally in form of a tube closed on one end, which is attached to the ordinary water cock. The water thus filters through the pores of this unglazed porcelain under the pressure of the waterworks system.

Mineral Water. — Waters containing special mineral ingredients or dissolved gases are frequently used for medicinal purposes. Among the mineral waters are distinguished : (1) bitter waters that are rich in magnesium salts ; (2) chalybeate waters that contain iron salts ; (3) sulphur waters which con-

tain hydrogen sulphide; (4) carbonated waters which are charged with carbon dioxide so that they effervesce; (5) lithia waters containing lithium salts. Thermal waters are those which have a higher temperature than the surrounding atmosphere. They frequently also contain special mineral ingredients which are considered valuable for therapeutic purposes.

Composition. — Chemically pure water is a compound of oxygen and hydrogen, two volumes of the latter uniting with one volume of the former to form water. By weight water consists of 88.864 per cent oxygen and 11.136 per cent hydrogen. Knowing that by the electrolysis of water two volumes of hydrogen and one volume of oxygen are produced, and having found the weight of a liter of hydrogen and that of a liter of oxygen, the composition of water by weight can readily be computed.

When hydrogen is passed over copper oxide heated to a dull redness, the oxide is reduced to metallic copper and water is formed. Consequently, by heating a known amount of dry copper oxide in a tube, in a current of dry hydrogen, and collecting and weighing the water formed, and also weighing the metallic copper obtained, the percentage composition of water may be computed. Obviously, the loss of weight of the copper oxide represents the oxygen that has entered into combination in the water formed; and the difference between the weight of the latter and the oxygen given off by the copper oxide is the weight of the hydrogen in the water produced. This method of determining the composition of water was used by Dulong and Berzelius in 1819. It was also employed by Dumas in 1842 with greater refinements.

The researches on the composition of water have yielded the result that for each gram of hydrogen, water contains 7.94 grams of oxygen; that is to say, the ratio of hydrogen to oxygen in water is nearly 1 to 8.

Gay-Lussac's Law of Combination of Gases by Volume. — When two volumes of hydrogen and one volume of oxygen unite chemically, and the water formed is not allowed to condense to the liquid state, it is found that the steam obtained occupies two volumes, measured, of course, at the same temperature and pressure as the oxygen and hydrogen. To demonstrate this, the apparatus of Hoffman (Fig. 21) is convenient. The inner

long eudiometer tube *A* is filled with mercury and then inverted in the mercury bath *B*. Thus, a Torricelli vacuum is formed in *A*, whose upper end is provided with a pair of plati-

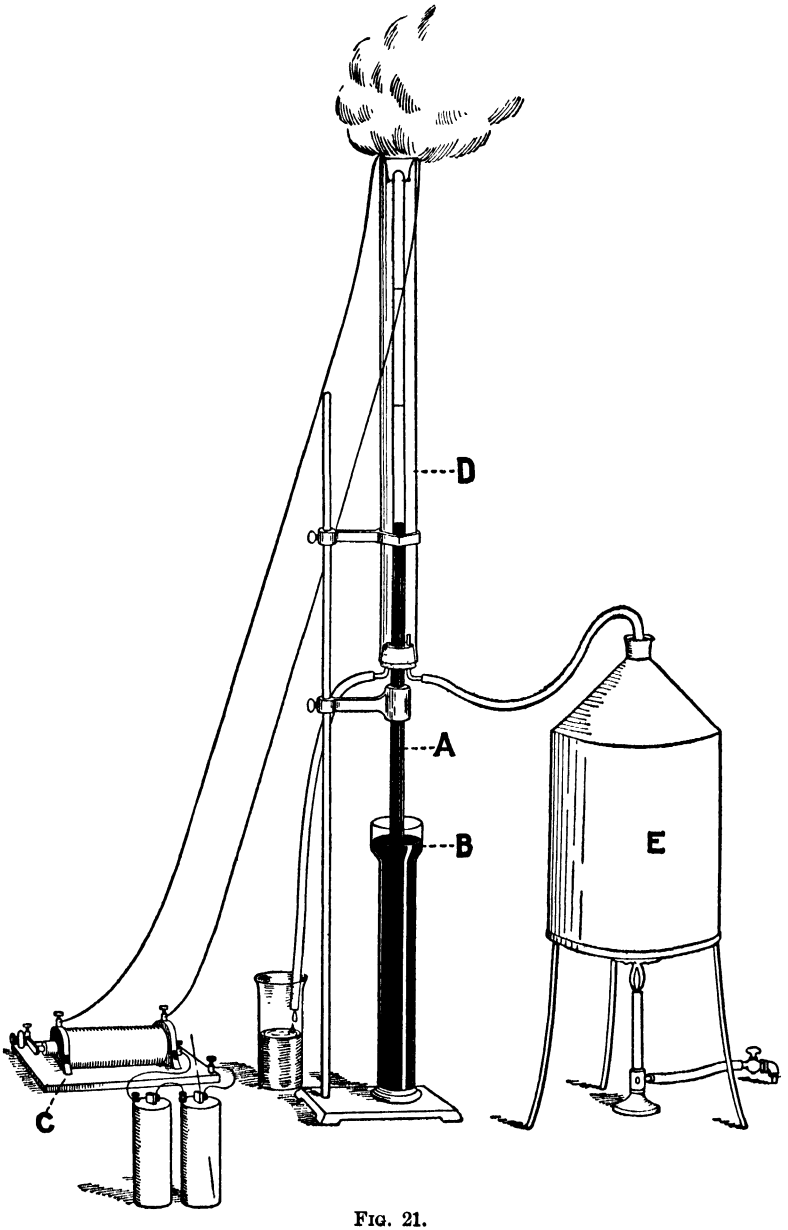


FIG. 21.

num terminals, across which an electric spark may be passed by connecting with the induction coil *C*. The eudiometer tube *A* is placed inside of the larger tube *D*, which is filled with steam from the boiler *E*. By this means the eudiometer tube is heated to the boiling point of water. If now a mixture of two volumes of hydrogen and one volume of oxygen is introduced into the eudiometer tube *A*, the volume carefully noted, and then the mixture is exploded by passing the electric spark, the resulting water vapor will be found to have two thirds of the volume of the mixture of the oxyhydrogen gas introduced, when the level of the mercury in the eudiometer has been restored to its original place. Therefore, *two volumes of hydrogen and one volume of oxygen unite to form two volumes of water vapor.* This very simple relation is typical of the volume relations in general which have been found to obtain when gases combine chemically. Expressed in general terms we may say: *When gases combine chemically with one another, the volumes that unite bear a simple relation to one another; and if the product formed be gaseous, its volume also bears a simple relation to the volumes of the original gases that have entered into combination.* This law was discovered by Joseph Louis Gay-Lussac, professor of chemistry at the Sorbonne, Paris. We shall meet with further specific illustrations of this law, which is known as the **law of Gay-Lussac of combination of gases by volume.** It is of great importance in chemistry, as will appear in the succeeding chapters.

Properties of Water. — In thin layers, pure water is colorless, but in deep layers it has a greenish blue color. This explains the beautiful hue of the waters of the sea and many lakes. River waters are commonly brownish in color, due to the humus material which they contain from the soils through which they have coursed. The freezing point of water is taken as the zero of the centigrade scale, and the boiling point under a pressure of 76 cm. of mercury is taken as the 100° point of that scale. At and below 360° C water may be condensed to a liquid; above this point, which is the critical temperature, water is a gas which cannot be condensed to a liquid even though very high pressures be applied.

Like liquids in general, water is but slightly compressible. Thus, by placing a liter of water at 20° under a pressure of two

atmospheres its volume is diminished only by 0.046 of a cubic centimeter. The volume of a given weight of water varies with the temperature. Water expands in volume when heated above 4°, and also when cooled below that temperature to its freezing point. Water, therefore, has its maximum density at 4°. Most substances show a continuous diminution in volume when cooled. The fact that water expands when cooled below 4° is therefore a very exceptional behavior. At 4° a cubic centimeter of water weighs one gram. Water at its maximum density is commonly taken as the standard liquid with which the weights of equal volumes of other liquids and solids are compared. In other words, water at 4° is the standard of comparison of the specific gravities of liquids and solids. At 100° the volume of water is about 4.3 per cent greater than at 0°.

The amount of heat required to raise the temperature of one gram of water one degree is called a calorie (cal.); it is the unit used in the measurement of heat. It requires 80 cal. to transform one gram of ice at 0° to water of the same temperature; *i.e.* the latent heat of fusion of ice is 80 cal. To convert one gram of water at 100° into vapor of the same temperature requires 537 cal., which is the so-called latent heat of evaporation of water. The specific heat, the latent heat of fusion, and the latent heat of evaporation of water are very high indeed, as compared with similar constants of most other substances.

When water freezes it expands, and the ice at 0° occupies 1.0908 times the volume of the water at the same temperature. This behavior of water is again unusual, for most substances contract during the act of congealing, thus forming a solid that is heavier than the liquid. The fact that water increases in volume as it solidifies is an important factor in the disintegration of rocks, for the force exerted by water in freezing is enormous. The bursting of frozen water pipes and other containers in winter is also due to the expansion of water in freezing. But the fact that ice is lighter than water is of further importance in nature; for were it not for this, many of our lakes and rivers would freeze to the bottom in winter, and thus fishes and other organisms in these waters would be destroyed. The huge masses of ice that would accumulate in winter also would

materially reduce the temperature for the remainder of the year.

Supercooled Water. — Ice melts at 0°, but when water is cooled to 0°, it does not necessarily freeze. In fact, water may be cooled several degrees below zero and still be liquid. Water in this condition is said to be supercooled, or in a metastable condition. If water thus supercooled is brought in contact with a piece of ice, the whole mass freezes to a solid. If supercooled water is cooled still further, a point is finally reached at which it will congeal without being touched with ice. Supercooled water may be kept in the liquid condition for a long time. Sometimes shaking, jarring, or brisk stirring induces freezing of supercooled water, but this is not necessarily the case. The lower the temperature of the metastable water, the more likely is jarring to induce ice formation. However, touching supercooled water with ice, always causes freezing.

The freezing point and the melting point of water are the same; namely, 0°. This is the temperature at which ice and water are in equilibrium with each other at ordinary pressure. Raise the temperature above 0° and all ice disappears; cool below 0° in the presence of ice and the whole mass freezes; *i.e.* liquid water disappears. Similarly, *the freezing or melting point of any solid is an equilibrium temperature at which the solid and liquid can exist side by side in contact with each other without change.*

Change of Freezing Point with Pressure. — The freezing point of ice is altered by change of pressure. Since water expands on congealing, an increase of pressure on its surface would make it more difficult for ice to form. In other words, we should then have to cool water under pressure to a lower temperature in order to freeze it; or what comes to the same thing, ice under pressure melts at a lower temperature than at ordinary pressure. Substances which do not expand, but contract as they congeal, act just the opposite from water in this respect when put under pressure; *i.e.* increase of pressure causes them to freeze at a higher temperature, the increase of pressure aiding contraction which accompanies the solidification in these cases.

These instances of the alteration of the freezing point of substances with increase of pressure are illustrations of a far-

reaching principle which may be stated as follows: *When chemical or physical equilibrium exists, and one of the factors upon which it depends is altered, a change is produced which opposes the first alteration.*

This is known as the **principle of Le Chatelier,** who first enunciated it. Thus increase of pressure upon any solid or liquid tends to diminish its volume. When ice and water exist in equilibrium at 0° and the pressure is increased, the ice melts, which process is accompanied with a diminution in volume, which has a tendency to lessen the pressure. In the case of increase of pressure upon solid and liquid tin in equilibrium with each other at the melting point of tin, the liquid tin will congeal, for thus contraction is brought about and consequently the pressure exerted upon the tin is lessened. The principle of Le Chatelier is of far-reaching importance, and we shall have further examples of it later.

Crystalline Nature of Ice. — When water solidifies, it tends to take on regular forms. This is evident from the frost on the windows, from the shapes of snowflakes, and the radial structure of ice. The needles that form as ice congeals tend to arrange themselves so as to form angles of 60°. These forms are most perfect perhaps in the case of snowflakes, which as they fall on a still day are frequently quite large and perfect.

Water crystallizes in the hexagonal system, which is one of the six systems into which all known crystals may be divided (see Crystal Systems). Not only do crystals exhibit outward regularity of form, but they also show different degrees of hardness, tenacity, refrangibility, light absorbing power, etc., in different directions. We therefore distinguish crystalline substances, which show these characteristics, from amorphous substances, which do not have regularity of form and which exhibit the same properties irrespective of the direction through them. Ice is a typical crystalline substance, while glass is a typical amorphous substance. Amorphous means without form. Crystalline substances commonly have a definite melting point and definite solubility, while amorphous substances do not.

Thus glass has no definite temperature at which it melts. It softens when heated and gradually passes through all stages

of gradations to the liquid state on further heating. Not so with water, for it has a sharp melting point at 0°. Many definite chemical compounds tend to form crystals; and since the same compound tends to take on the same shape under given conditions, the study of crystallography is of value to the chemist in aiding him in purifying and identifying substances. However, many definite chemical compounds have never been obtained in the crystalline condition.

Compounds with Water. — Many salts, like copper sulphate, Glauber's salt, and Epsom salt, crystallize with water. The water in these salts is spoken of as *water of crystallization.* On exposure to the air, some of these salts lose a portion of this water of crystallization and become opaque or crumble to a powder. They are said to *effloresce.* Other salts, like calcium chloride, have such a strong attraction for water, that on exposure to the air they take on water from the air and finally become completely dissolved. They are said to *deliquesce.* Substances that have attraction for water are also called *hygroscopic.* Concentrated sulphuric acid, phosphorus pentoxide, calcium chloride, lime, and caustic potash are strongly hygroscopic. Gases passed over these are deprived of their moisture, and many solids left with them for a time in a confined space are dried or desiccated. A typical form of desiccator is shown in Fig. 22. The strongly hygroscopic substance is placed in the bottom of the vessel, and the substance to be dried is placed on the support in the upper part of the apparatus. Through the cock the air can be exhausted from the apparatus and thus the drying process be aided still further. Such desiccators are frequently used in chemical work, for many substances like glass, porcelain, and even metallic utensils attract moisture and form a film of it on their surface. This film varies in thickness and weight with the degree of humidity of the atmosphere. In accurate quantitative experiments it is

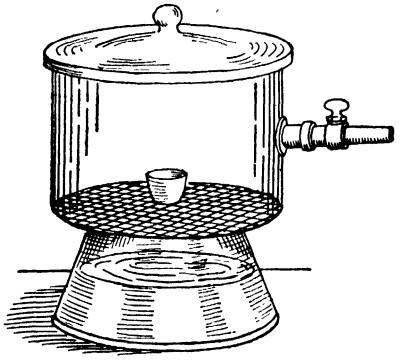


FIG. 22.

necessary to eliminate this film of moisture, and for this purpose desiccators are commonly used. If permissible, the objects are heated to drive off moisture, and then cooled in the desiccator. If heating is not permissible in a given case, the substance is introduced into the desiccator and kept there for a longer time, frequently in a vacuum. It is evident that in a desiccator, the drying material used must have a greater affinity for water than the substance to be dried.

When water simply adds itself to another compound, the product is commonly termed a *hydrate*. Such hydrates are quite common; thus ferric chloride forms several hydrates with water, which follow the laws of definite and multiple proportions.

When oxides unite with water, or when a metal like sodium acts on water, crowding out a portion of its hydrogen, the product formed is commonly termed an *hydroxide*. In these cases it is always possible to regard the resulting substance as water in which a portion of the hydrogen has been replaced by another element. So when lime and water act on each other they unite and form slaked lime, which is hydroxide of calcium. Caustic potash, which may be formed by the action of potassium on water, with concomitant evolution of hydrogen, is potassium hydroxide.

Water as a Solvent. — Many substances are soluble in water. Indeed, of so many is this the case that water has at times been termed a universal solvent. There are, however, very many compounds that are not soluble in water. In general, the ordinary acids, alkalies, and salts used in the chemical laboratory are soluble in water to a greater or lesser degree. The rocks of the earth's crust are all soluble to some extent, though to a very slight degree in some cases; yet this slight solubility of rocks is of the highest importance to plants whose rootlets are thus able to take up mineral matter needed for their economy and growth. In geological transformations, such as the weathering of rocks, the formation of soils, and the deposition of ores, this slight solubility is nevertheless the determining factor, without which these processes could not proceed.

Fats, waxes, oils, and kindred substances are generally not soluble in water. Yet many of these have some degree of

attraction for water, which is shown by the fact that they are often slightly hygroscopic. And again, in the bodies of plants, and particularly in those of animals, fatty material is very closely associated with tissues which are rich in water. So that although fats are generally not soluble in water to speak of, yet in many cases there is evidence that some degree of attraction between them and water does exist. Solutions will receive further consideration later.

REVIEW QUESTIONS

1. Describe three different methods of demonstrating that water consists of hydrogen and oxygen and nothing else.

2. What impurities are found in rain water? In well water? In ocean waters?

3. What impurities are removed from a natural water by the process of distillation? Why are natural waters never pure?

4. (*a*) Mention the essential characteristics which every good drinking water ought to possess.

(*b*) What tests must be made to ascertain whether a water is fit to drink?

(*c*) Why is it well to boil contaminated water before drinking it?

5. What impurities are removable from water by the process of filtration?

6. Mention five different kinds of mineral waters.

7. How much hydrogen could be prepared from 50 kilograms of water? Give two methods that are essentially different in character by means of which the hydrogen could be liberated from the water. State also what volume the hydrogen would occupy under standard conditions.

8. State the Law of Gay-Lussac of the combination of gases by volume, and show how the composition of water, by volume, illustrates this law.

9. Make a list of the more important physical properties of water.

10. Define the following terms: water of crystallization, efflorescence, deliquescence, hydrate, hydroxide. Give an example in each case.

11. Name some of the more important substances that are soluble in water. What substances are not soluble in water? Why is the slight solubility of the rocks of the earth's crust nevertheless of great importance in the economy of nature?

12. What is the difference between an unsaturated, a saturated, and a supersaturated solution?

13. How may a supersaturated solution of common salt in water be prepared?

CHAPTER V

HYDROCHLORIC ACID AND CHLORINE

Preparation and Properties of Hydrochloric Acid. — When concentrated sulphuric acid is poured upon common salt, an effervescence ensues, a gas being evolved which is colorless, has a pungent odor, and is neither combustible nor a supporter of combustion. This gas has a very sour taste, and produces suffocation when inhaled in quantity. It reddens moist blue litmus paper, and is very soluble in water. At 0° one volume of water will absorb 503 volumes of the gas, while at room temperature about 450 volumes are thus absorbed. This gas, which was at first called "spirit of salt," was discovered by Johann Rudolf Glauber in 1658. It is hydrochloric acid. Priestley called it "marine acid air"; he collected the gas over mercury.

Hydrochloric acid is sometimes emitted during volcanic eruptions. It also occurs in the gastric juice of man and other animals. In normal condition the human gastric juice contains about 0.33 per cent of hydrochloric acid, which is essential in the process of digestion.

Hydrochloric acid comes in the market as a solution of the gas in water. It also goes by the name of *muriatic acid.* On dissolving pure hydrochloric acid gas in distilled water, a colorless solution is obtained. However, much of the commercial muriatic acid is colored yellowish by the impurities, especially salts of iron, that it contains.

The attraction between hydrochloric acid gas and water is so great that the gas fumes strongly in the air. This is due to the fact that it condenses moisture from the air in drops, which consist of an aqueous hydrochloric acid solution. When the gas is conducted into water, heat is evolved. The thermal change accompanying the solution of any substance is termed the *heat of solution* (see Thermochemistry). Aqueous solutions of hydrochloric acid are heavier than water. Thus, a solution of specific gravity 1.024 at 15° contains 5 per cent hydrochloric

acid, while solutions having the specific gravities 1.049, 1.100, 1.152, and 1.200 contain 10, 20, 30, and 40 per cent, respectively. A solution which is saturated with hydrochloric acid at 15° contains 42.9 per cent and has a specific gravity of 1.212. The usual "pure," commercial, concentrated hydrochloric acid is about 38 per cent strong and has a specific gravity of 1.19. It fumes strongly when exposed to the air.

On boiling a saturated solution of hydrochloric acid, the gas is in part expelled, and finally a 20.2 per cent solution with a boiling point of 110° is obtained. At ordinary pressure, this solution distills over without change of composition. The same strength of solution is finally obtained when a dilute solution is boiled. In this case water is mainly expelled until the solution reaches a strength of 20.2 per cent, when it distills over without decomposition. The final acid thus obtained at *different pressures*, however, has a slightly different composition.

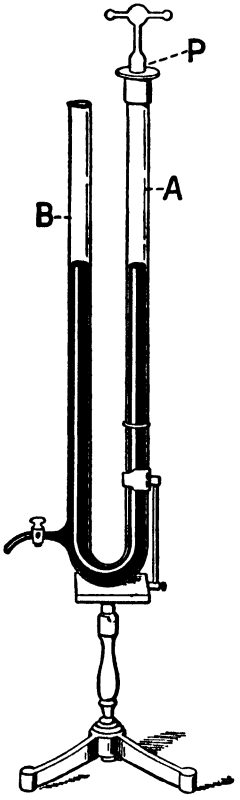


FIG. 23.

Pure, dry hydrochloric acid gas may be condensed to a liquid at 10° under a pressure of 40 atmospheres. Under atmospheric pressure the liquid, which is colorless, boils at − 84° and freezes at about − 110°.

Composition and Chemical Behavior of Hydrochloric Acid. — When metallic sodium is introduced into pure hydrochloric acid gas, the metal burns in the gas, forming common salt and hydrogen. This fact shows that hydrogen is one of the constituents of hydrochloric acid.

The right limb of the apparatus (Fig. 23) is filled with pure, dry hydrochloric acid gas. The press *P*, which fits securely on the top of the glass tube, contains metallic sodium. When the latter metal is pressed out into the tube *A*, by turning the screw of the press, the sodium and hydrochloric acid react and form common salt and hydrogen with concomitant evolution of light and heat. If the level in the limbs *A* and *B* is kept constant by pouring

mercury into *B* as required, it will be seen that when further addition of sodium no longer produces any action in *A*, *the hydrogen obtained occupies just one half of the volume of the original hydrochloric acid gas.*

Hydrochloric acid is a very powerful acid and acts strongly on many metals, hydrogen being liberated and chlorides of the metals being formed during the reaction.

When a concentrated aqueous solution of hydrochloric acid is subjected to electrolysis (*Fig.* 24), *equal volumes of hydrogen and*

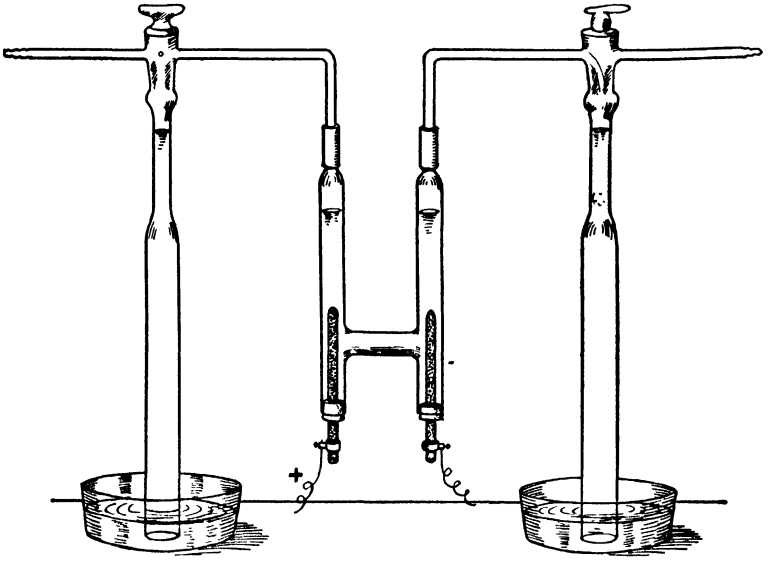


FIG. 24.

a greenish yellow gas, chlorine, appear. Carbon electrodes are used in this electrolysis, for platinum would be attacked by the chlorine. This apparatus, designed by Lothar Meyer, differs from that in Fig. 2, because chlorine when collected over an aqueous hydrochloric acid solution under pressure is quite appreciably absorbed, so that the volume of the chlorine gas would be diminished.

When equal volumes of dry chlorine and dry hydrogen contained in the two parts of the strong tube (Fig. 25) are allowed to mix by opening the stopcock, and the mixture is then exposed to diffused daylight, hydrochloric acid is formed, and neither hydrogen nor chlorine is left uncombined. Moreover,

the volume of the hydrochloric acid gas formed is exactly equal to that of the hydrogen plus chlorine. That is, *equal volumes of hydrogen and chlorine unite to form hydrochloric acid without change of volume*, which is demonstrated by the fact that when the stopper at the lower end of the tube (Fig. 25) is removed *under mercury* after the hydrochloric acid has formed, neither gas escapes nor mercury enters the tube. In direct sunlight or on exposure to a strong magnesium flash light the union takes place with explosive violence. Thus it is *that one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrochloric acid gas.* This is another example illustrating the law of Gay-Lussac of combination of gases by volume.

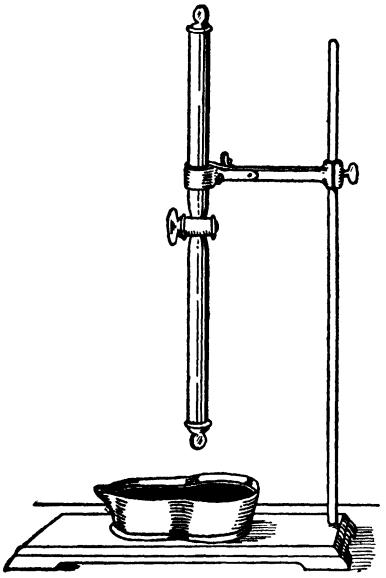


FIG. 25.

It has been found that one volume of chlorine is 35.45 times as heavy as an equal volume of hydrogen. From this and the fact that equal volumes of hydrogen and chlorine unite to form hydrochloric acid, it is evident that *by weight*, 1 *part of hydrogen unites with* 35.45 *parts of chlorine to form hydrochloric acid.*

According to H. Sainte-Claire Deville, hydrochloric acid gas is partially decomposed into hydrogen and chlorine when heated to temperatures of 1300° or above.

Enormous quantities of hydrochloric acid are manufactured as a by-product of the Le Blanc soda process (which see).

Occurrence, History, and Preparation of Chlorine. — Chlorine occurs in nature only in combination with other elements. The chlorine-bearing compounds are chiefly common salt, the chloride of sodium, and the chlorides of potassium, magnesium, and calcium. Chlorine is also found in the native chlorides of lead, copper, and silver. In combination with hydrogen, it occurs in the gastric juice, and as sodium chloride and potassium chloride it forms an essential constituent of the bodies of animals.

It is also an important constituent of plants, in which it is probably mainly combined with potassium.

Chlorine was first prepared in the free state by Scheele in 1774, who treated manganese dioxide with hot hydrochloric acid. He called the gas "dephlogisticated hydrochloric acid," for at that time hydrogen was regarded as the phlogiston of Stahl. However, in 1785 Berthollet, who belonged to the anti-phlogistic school, called chlorine "oxidized hydrochloric acid." He was of the opinion that chlorine contained oxygen, and this view prevailed till 1807; when, on the basis of their researches, Gay-Lussac and Thenard showed the gas to be a simple substance, *i.e.* an element. The gas was named chlorine by Sir Humphry Davy. The name comes from the Greek, meaning greenish yellow.

We have seen that chlorine is one of the products of the electrolysis of hydrochloric acid. The simplest way of preparing chlorine is by treating hydrochloric acid with an oxidizing agent, whose oxygen unites with the hydrogen of the hydrochloric acid, thus forming water and setting the chlorine free. As such an oxidizing agent, manganese dioxide is commonly employed. Chlorine may be formed by treating manganese dioxide with the aqueous solution of hydrochloric acid and heating gently; or by mixing common salt with manganese dioxide and treating the mixture with sulphuric acid. In the latter case, the sulphuric acid acts on the sodium chloride forming hydrochloric acid, which then acts upon the manganese dioxide as before. In these processes manganous chloride is also formed. In place of manganese dioxide, other oxidizing agents, like potassium dichromate, potassium chlorate, red lead, or bleaching powder, may be employed. In preparing chlorine by subtracting the hydrogen from the hydrochloric acid by an oxidizing agent, the oxygen of the air may be employed. By passing a mixture of air and hydrochloric acid at about 400° over porous bricks which have been soaked with copper sulphate solution, chlorine is liberated. The method is called the **Deacon process** and is used on a commercial scale. In this process cupric chloride is formed, and this is decomposed into cuprous chloride and chlorine. The cuprous chloride is then again converted into cupric chloride, which suffers decomposition as before, and so on.

Properties of Chlorine. — Chlorine is a greenish yellow gas which is 2.5 times as heavy as air. It has a very disagreeable odor, attacks the mucous membranes strongly, giving rise to a cough, and causes death by suffocation. At 0° it may be liquefied by means of six atmospheres of pressure. The critical temperature of the gas is 146°, and the critical pressure is 84 atmospheres. Thus, at ordinary temperatures chlorine is a condensable vapor. Under atmospheric pressure it becomes a liquid at − 34°, its boiling point. Liquid chlorine has a golden yellow color. At − 102° it freezes, forming yellow crystals. Liquid chlorine is now obtainable in the market in lead-lined steel flasks (Fig. 13). In this form it is shipped for use in laboratories and various industrial plants.

Chemically, chlorine is a very active element, combining at ordinary temperatures with evolution of light and heat with sodium, phosphorus, arsenic, antimony, and many other metals when these are introduced into an atmosphere of the gas in the form of powder or very thin sheets. In all such cases chlorides form by direct union of the chlorine with the other element. An apparatus for burning arsenic in chlorine is shown in Fig. 26. The cork fits loosely. When the test tube containing the powdered arsenic is raised, the latter falls into the bottle and unites with the chlorine with evolution of light.

FIG. 26.

Chlorine does not act directly on carbon or nitrogen; but chlorides of these elements may be formed by the indirect methods of double decomposition, as will appear later. Chlorine and hydrogen have a strong affinity for each other. A jet of hydrogen will burn in an atmosphere of chlorine, or a jet of chlorine in an atmosphere of hydrogen. In either case hydrochloric acid is formed as the product. A lighted taper or gas jet will continue to burn in chlorine, forming hydrogen chloride and carbon, which forms dense clouds of soot. Similarly, when a strip of filter paper moistened with turpentine is introduced into an atmosphere of chlorine, hydrochloric acid is formed, much soot escapes in dense clouds, and the paper instantly catches fire.

Chlorine is soluble in water. At 10° 1 volume of water absorbs about 3 volumes of chlorine, and at 50° about 1.5 volumes. The solution is commonly called chlorine water. When it is exposed to sunlight, the chlorine gradually unites with the hydrogen of the water, forming hydrochloric acid and oxygen. By filling a retort (Fig. 27) with chlorine water and exposing it to sunlight, the solution becomes colorless, hydrochloric acid being formed and oxygen liberated. The latter gas collects in the bulb, as shown in Fig. 27. By tilting the retort, this gas may be brought into the neck of the vessel and tested with a glowing splint.

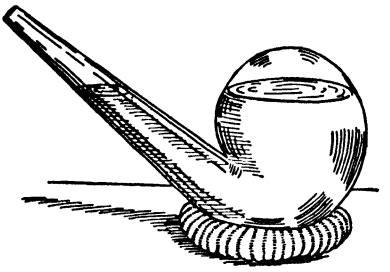


FIG. 27.

Because chlorine thus unites with the hydrogen of water and sets oxygen free, which in turn is capable of oxidizing substances, chlorine is spoken of as a powerful oxidizing agent. Upon this power to set free oxygen from water depends the bleaching action of chlorine. When moist flowers, green leaves, colored cloth, and paper on which marks have been made with ordinary ink are introduced into an atmosphere of chlorine, they are bleached; that is, the color is destroyed. Moisture is essential to have the bleaching take place; for the chlorine unites with the hydrogen of the water, forming hydrochloric acid and setting oxygen free. The latter then unites with the coloring matter and destroys it. Printer's ink consists largely of carbon, which at ordinary temperatures is not attacked either by oxygen or chlorine; it consequently is not bleached. It should further be stated that fabrics dyed with some of the aniline dyestuffs also retain their color, even when treated with chlorine water. By the action of chlorine on water, some hypochlorous acid is always formed.

Other Uses of Chlorine. — The oxygen liberated when chlorine acts upon water as explained is very destructive to organic life; for this reason chlorine is used as a disinfectant. Fungi and disease germs are rapidly destroyed by the action of chlorine.

Chlorine is also sometimes used in extracting gold from its ores. By direct union with the metallic gold, the chloride of

that metal is formed; and this salt being readily soluble in water, can then be leached out of the ores.

Some Compounds of Chlorine with Oxygen. — Chlorine does not form compounds with oxygen by direct union of the two gases. However, by the indirect method of double decomposition, compounds of oxygen and chlorine may be obtained. These compounds are gases which readily decompose.

The compounds of oxygen and chlorine will be considered in Chapter VIII. Here only two of these compounds will be mentioned briefly.

Chlorine Monoxide. — When dry chlorine is passed over red oxide of mercury in the cold, a pale yellow gas is formed, which does not have the greenish tint of the chlorine and readily decomposes with explosive violence, even when moderately heated. At 5° it may be condensed to a liquid of orange-yellow color, which readily explodes in sunlight or on slight heating, at times even on pouring it from one dish to another. The gas is soluble in water. One volume of water absorbs about 200 volumes of chlorine monoxide gas at 0°.

This substance is an oxide of chlorine, and consists of 35.45 parts of chlorine to 8 parts of oxygen by weight. It is called chlorine monoxide.

Chlorine Dioxide. — By carefully treating powdered potassium chlorate with concentrated sulphuric acid added in *very small quantities* at a time, a heavy, deep yellow gas is evolved which has a very disagreeable odor, attacks mercury, and is readily soluble in water. It is very unstable, exploding in the sunlight, or when heated by means of the electric spark or a hot iron rod. In the cold, it may be condensed to a liquid of dark red color, which is of a highly explosive nature.

This compound is an oxide of chlorine, which contains 35.45 parts of chlorine and 32 parts of oxygen by weight. It is called chlorine dioxide or chlorine peroxide.

Thus, in the case of these two oxides of chlorine we have another illustration of the law of multiple proportions; for in the monoxide 35.45 parts of chlorine are united with 8 parts of oxygen by weight, whereas in the peroxide 35.45 parts of chlorine are united with 4 times 8 parts of oxygen.

The Law of Reciprocal Proportions. — We have learned that in water hydrogen and oxygen are united in the proportions of

1 part of hydrogen to 8 parts of oxygen by weight. In hydrochloric acid 1 part of hydrogen is united with 35.45 parts of chlorine by weight. In chlorine monoxide we find that 35.45 parts of chlorine are united with 8 parts of oxygen by weight; and in chlorine peroxide 35.45 parts of chlorine are united with 4 times 8 parts of oxygen.

Thus we see that *the proportions by weight in which hydrogen and oxygen combine, and in which hydrogen and chlorine combine, also determine the proportions in which chlorine and oxygen combine with each other.* This is an illustration of a general law which holds in all chemical combinations. It may be stated thus in general terms: *If three elements, A, B, and C, are able to unite to form chemical compounds with one another, the proportions by weight with which A and B unite to form the compound AB, and the proportions in which A and C unite, also determine the proportions in which B and C unite with each other.* This law is known as the **law of reciprocal proportions.** It was discovered by Jeremias Benjamin Richter, and is one of the fundamental laws of chemical combination by weight. In the further study of chemistry, the student will meet numerous illustrations of this law.

REVIEW QUESTIONS

1. Describe the common way of preparing hydrochloric acid gas.
2. About how much hydrochloric acid gas will a liter of water absorb at ordinary temperature, 15° C.? What different names are given to an aqueous solution of hydrochloric acid gas? What properties has the gas?
3. How many liters of hydrogen will be required to unite with 25 liters of chlorine to form hydrochloric acid gas? What would be the volume of the latter? What law is illustrated by these facts?
4. Describe two different methods of proving that hydrochloric acid consists of hydrogen and chlorine, and that these are present in the proportion of 1 part of hydrogen to 35.5 parts of chlorine by weight.
5. Why is the method of preparing chlorine by acting upon hydrochloric acid with any of the following substances one and the same in principle: manganese dioxide, potassium chlorate, red lead, potassium dichromate? Give a method of preparing chlorine which is essentially different in principle.
6. Mention the properties of chlorine. What use is made of chlorine?
7. Name two oxides of chlorine and state what law these illustrate.
8. What is the law of reciprocal proportions? Illustrate.
9. How much chlorine is there in a barrel of common salt containing 280 lb. net? How much hydrochloric acid could be made from this salt?

CHAPTER VI

THE LAWS OF COMBINING WEIGHTS AND COMBINING VOLUMES AND THE ATOMIC AND MOLECULAR THEORIES

Retrospect.—In the preceding chapters we have found that certain general laws regulate the quantities in which the chemical elements combine to form compounds. The laws governing the combination of the elements by weight are as follows:

(1) **The Law of Definite Proportions.**—*A chemical compound always contains the same elements in the same proportions by weight.* No matter when, where, or by what process hydrochloric acid, for example, is formed, it always contains only the elements hydrogen and chlorine in the proportions of 1 gram of hydrogen to 35.45 grams of chlorine. Water always consists of hydrogen and oxygen united in the proportions of 1 gram of hydrogen to 8 grams of oxygen. Common salt is made up of 23 parts of sodium to 35.45 parts of chlorine by weight; and similarly every other chemical compound always has exactly the same invariable qualitative and quantitative composition. The law of definite proportions, it will be recalled, was discovered by Lavoisier.

(2) **The Law of Multiple Proportions.**—*When any two elements, A and B, form more than one compound with each other, the amounts of B that unite with one and the same weight of A are simple rational multiples of one another.* Thus iron and sulphur form ferrous sulphide, which consists of 28 grams of iron to every 16 grams of sulphur; and pyrite or fool's gold, a native sulphide of iron, always contains 28 grams of iron to every 32 (*i.e.* 2 times 16) grams of sulphur. Again, in chlorine monoxide, every 35.45 grams of chlorine are united with 8 grams of oxygen. In chlorine peroxide, every 35.45 grams of chlorine are united with 32 (*i.e.* 4 times 8) grams of oxygen; and in chlorine heptoxide (which see) every 35.45 grams of chlorine

are combined with 56 (*i.e.* 7 times 8) grams of oxygen. In the oxides of lead the proportions of lead and oxygen by weight are as follows: —

(*a*) In the black oxide, Lead : Oxygen : : 1 : 0.0387
(*b*) In the yellow oxide, Lead : Oxygen : : 1 : 0.0773
(*c*) In the red oxide, Lead : Oxygen : : 1 : 0.103
(*d*) In the orange oxide, Lead : Oxygen : : 1 : 0.1160
(*e*) In the brown oxide, Lead : Oxygen : : 1 : 0.1547

Now, 0.0387 : 0.0773 : 0.103 : 0.1160 : 0.1547 : : 1 : 2 : $\frac{8}{3}$: 3 : 4.

The compounds of oxygen with nitrogen (which see) are five in number, and these furnish a further good illustration of the law of multiple proportions. These oxides are all gases, in which the proportion of nitrogen to oxygen by weight is as follows: —

(*a*) In nitrous oxide, Nitrogen : Oxygen : : 1 : 0.5710
(*b*) In nitric oxide, Nitrogen : Oxygen : : 1 : 1.142
(*c*) In nitrogen sesquioxide, Nitrogen : Oxygen : : 1 : 1.713
(*d*) In nitrogen dioxide, Nitrogen : Oxygen : : 1 : 2.28
(*e*) In nitrogen pentoxide, Nitrogen : Oxygen : : 1 : 2.855

Now, 0.5710 : 1.142 : 1.713 : 2.28 : 2.855 : : 1 : 2 : 3 : 4 : 5.

As already stated, the law of multiple proportions was first recognized by John Dalton of Manchester, England.

(3) **The Law of Reciprocal Proportions.** — *When three elements, A, B, and C, are able to form chemical compounds with one another, the proportions by weight in which A and B unite to form the compound AB, and the proportions in which A and C unite to form the compound AC, also determine the proportions in which B and C unite to form the compound BC.* Thus, hydrogen, oxygen, and chlorine are three elements which can form compounds with one another. In water we have, for every 8 grams of oxygen, 1 gram of hydrogen; in hydrochloric acid, we have, for every 35.45 grams of chlorine, 1 gram of hydrogen; and in chlorine monoxide we have, for every 35.45 grams of chlorine, 8 grams of oxygen; whereas in chlorine peroxide every 35.45 grams of chlorine are united with 4 times 8 grams of oxygen. Again, in sodium chloride every 35.45 grams of chlorine are combined with 23 grams of sodium; in sodium oxide, every 23 grams of sodium are united with 8 grams of oxygen; in chlo-

rine monoxide every 35.45 grams of chlorine are united with 8 grams of oxygen. Further, take the elements hydrogen, sulphur, and oxygen: — In hydrogen sulphide (which see) every 16 grams of sulphur are combined with 1 gram of hydrogen; in water every 8 grams of oxygen are combined with 1 gram of hydrogen; in sulphur dioxide, which gas is formed when sulphur is burned in the air or in oxygen, every 16 parts of sulphur are united with 16 (*i.e.* 2 times 8) parts of oxygen. As mentioned in the previous chapter, the law of reciprocal proportions was first recognized through the work of the German chemist, Jeremias Benjamin Richter.

The subject of the study of the weight relations that obtain when chemical changes take place is called **stoichiometry**, and the three laws just elucidated are the fundamental **laws of stoichiometry**.

In connection with the study of hydrogen, it was found that 23 grams of sodium will liberate 1 gram of hydrogen from water; 32.5 grams of zinc by acting on dilute hydrochloric acid will also liberate 1 gram of hydrogen; 9 grams of aluminum, or 12 grams of magnesium, will similarly set free 1 gram of hydrogen. Therefore, 23, 32.5, 9, and 12 are termed the hydrogen equivalents of sodium, zinc, aluminum, and magnesium, respectively. Now in water, which is an oxide of hydrogen, 1 gram of hydrogen is united to every 8 grams of oxygen; in sodium oxide, 23 grams of sodium are united to 8 grams of oxygen; in the oxide of zinc, 32.5 grams of zinc are united to 8 grams of oxygen; in oxide of aluminum, 9 grams of aluminum are united to 8 grams of oxygen; in oxide of magnesium, 12 grams of magnesium are united to 8 grams of oxygen. In the chlorides of hydrogen, sodium, zinc, aluminum, and magnesium, these same equivalents, namely, 1, 23, 32.5, 9, and 12, respectively, are each united with 35.45 parts by weight of chlorine. Thus, one might look upon hydrochloric acid as water in which the 8 parts of oxygen that are united to 1 part of hydrogen are replaced by 35.45 parts of chlorine. Similarly, for instance, oxide of magnesium might be regarded as water in which each gram of hydrogen is replaced by 12 grams of magnesium; or the chloride of magnesium might be looked upon as hydrochloric acid in which each gram of hydrogen is replaced by 12 grams of magnesium; sodium chloride might be viewed as sodium

oxide in which every 8 grams of oxygen are replaced by 35.45 grams of chlorine, etc.

It thus becomes clear that these so-called chemical equivalents are the weights of the elements that enter into chemical combination with one another. So for each chemical element a definite weight can be found experimentally, in which, or in multiples of which, it enters into combination with other elements. A table of such weights is called a table of **combining weights** or **chemical equivalents.** While the actual numerical value of such combining weights or chemical equivalents will vary according to the unit of comparison chosen, the relative values of the combining weights are fixed and invariable. So we might arbitrarily agree to call the combining weight of oxygen 100, and then determine the combining weight of the other elements accordingly. Thus in water 100 parts of oxygen are combined with 12.5 parts of hydrogen, and the latter figure would be the combining weight of hydrogen, if that of oxygen is taken as 100. Similarly, on this basis, the combining weight of chlorine would be 443.1, for in hydrochloric acid 12.5 parts of hydrogen by weight are combined with 443.1 parts of chlorine. As a matter of fact, the great Swedish chemist Berzelius, who lived in the former half of the nineteenth century, and to whose careful, painstaking labors we owe the first really reliable table of the combining weights of the chemical elements, actually computed the values he found experimentally by choosing arbitrarily the combining weight of oxygen as 100. On the other hand, Wollaston, an English chemist and contemporary of Berzelius, arranged the table on the basis of oxygen equals 10. It is clear that one might arrange such a table by taking the combining weight of any element equal to any fixed number, and then computing the combining weights of the other elements accordingly, from experimental results gathered by ascertaining the ratios in which the elements combine with one another by weight. At the beginning of the nineteenth century, John Dalton suggested that the table of combining weights be arranged by arbitrarily choosing the combining weight of hydrogen equal to one. Since hydrogen is the lightest of substances, and the quantity by weight in which it enters into combination with other elements is the smallest, it is clear that if its combining weight is chosen as unity, the combining weights of all the

other elements would be greater than unity. Now, as we have seen, hydrogen combines directly with but very few elements, whereas oxygen is a very active substance chemically, and combines directly with most of the other elements. For this reason a large number of the combining weights were determined from the compounds with oxygen; and this fact led Berzelius to take that element as the standard for his table, fixing the value of its combining weight arbitrarily at 100, as already stated. However, the distinct advantage of placing the combining weight of hydrogen equal to unity was so apparent, that for a long time tables were arranged on this basis. In computing the values of a table of combining weights on the basis that the combining weight of hydrogen equals 1, the ratio by weight in which oxygen and hydrogen combine clearly plays a very important rôle; for since most of the elements do not combine with hydrogen directly, their combining weights are actually determined from the ratios in which they unite with oxygen. Consequently the ratio in which the latter element unites with hydrogen is used to compute the combining weights on the basis of hydrogen equals unity. Now since hydrogen is a very light gas and consequently difficult to weigh with accuracy in large quantities, and moreover rather difficult to obtain in a high state of purity, the ratio in which oxygen and hydrogen unite to form water has been the object of a great deal of research by a goodly number of able, painstaking chemists. And every time this ratio was determined to a greater degree of accuracy, nearly all the values in the table of combining weights had to be recomputed. To avoid this, most chemists have of recent years returned to the oxygen basis, choosing the combining weight of oxygen arbitrarily as equal to 8. On this basis, the combining weight of hydrogen is very nearly 1.008, according to the latest researches. By this procedure, we retain the practical advantage of having hydrogen as the unit and avoid the necessity of recalculating nearly the whole of the table every time the ratio in which oxygen and hydrogen unite is redetermined with greater accuracy. Such experimental redetermination will then only necessitate a recomputation of the combining weight of hydrogen. From what has been said, it is evident, that if the combining weight of hydrogen is arbitrarily taken as equal to 1, that of oxygen is nearly 7.94.

The following is a table of the combining weights or chemical equivalents which have mainly engaged our attention thus far in this book, computed on the basis of oxygen equals 8: —

Hydrogen	1.008	Magnesium	12.16
Oxygen	8.00	Aluminum	9.03
Chlorine	35.46	Zinc	32.68
Sulphur	16.03	Iron	27.92
Sodium	23.00	Lead	103.55

For purposes of discussion, figures rounded off to the first decimal place are commonly used.

Chemical Symbols. — Thus far in all our considerations we have written the names of all elements and compounds. This is a somewhat cumbersome procedure, and chemists have adopted a system of symbols for designating substances. Even long before the rise of modern chemistry, which dates from the work of Lavoisier at the beginning of the nineteenth century, chemists had been wont to designate substances by means of certain symbols. So the moon ☽ was the symbol of silver, ▽ was the symbol for water, ⊖ was the symbol for a salt, etc. Such arbitrary signs were still used by the great Swedish chemist Scheele, who was a contemporary of George Washington. It was Berzelius who, in the early part of the nineteenth century, made the suggestion that each of the chemical elements be designated by the first letter of the name of the element, and that whenever the names of two or more elements begin with the same letter, a second characteristic letter from the name of the element be added to the symbol. This is still the usage at the present time. Thus, the symbol of hydrogen is H, that of oxygen O, that of carbon C, that of chlorine Cl, that of cobalt Co, etc. In some cases the symbols are derived from the Latin names of the elements in the manner mentioned. So the symbol for silver, argentum, is Ag; for sodium, natrium, Na; for mercury, hydrargyrum, Hg; for lead, plumbum, Pb; etc. A complete list of all the names and symbols of the elements will be given later.

Having thus adopted the symbols for the elements, the compounds would naturally be designated by simply writing side by side the symbols of the elements that occur in the compounds. But since the elements always enter into combination in the ratio of their combining weights, it is easy to have

the symbol of a compound stand for both its qualitative and its quantitative composition. This is readily accomplished by letting the symbol of each element stand for not only the verbal name of that element, but also for its combining weight. Thus the symbols H and Cl would stand not only for hydrogen and chlorine, but also for 1 part of hydrogen by weight, and 35.45 parts of chlorine by weight, respectively. And so the symbol HCl stands not only for hydrochloric acid, but it also tells us that in that compound 1 part of hydrogen is combined with 35.45 parts of chlorine by weight. Likewise, the symbol for common salt, NaCl, denotes that this compound consists of sodium and chlorine united in the proportions of 23 parts of sodium to 35.45 parts of chlorine by weight. Again, the symbol HO, which was formerly used for water, denoted that this compound consists of hydrogen and oxygen united in the proportions of 1 to 8 by weight. The symbol of ferrous sulphide, FeS, denoted that in this compound iron and sulphur are present and in the proportion of 28 parts of iron to 16 parts of sulphur by weight. The symbol FeS_2, the 2 being used as a subscript to the S, was the symbol for pyrite, and denoted that in it 28 parts of iron are combined with 2 times 16 parts of sulphur, *i.e.* two combining weights of sulphur. In general, whenever more than one combining weight of an element enters into the compound, that fact is indicated by the appropriate figure used as a subscript. So, for instance, the symbol for red lead is Pb_3O_4, indicating that in that compound 3 combining weights (3×103.5) of lead are united with 4 combining weights (4×8) of oxygen. This mode of designating chemical compounds by having the symbols stand for equivalent or combining weights was in vogue for many years; and with a slight modification it is still in use at present. The nature of this modification lies merely in the fact that we do not always designate the chemical equivalent by the symbol of the element, but frequently the symbol stands for some other simple multiple of the chemical equivalent, for reasons that will presently be explained.

The Atomic Theory of Matter. — The fact that the chemical elements always unite in definite proportions by weight in accordance with the three laws of definite, multiple, and reciprocal proportions, finds a ready explanation in a simple assumption as to the nature of matter. If we assume that each

elementary substance is made up of extremely minute, ultra-microscopic, indivisible particles, termed **atoms** (from the Greek meaning indivisible), and that these atoms are of exactly the same weight and also otherwise alike in the case of any one element, but different in weight and other properties in the case of different elements, and that chemical compounds are formed by the union of the atoms of the various elements with one another, the experimental facts expressed in the laws of definite, multiple, and reciprocal proportions are readily explained. So, for instance, by this hypothesis, hydrogen would be considered as made up of minute particles, atoms, all of the same weight and otherwise also alike. Chlorine would similarly be regarded as composed of atoms which are of the same weight and otherwise alike among themselves, but quite different in weight and other properties from the atoms of hydrogen or those of any other element. Each element would similarly be composed of atoms that are alike in weight and otherwise, but different in weight and other characteristics from the atoms of all other elements.

Since the atoms of each element are assumed to be indivisible, in forming compounds a whole number of atoms of one element must always unite with a whole number of atoms of another element or elements. Consequently the proportions by weight in which, for instance, two elements A and B unite with each other to form a compound AB, are proportional to the atomic weights of A and B; in other words, *the combining weights of the elements are proportional to the atomic weights.* So, for example, 1 gram of hydrogen unites with 35.45 grams of chlorine to form 36.45 grams of hydrochloric acid, consequently, in the light of the atomic theory, 1 gram of hydrogen must contain a definite whole number of atoms of hydrogen, and similarly the 35.45 grams of chlorine must contain a definite whole number of atoms of chlorine. If we let x represent the actual weight of one of the hydrogen atoms, and n the number of atoms of hydrogen in 1 gram of hydrogen, then xn equals 1 gram. Similarly, if we let y represent the weight of 1 atom of chlorine and n' the number of atoms of chlorine in 35.45 grams of that gas, then yn' equals 35.45 grams. We may consequently write the relation —

$$xn : yn' : : 1 \text{ gram} : 35.45 \text{ grams.}$$

It is clear that we might deduce a similar equation in the case of the union of any two or more of the chemical elements. Let us now view this equation more closely. It contains four unknown quantities: namely, the atomic weight of hydrogen x, the atomic weight of chlorine y, the number of atoms of hydrogen n, in 1 gram of hydrogen, and the number of atoms of chlorine n', in 35.45 grams of chlorine. Of course, neither of these values can be ascertained from the equation as it stands. If now we arbitrarily choose some definite value for either x or y, say we assume with Dalton the atomic weight of hydrogen as 1, the x will disappear from our equation as an unknown quantity; still we should have the three unknown quantities n, n', and y present in the equation. There is no way of determining how many atoms of hydrogen unite with how many atoms of chlorine in forming hydrochloric acid, and so it is customary to make the simplest possible assumption here, namely, that 1 atom of hydrogen unites with 1 atom of chlorine in forming a particle of hydrochloric acid. On the basis of this assumption, it becomes clear that 1 gram of hydrogen would contain as many atoms of hydrogen as 35.45 grams of chlorine contain atoms of chlorine; or in other words, in our equation n equals n'. Since we have assumed that x equals 1, and also that n equals n', the equation becomes —

$$1 : y : : 1 \text{ gram} : 35.45 \text{ grams};$$ whence y equals 35.45.

That is, the atomic weight of chlorine is 35.45, if the atomic weight of hydrogen is assumed to be 1, and it is further assumed that in forming hydrochloric acid 1 atom of hydrogen unites with 1 atom of chlorine. Similarly, the proportions by weight in which hydrogen and oxygen unite to form water, namely, 1 to 8 (if we were to make the simplest assumption, as Dalton did, that in forming water 1 atom of hydrogen unites with 1 atom of oxygen), lead to the conclusion that the atomic weight of oxygen is 8. And this value was assigned to it by Dalton, though it is not the one used at present, as will be explained shortly. However, if we thus take the atomic weight of hydrogen as 1, that of oxygen as 8, and that of chlorine as 35.45, then since in chlorine monoxide every 35.45 grams of chlorine are combined with 8 grams of oxygen, we should have in this compound 1 atom of chlorine united with 1 atom of

oxygen. In the chlorine peroxide again, in which every 35.45 grams of chlorine are combined with 32 grams of oxygen, we should have 1 atom of chlorine combined with 4 atoms of oxygen. Thus on this basis the formulæ for hydrochloric acid, water, chlorine monoxide, and chlorine peroxide would be HCl, HO, ClO, and ClO_4, respectively. In these formulæ the symbols of the elements simply stand for the combining or equivalent weights. Thus by introducing the assumptions: (1) that the elements are made up of atoms, (2) that the atomic weight of hydrogen is 1, (3) that in water 1 atom of hydrogen is united with 1 atom of oxygen, and (4) that in hydrochloric acid 1 atom of chlorine is united with 1 atom of hydrogen, we simply arrive at the conclusion that the combining weights are the relative atomic weights; the lowest combining weight of an element found in any compound into which it enters being, of course, taken as the atomic weight. This system of using the equivalent weights as the atomic weights was employed by many chemists during the first half of the 19th century.

Thus, in the atomic theory, the law of definite proportions finds a ready explanation, for each compound would always contain the same relative number of atoms of each of the elements of which it is composed. The law of multiple proportions is readily explained by the theory, since according to it a fixed number of atoms of one element can only combine with one atom or some other whole number of atoms of another element. And finally, the law of reciprocal proportions also is easily accounted for by the theory, since according to it the weight of an atom of any one element is constant and different from that of any other element, and combination can only take place by whole numbers of atoms, from which it follows that the proportion by weight in which an element occurs in one compound will be either the same as, or some multiple of, the proportion in which it occurs in any other compound.

It should thus be borne in mind that the modern atomic theory of matter is based upon the weight relations that obtain when the elements unite chemically, and these weight relations are expressed in the three fundamental stoichiometrical laws.

It is of interest to note that, though Dalton promulgated the modern atomic theory in 1802, the basis for that theory has been furnished by chemists of three different nations; for the

law of definite proportions was discovered by Lavoisier and Proust, the law of multiple proportions by Dalton, and the law of reciprocal proportions by Richter.

The atomic conception of matter was not original with Dalton; indeed, its origin dates back to the times of classical Greece. Democritus, Epicurus, and Leucippus taught that matter is made up of indivisible particles or atoms, whereas according to the doctrine of Anaxagoras, matter is infinitely divisible. However, the atomic conception of matter of the Greeks was a mere metaphysical speculation, not founded upon experimental facts. It was Dalton who first used the conception of the atomic nature of matter in explaining actual facts established by experiments, and to him consequently we rightly ascribe the origin of the modern atomic theory.

Difference between Theory and Law. — The student must always clearly bear in mind the distinction between a theory on the one hand, and facts and laws on the other hand. *Facts are the results of actual observation and experiment. When a large number of similar facts have been found and these are expressed in a general statement, the latter is a law.* Thus we actually find that the composition of salt, water, lime, sal ammoniac, etc., is constant, no matter when or where prepared. We have here a series of facts. If now we formulate this into the general statement, that a chemical compound always has the same composition, we have a law. *A theory or hypothesis, however, is neither a fact nor a general statement of fact, it is merely an assumption made for the purpose of correlating, explaining, or accounting for facts that have been collected and formulated into laws.* So the atomic theory is a theory which enables us to correlate and comprehend better the facts expressed in the stoichiometrical laws. *A theory, however, not only enables one to see facts in their relations and thus satisfies the natural craving of the human intellect for a better comprehension of things observed, but it also suggests new avenues of inquiry and experimentation by means of which further facts may be acquired.* A theory is thus a powerful stimulus to scientific research, and is consequently of almost inestimable value. On the other hand, it is to be remarked that *theories by implication also suggest that it is useless for actual inquiry to proceed in certain directions, and that certain things are impossible, when after all they are quite possible,*

and thus a theory may be a bar to progress. Carefully ascertained facts formulated into laws constitute the unchangeable, the eternal part of science. Theories and hypotheses on the other hand are the changeable, the ephemeral part of science; for the views we entertain concerning the relationship of natural phenomena frequently change as new facts are acquired. A theory is a cord by which the precious pearls of truth are held together, but when the pearls found become too numerous or too heavy so that the old cord can no longer hold them together, it must be discarded, and the pearls must ultimately be arranged on a new cord of adequate length and strength. Thus theories and hypotheses are frequently discarded in science. In fact, the pathway of the progress of science is strewn with defunct theories. As we continue our considerations, we shall see that the atomic theory, simple and even crude as it seems, has been in a high degree useful in correlating even facts other than those upon which it is actually based, and has suggested many new avenues of further experimental inquiry. It has thus fulfilled in a high degree the function of a theory.

The Law of Combination of Gases by Volume. — It will be recalled that Gay-Lussac discovered the law that *when gases combine to form chemical compounds the volumes of the gases that enter into combination bear a simple relation to one another; and if the product formed be gaseous, its volume also bears a simple relation to the volumes of the original gases.* This law was established at about the time when Dalton formulated the atomic theory. In viewing the fact that 1 volume of hydrogen and 1 volume of chlorine unite to form hydrochloric acid gas, in the light of the atomic theory of Dalton, according to which hydrogen and chlorine are made up of atoms and 1 atom of the one unites with 1 atom of the other to form one particle of hydrochloric acid, it follows at once that 1 volume of hydrogen must contain exactly as many atoms of hydrogen as the same volume of chlorine contains atoms of the latter element; for were this not the case, there would be either hydrogen or chlorine left uncombined when exactly equal volumes act on each other chemically. Thus the idea was naturally formed that equal volumes of gases under the same conditions of temperature and pressure contain the same number of atoms. This is, of course, not a law, but simply an hypothesis evolved

to explain the law of Gay-Lussac of combination of gases by volume. To the hypothesis in the form stated, Berzelius interposed a serious objection. Thus he called attention to the fact that when 1 volume of hydrogen and 1 volume of chlorine unite, 2 volumes of hydrochloric acid are formed; and if 1 atom of hydrogen unites with 1 atom of chlorine, there will of course be formed as many particles of hydrochloric acid as there are particles of hydrogen, or what amounts to the same thing, as there are particles of chlorine. Therefore, if equal volumes of hydrogen, chlorine, and hydrochloric acid contain the same number of atoms or particles, the hydrochloric acid formed by the union of equal volumes of hydrogen and chlorine ought to occupy the same volume as the original hydrogen; that is, it ought to occupy one half of the volume that it actually does occupy. To hold the volume hypothesis, a scheme consequently had to be proposed whereby 1 atom of hydrogen would unite with 1 atom of chlorine and form 2 particles of hydrochloric acid; for only then the actual volume relations that obtain when the latter substance is formed by the union of hydrogen and chlorine would be accounted for. Such a scheme was proposed in 1811 by Amadeo Avogadro, who was then professor of physics at the University of Turin. He made the bold assumption that the particles of hydrogen gas really are double atoms, that is, that they consist of 2 atoms joined together, and that the particles of chlorine gas are similarly made up each of 2 chlorine atoms. These double atoms of hydrogen and double atoms of chlorine he called *molecules*, and then stated the hypothesis as follows: *Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.* This is known as **Avogadro's hypothesis.** It is very important in chemistry. Thus, Avogadro considered the molecule of hydrogen as H_2, and the molecule of chlorine as Cl_2; and when these react with each other we should have —

$$\begin{aligned} H_2 \quad &+ \quad Cl_2 \quad = 2\,HCl. \\ 1 \text{ molecule} &+ 1 \text{ molecule} = 2 \text{ molecules}. \\ 1 \text{ volume} \quad &+ 1 \text{ volume} \quad = 2 \text{ volumes}. \end{aligned}$$

On this basis, there would be twice as many molecules of hydrochloric acid formed as there were molecules of hydrogen or molecules of chlorine, and consequently one would expect

the hydrochloric acid formed to occupy twice the volume of the original hydrogen; or, what is the same, twice the volume of the chlorine.

Let us now review the volume relations that obtain when hydrogen and oxygen combine to form water vapor. We have by experiment—

2 volumes of hydrogen + 1 volume of oxygen
= 2 volumes of water vapor.

If, now, we desire to hold Avogadro's hypothesis, we clearly must assume the molecules of hydrogen, oxygen, and water so constituted that: —

2 molecules of hydrogen + 1 molecule of oxygen
= 2 molecules of water vapor.

But in connection with the synthesis of hydrochloric acid, it was already assumed that the molecule of hydrogen consists of 2 atoms (*i.e.* that it is H_2); we must consequently adhere consistently to this assumption wherever hydrogen gas is considered. Now if we assume that the oxygen molecule is made up of 2 atoms of oxygen (*i.e.* is O_2), the volume relations in the case of the synthesis of water are readily explained; the water molecule then, however, must be considered as composed of 2 atoms of hydrogen and 1 atom of oxygen. In form of an equation we should have —

2 volumes of hydrogen + 1 volume of oxygen = 2 volumes of water vapor.
2 molecules of hydrogen + 1 molecule of oxygen = 2 molecules of water vapor.
i.e. $2H_2 + O_2 = 2H_2O$.

Thus it appears that if we hold Avogadro's hypothesis, and assume with him, that in hydrogen gas and oxygen gas there are molecules that consist of 2 atoms of these respective elements, we are bound to conclude that the molecule of the very common compound water is not made up of 1 atom of hydrogen united with 1 atom of oxygen, but rather of 2 atoms of hydrogen united with 1 atom of oxygen. We should thus have to assign to water the formula H_2O instead of HO. Further, since by weight 1 part of hydrogen unites with 8 parts of oxygen, and since we assume with Dalton that the atomic weight of hydrogen is 1, we consequently must assume the atomic weight of oxygen as equal to 16 instead of 8.

All this seemed to many chemists of the early part of the nineteenth century as a set of rather violent changes to make. In fact, Avogadro's molecules, his double atoms as they were frequently termed in the literature, were not regarded seriously by many able chemists for nearly half a century; they simply continued to work with the tables of equivalent or combining weights in which the value for oxygen was 8. One of the reasons why Avogadro's hypothesis was laid aside for a time was that in the study of the ammonium salts certain apparent contradictions were met. These will be considered when those salts are discussed. Suffice it here to say that Avogadro's hypothesis has gained general acceptance and is now commonly regarded as of vital consequence in chemistry. Thus, *while the atomic theory is based upon the weight relations that obtain when substances unite chemically, the molecular theory came into being as a consequence of the acceptance of Avogadro's hypothesis, which in turn grew out of Gay-Lussac's law of the combination of gases by volume. Avogadro's hypothesis is further supported by the fact that all gases contract and expand alike under the same changes of temperature and pressure.*

Molecular Weight Determinations. — If equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules, it is clear that *the weights of equal volumes of gases are to one another as the molecular weights of the gases.* To fully appreciate Avogadro's hypothesis, the student must bear in mind that on the basis of the molecular theory a gas consists of molecules that are entirely remote from one another. So, for example, if the molecules of a gas were, say by pressure, all crowded together so that they touched one another, they would occupy but a small portion of the volume originally occupied by the gas. In other words, the actual volume of a gas consists largely of space or interstices between the molecules, as it were. Bearing this in mind, it is clear that equal volumes of gases may well contain equal numbers of molecules, though the individual molecules of each of the gases may occupy very different volumes. According to Avogadro's hypothesis, the volume of any gas, at constant temperature and pressure, depends not upon the size, weight, or kind of molecules it contains, but solely upon the *number* of molecules present. *Hence at constant temperature and*

pressure, the volumes of any two gases are to each other as the number of molecules in the volumes. Thus, for instance, 10 liters of any gas contain 10 times as many molecules as 1 liter of the same gas or any other gas. Again, take any volume of hydrogen, say 1 liter, and compare its weight with the weight of the same volume of some other gaseous substance, say chloroform vapor, at the same temperature and pressure. Now since by Avogadro's hypothesis each of these volumes contains the same number of molecules, which we shall call n, then we should have —

The wt. of 1 liter of Chloroform Vapor : wt. of 1 liter Hydrogen : : $mn : 2n$,

where m is the molecular weight of chloroform, and 2 that of hydrogen. From the equation,

$$m = 2 \times \frac{\text{wt. of liter of Chloroform Vapor}}{\text{wt. of liter of Hydrogen}}.$$

That is, the molecular weight of chloroform is equal to twice its vapor density as compared with hydrogen. Hence the rule for finding molecular weight of any gas: find the density of the gas with respect to hydrogen, and multiply the result by 2. The volume occupied by 2 grams of hydrogen under standard conditions, 0° and 760 mm. pressure, is 22.38 liters. The same volume is occupied by 32 grams of oxygen, 70.9 grams of chlorine, 18 grams of water vapor, and in short, by the molecular weight in grams of any gaseous substance whatever, under standard conditions. Consequently 22.38 liters is termed the molecular volume of all gases. We may also state that to find the molecular weight of any gas, we simply need to determine the weight of 22.38 liters of that gas at 0° and 760 mm. pressure, and the result is the molecular weight in grams. The student should assure himself that this really comes to the same thing as finding the density of the gas with respect to hydrogen and multiplying the result by 2.

The molecular weights of substances that can be obtained in the vapor state can thus readily be determined. But there are liquid and solid substances that cannot be vaporized without decomposition, and so their vapor densities cannot be determined. In the case of substances that can be dissolved, it is possible to make molecular weight determinations by studying the freezing point, boiling point, or vapor pressure of the solu-

tion. This will be explained later in connection with the subject of solutions.

Determination of Atomic Weights.— The proportions by weight in which the elements combine with one another are determined by very exact chemical analyses of the compounds containing the elements in question; or, if the latter will unite directly, by ascertaining the weights of the elements that enter into combination, when compounds are thus formed by synthesis. The values so found are the combining weights. Dalton took the combining weight of hydrogen as equal to unity, and expressed the combining weights of the other elements on this basis. We now, for reasons already stated above, take the combining weight or chemically equivalent weight of oxygen as equal to 8, on which basis that of hydrogen equals 1.008.

We have seen that Gay-Lussac's law of combination of gases by volume led to Avogadro's hypothesis, which in turn led to the idea of molecules, and to the conception that a molecule of oxygen consists of 2 atoms. This further made it necessary to adopt for water the formula H_2O, instead of HO, and consequently for oxygen the atomic weight 16 instead of 8. Thus the experimental fact that 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of water vapor really determined us in choosing the atomic weight of oxygen as 16 instead of 8; in other words, the vapor density of water has really been used in deciding whether we should use 8 or some multiple of that figure as the atomic weight of oxygen. Similarly, the vapor density of substances has in many other cases been used in choosing the atomic weights, the combining weights being known. Thus, in hydrochloric acid hydrogen and chlorine are combined in the proportions of 1 to 35.45 by weight. By volume, on the other hand, we have, 1 volume of hydrogen uniting with 1 volume of chlorine to form 2 volumes of hydrochloric acid. We have seen that this volume relation led Avogadro to distinguish between the atom of hydrogen, H, and the molecule of hydrogen, H_2, and also between the atom of chlorine, Cl, and the molecule of chlorine, Cl_2. We have also noted, that having assumed each of the molecules of hydrogen and chlorine to consist of 2 atoms, the composition of the molecule of hydrochloric acid could still be expressed by the simple formula, HCl; and thus the volume

relations that obtain when hydrochloric acid is formed from the elements could be explained in the light of Avogadro's hypothesis, and 35.45 be regarded as the atomic weight of chlorine. Here again, the vapor density of hydrochloric acid gas has been the determining factor in choosing the atomic weight of chlorine as 35.45 rather than some multiple thereof.

In marsh gas, which consists of hydrogen and carbon, 1 gram of hydrogen is combined with every 3 grams of carbon. The combining weight or chemical equivalent of carbon is therefore 3. How now proceed to ascertain the atomic weight of carbon? Marsh gas is 8 times heavier than hydrogen; whence 22.38 liters of marsh gas weigh 16 grams. From what has been stated above, 16 is therefore the molecular weight of marsh gas. But in 16 grams of marsh gas there are 4 grams of hydrogen, which is 4 times the atomic weight of hydrogen in grams. The molecule of marsh gas therefore contains 4 atoms of hydrogen. Now if in the case of this compound, which of all the compounds of hydrogen with carbon contains the *least* amount of carbon by weight as compared with the hydrogen, we assume that there is but 1 carbon atom to the 4 hydrogen atoms, we must ascribe to the carbon atom the weight of 12. Thus it is clear that the vapor density of marsh gas has not only fixed its molecular weight, but has also led us to choose the atomic weight of carbon as 12, rather than as some other multiple of 3, the combining weight. Further, we find that by thus taking 12 as the atomic weight of carbon, the composition of other compounds into which that element enters can readily be expressed. Of compounds of carbon with oxygen, the one that contains the least carbon as compared with the oxygen is carbonic acid gas. In this 3 grams of carbon are combined with every 8 grams of oxygen. The gas is 22 times heavier than hydrogen, that is 22.38 liters of carbonic acid gas weigh 44 grams, and the molecular weight of this substance is consequently 44. Since it contains the least carbon of any of the known compounds of oxygen and carbon, it would be natural to hold that it contains but 1 atom of carbon. Now if the atomic weight of carbon be 12, that of oxygen 16, and the molecular weight of carbonic acid gas 44, we have (since in 44 grams of carbonic acid gas there are 12 grams of carbon and 32 grams of oxygen) in the carbonic acid molecule

1 atom of carbon united with 2 atoms of oxygen, which is expressed by the formula CO_2. Since this compound contains but two elements, it is a so-called *binary compound.* The names of all binary compounds, *i.e.* compounds consisting of but two elements, end in *ide.* Since carbonic acid gas contains twice as much oxygen as the lower oxide of carbon, carbon monoxide, and as we have assigned to the former the formula, CO_2, indicating that the molecule contains 2 atoms of oxygen, it is called carbon dioxide. In carbon monoxide there are 3 grams of carbon combined with every 4 grams of oxygen, and carbon monoxide is 14 times heavier than hydrogen; its molecular weight is consequently 28. The atomic weights 12 for carbon and 16 for oxygen would consequently lead us to write the formula for carbon monoxide as CO. The name carbon monoxide is given to the compound because it contains but 1 atom of oxygen in its molecule.

When carbon is burned in oxygen, the carbon dioxide formed is of exactly the same volume as the original oxygen, as will appear later. In other words: 1 volume of oxygen yields 1 volume of carbon dioxide. Accepting Avogadro's hypothesis, there are then as many molecules of carbon dioxide formed as there are molecules of oxygen. The process may be expressed by the equation,

$$C + O_2 = CO_2,$$

which, like all so-called chemical equations, simply expresses the march of the reaction. The sign = stands for yields. Some use the sign $\rightarrow$ instead of =. The latter is, however, more frequently employed.

When carbon monoxide is burned in oxygen, 2 volumes of the former unite with 1 volume of the latter to form 2 volumes of carbon dioxide. Assuming Avogadro's hypothesis, there must consequently be formed as many molecules of carbon dioxide as there were molecules of carbon monoxide. These relations are expressed by the simple equation:

$$2\,CO + O_2 = 2\,CO_2.$$

The above illustrations may suffice to indicate how the vapor densities of substances have been employed in choosing the atomic weights, the combining weights having been ascertained by careful quantitative analytical or synthetical experiments.

When Avogadro put forth his hypothesis in 1811, it was by no means at once generally accepted. Indeed, it was not till the vapor densities of a very considerable number of substances had become known, that the value of the hypothesis was really recognized. It was Charles Gerhardt, professor of chemistry at the University of Montpellier, who in 1842 used the vapor densities of substances as a guide in determinining their formulæ and in choosing the atomic weights from the equivalents or combining weights, which were at that time in almost general use. But it was Auguste Laurent, professor of chemistry at the University of Bordeaux, who in 1846 grasped the great value of Avogadro's hypothesis and paved the way for its general acceptance. *He distinguished clearly between atomic and molecular weights, defining the molecule as the smallest weight of any substance that can exist by itself, and the atom as the smallest weight of a substance that can enter into combination.*

But there are elements which do not enter into compounds that can be vaporized, and consequently the atomic weights of such elements cannot be chosen from the combining weights by means of the vapor density, as described. This is particularly true of many of the metals. In determining the atomic weights of the latter, Berzelius simply took the number of parts by weight of the metal that united with 16 parts by weight of oxygen as the atomic weight of the metal. In case a metal formed more than one oxide — recall the oxides of lead, for instance — Berzelius assumed the one most commonly found as containing 1 atom of the metal to 1 atom of oxygen, and then computed the formulæ of the other oxides accordingly. When there was but one oxide known, as in the case of zinc, for instance, he assumed that the molecule consisted of 1 atom of the metal to 1 atom of oxygen. Thus he proceeded on the basis of simplicity, guarding himself by assigning similar formulæ to substances that exhibit similar chemical properties. Gerhardt, however, considered it likely that the molecules of the oxides of the metals are similar to the molecule of water in construction, and consequently contain 2 atoms of metal to 1 atom of oxygen, which, of course, led him to adopt atomic weights for the metals which were just half of the values adopted by Berzelius. This led to considerable discussion. But in 1858 Stanislao Cannizzaro, then professor of

chemistry at Genoa, brought order into the confusion that had arisen by pointing out that the specific heats of the elements in the solid state may be employed with great advantage in choosing the true atomic weights from the combining weights.

The Law of Dulong and Petit. — Cannizzaro recalled a simple relation, discovered by Dulong and Petit of Paris in 1819, between the atomic weight of an element and its specific heat. This relation is that *the product of the specific heat of an element in the solid state and its atomic weight is constant.* This law, which is known as the **law of Dulong and Petit**, may also be expressed by saying that *the atoms of the elements have the same heat capacity.* The experimental researches of Victor Regnault, the great French physicist (1810–1878), added many new data to confirm this law; but, like the hypothesis of Avogadro, its value was not clearly recognized till Cannizzaro showed how useful it is in fixing the atomic weights of many of the elements. *The product of the atomic weight and the specific heat of an element in the solid state is approximately* 6.4. The following table gives the specific heats of a number of elements in the solid state: —

Element	Symbol	Atomic Weight	Specific Heat	Atomic Heat
Lithium	Li	6.94	0.941	6.53
Sodium	Na	23.00	0.293	6.74
Magnesium	Mg	24.32	0.245	5.95
Aluminum	Al	27.1	0.214	5.80
Phosphorus	P	31.0	0.202	6.26
Sulphur	S	32.07	0.203	6.50
Potassium	K	39.10	0.166	6.49
Iron	Fe	55.85	0.112	6.26
Copper	Cu	63.57	0.095	6.04
Zinc	Zn	65.37	0.093	6.08
Silver	Ag	107.88	0.057	6.15
Platinum	Pt	195.2	0.0325	6.34
Gold	Au	197.2	0.0324	6.40
Mercury	Hg	200.6	0.0333	6.68
Lead	Pb	207.1	0.0315	6.52
Glucinum	Gl	9.1	0.42	3.82
Boron	B	11.0	0.24	2.64
Carbon (Graphite)	C	12.0	0.200	2.40
Silicon	Si	28.3	0.177	5.01

As the specific heat of a substance is a function of the temperature at which it is determined, one would clearly not expect the product of the atomic weight and the specific heat to yield exactly the same value. An inspection of the table shows that the atomic heat is generally about 6, except in the case of the last four elements, where it varies greatly from that value. Now it is found that the specific heats of glucinum, boron, carbon, and silicon increase greatly with rise of temperature, finally becoming nearly constant. So the specific heat of graphite is 0.160 at 10°; 0.199 at 60°; 0.445 at 600°; and 0.460 at 900°. The specific heat of silicon is 0.20 at 200° and 0.203 at 300°; that of glucinum is 0.617 at 400°, and 0.620 at 500°. Thus at higher temperatures these elements approximately obey the law of Dulong and Petit, though at room temperatures they apparently are exceptions.

By means of the law of Dulong and Petit the atomic weight of an element may be found by dividing the atomic heat, approximately 6.4, by the specific heat; that is,

$$\text{Atomic Weight} = \frac{6.4}{\text{Specific Heat}}.$$

This method can obviously not be used for determining atomic weights with accuracy; but it is of great value in choosing the true atomic weight from the combining weights, and it is in this way that it was employed with great success by Cannizzaro. The latter thus showed that in nearly all cases the values that Berzelius had assigned to the atomic weights of the metals were the correct ones; and that only in a few instances, like potassium, sodium, and silver, did the oxides have two atoms of the metal in the molecule, though Gerhardt had assumed this in all cases. Cannizzaro also showed that wherever volatile metallic compounds were known, the choice of the atomic weights from the vapor density of these agreed with the values deduced from the specific heats.

Other Methods of choosing the Atomic Weights from the Combining Weights. — Many substances form crystals. Crystals are solids bounded by plane faces which are the outcome of a regular internal structure. Substances which do not crystallize, that is, are non-crystalline, are called amorphous. All crystals may be classified into six crystal systems (which see).

In 1819, Eilhard Mitscherlich discovered that *chemical compounds which are similar in character crystallize in the same forms.* This is the **law of isomorphism,** for isomorphous substances are such as crystallize in the same form. Whenever compounds are isomorphous, they are chemically analogous; and so if the formula of one compound has been determined, the formulæ of other compounds that are isomorphous with it are readily deduced by analogy. Ismorphism may consequently be used in choosing the atomic weights from the combining weights. It was so employed by Berzelius. Thus, the sulphate of magnesium is isomorphous with that of zinc. If the atomic weight of the latter metal has been fixed as 65.5, with the aid of the law of Dulong and Petit, then the amount of magnesium that is required to replace 65.5 parts of zinc by weight in the sulphate, namely 24.32, is the atomic weight of magnesium. In this way isomorphism has been of great use in atomic weight determinations. It must be applied with great care, however, for it is true there are many cases where compounds are chemically dissimilar and yet possess like crystal forms. For this reason, isomorphism is not so reliable a guide as the specific heat or vapor density method, and is only employed when other methods cannot be used.

In choosing the atomic weights from the combining weights, the principle of simplicity and analogy was employed with much success by Berzelius. As already stated, in the case of metals, like zinc and magnesium, that form but one compound with oxygen, he assumed that the oxide contains 1 atom of the metal to 1 atom of oxygen. Since the atomic weight of oxygen was taken as 16, the atomic weight of the element combined with oxygen could readily be found. Further, Berzelius sought to assign analogous formulæ to compounds that are actually analogous in their chemical behavior. By this method he consequently chose the atomic weight of the element in question in accordance with the formulæ assigned.

Finally, the arrangement of the atomic weights of the elements in the so-called periodic system (which see) has in some cases influenced the choice of the atomic weights. *In summary, then, the methods of choosing the atomic weights from the combining weights are:* (1) *the vapor density,* (2) *the specific heats in the solid state,* (3) *isomorphism,* (4) *the principle of simplicity*

and chemical analogy, and (5) *the periodic system.* Concerning the last two of these it should be said at this juncture that the manner of their application cannot be elucidated before more substances have been studied.

Table of Atomic Weights. — The following is a table of the atomic weights of the elements as adopted by the International Commission on Atomic Weights: —

INTERNATIONAL ATOMIC WEIGHTS

Element	Symbol	Atomic Weight	Element	Symbol	Atomic Weight
Aluminum	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.88	Nickel	Ni	58.68
Arsenic	As	74.96	Niton (radium emanation)	Nt	222.4
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Cæsium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.5
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	3.99	Thallium	Tl	204.0
Holmium	Ho	163.5	Thorium	Th	232.4
Hydrogen	H	1.008	Thulium	Tm	168.5
Indium	In	114.8	Tin	Sn	119.0
Iodine	I	126.92	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Iron	Fe	55.84	Uranium	U	238.5
Krypton	Kr	82.92	Vanadium	V	51.0
Lanthanum	La	139.0	Xenon	Xe	130.2
Lead	Pb	207.10	Ytterbium (Neoytterbium)	Yb	172.0
Lithium	Li	6.94	Yttrium	Yt	89.0
Lutecium	Lu	174.0	Zinc	Zn	65.37
Magnesium	Mg	24.32	Zirconium	Zr	90.6
Manganese	Mn	54.93			
Mercury	Hg	200.6			
Molybdenum	Mo	96.0			

Interpretation of a Chemical Formula. — A chemical formula expresses (1) what elements occur in the compound, (2) the relative weights in which these elements occur in the compound, and (3) the weight of 22.38 liters of the vapor of the compound under standard conditions. In case the compound cannot be converted into the vapor state, the formula is derived from a study of the freezing or boiling point of its solution, the crystalline form, the specific heat, or from its chemical behavior and analogy to other compounds. These facts are thus recorded in the formula. So the formula of carbonic acid gas CO_2 tells us that this compound consists of carbon and oxygen in the proportions of 12 parts of the former to 32 parts of the latter by weight. It also tells that the weight of 22.38 liters of the gas under standard conditions is 44 grams, or that the gas is 22 times as heavy as hydrogen. Thus we see that chemical formulæ are a system of shorthand writing, as it were, for they express in a small space the salient facts known about a compound.

Valence and Structural Formulæ. — For hydrochloric acid we have developed the formula HCl. In this compound 1 atom of hydrogen is combined with 1 of chlorine. In water H_2O, on the other hand, 2 atoms of hydrogen are combined with 1 of oxygen. The power which an atom of one element has to unite with one or more atoms of other elements is called its **valence.** Thus in hydrochloric acid, hydrogen and chlorine each have a valence of one. Hydrochloric acid is said to be a *saturated compound*, for it will unite with neither more hydrogen nor more chlorine. Hydrogen always has a valence of one, it is consequently called a *univalent element* or a *monad. The number of hydrogen atoms, or other univalent atoms, with which an atom of a given element combines determines the valence of the latter.* In water, we have 2 hydrogen atoms united with 1 oxygen atom. Oxygen, consequently, has a valence of 2; *i.e.* it is a *bivalent element* or *dyad.*

The formula for water is also written H — O — H to indicate that each of the atoms of hydrogen is bound to oxygen, which idea may be deduced from the fact that when sodium acts on water only half of the hydrogen of the latter is displaced, and that the other half of the hydrogen is set free when the resulting sodium hydroxide

is treated with zinc, as indicated by the equations (compare Chapter II) —

$$H-O-H + Na = NaOH + H.$$
Water + sodium = sodium hydroxide + hydrogen.

$$2\,NaOH + Zn = Na_2O_2Zn + H_2.$$
Sodium hydroxide + zinc = sodium zincate + hydrogen.

The formula H – O – H is therefore the structural formula for water. It is clear that it is derived from reactions that water will undergo, and is consequently merely a brief way of expressing these changes. Structural formulæ are often used in chemistry, particularly in connection with the compounds of carbon. It is not to be thought that such a formula expresses the actual conditions that exist within the molecule itself; it is rather simply a concise expression of the reactions which the compound in question will undergo with other chemical compounds.

In chlorine monoxide Cl_2O chlorine is univalent and oxygen is bivalent. The structural formula of the compound is Cl – O – Cl; we may consider it as water in which the hydrogen atoms are replaced by chlorine. In chlorine dioxide ClO_2 the oxygen is bivalent, and the chlorine has a valence of four; *i.e.* it is quadrivalent, the formula being O = Cl = O. Oxygen is always bivalent except in very rare cases. It is thus clear that *the number of oxygen atoms, or other atoms of known valence, with which an atom of another element combines, may also serve to ascertain the valence of the latter.* In carbon dioxide CO_2 carbon is quadrivalent; thus, O = C = O. In carbon monoxide CO carbon is bivalent; thus, C = O; or sometimes it is considered as quadrivalent, two combining powers or *bonds* being *free* or *unsaturated*, thus, = C = O. This at once brings us to the question whether the valence of an element is always the same or not. There has been considerable dispute over this question, but now it is quite generally held that the valence of an element may vary in different compounds. The highest valence which an element exhibits in any known compound is called its *maximum valence.*

The valence of an element may vary from one to eight, though in case of most elements it varies but slightly. As already stated, hydrogen is always univalent; oxygen is almost

always bivalent; and carbon may practically always be considered as quadrivalent, though in some compounds it is bivalent and even trivalent. Chlorine is always univalent toward hydrogen, while toward oxygen it may be either univalent, bivalent, quadrivalent, or heptavalent. The valences of the various elements will be taken up in connection with the description of each element, for the subject cannot be considered fully except in connection with actual illustrations.

Nomenclature. — The names of the metallic elements end in *um*, like lithi*um*, sodi*um*, bari*um*, etc., except in case of some metals that have been known for a very long time, which retain their old names, as iron, lead, gold, silver, etc. The elements selenium and tellurium are not metals. They were thought to be such when discovered, on account of their outward properties, hence the ending *um* in their names.

Substances containing but two elements are called *binary compounds;* their names end in *ide*. Thus, common salt NaCl is sodium chlor*ide;* magnesia is magnesium ox*ide* MgO; lime is calcium ox*ide* CaO, etc. In some cases the suffix *ide* is used in connection with compounds containing more than two elements. In all these, however, two or more of the elements act as a group, *i.e.* a unit or *radical*, so called, which may pass from compound to compound; thus, sodium hydroxide NaOH contains the OH group, which is called the *hydroxyl group*. This OH group passes from one compound to another as a unit, and when elements or other groups are combined with this group, the compounds formed are termed *hydroxides*. So we have calcium hydroxide $Ca(OH)_2$ formed when calcium acts on water,

$$Ca + 2\,H_2O = Ca(OH)_2 + H_2;$$

or when lime, calcium oxide CaO, is treated with water, *i.e.* is slaked, thus: —

$$CaO + H_2O = Ca(OH)_2.$$

In the hydroxyl group OH one of the two combining powers or *bonds* of oxygen is satisfied by hydrogen, the other bond being free. The group is therefore univalent, and we may write it thus: $-O-H$.

When two elements form more than one compound with each other (which is frequently the case), a name indicating the num-

ber of atoms of the one element that are united with the other is given to each compound. Thus we have carbon monoxide CO, carbon dioxide CO_2, sulphur dioxide SO_2, sulphur trioxide SO_3, phosphorus trichloride PCl_3, phosphorus pentachloride PCl_5, lead sesquioxide Pb_2O_3. The ending *ous* is frequently used for one compound and the ending *ic* for another compound richer than the former in one of the ingredients. Thus SO_2 or sulphur dioxide is also called sulphur*ous* oxide, and SO_3 or sulphur trioxide is also called sulphur*ic* oxide. Again, PCl_3 is phosphorus trichloride or phosphor*ous* chloride, and PCl_5 is phosphorus pentachloride or phosphor*ic* chloride. When more than two compounds are formed by two elements, the endings *ous* and *ic* are retained and the prefixes *proto*, *hypo* or *sub*, and *per* are added as required. Thus litharge PbO is lead *mon*oxide, lead *pro*toxide or plumb*ic* oxide; black oxide of lead Pb_2O is lead *sub*oxide or plumb*ous* oxide; Pb_2O_3 is lead *sesqui*oxide; minium or red lead Pb_3O_4 is the *proto-sesqui*oxide of lead, *i.e.* $PbO \cdot Pb_2O_3$; brown oxide of lead PbO_2 is lead dioxide or lead *per*oxide. The prefix *per* stands for the highest oxidation stage in the case of oxides, for the highest chlorination stage in the case of chlorides, etc. Chlorine monoxide or protoxide Cl_2O is also called *hypo*chlorous oxide. Water H_2O is hydrogen *pro*toxide or *mon*oxide, or hydrogen hydroxide, or hydroxyl hydride. The prefix *hypo* is rarely used in case of binary compounds.

In *ternary compounds*, that is, those that are made up of three elements, somewhat similar designations are employed, which will be explained when compounds of this character are considered.

Chemical Equations. Retrospect. — Chemical compounds may be designated by means of symbols or formulæ, as we have seen, and chemical changes may be indicated by writing equations in which these formulæ are used instead of the names of the compounds. Reviewing the work on hydrogen, oxygen, and chlorine, and writing the principal chemical changes that have been studied in form of chemical equations, we have as follows: —

(1) **Preparation of Hydrogen**

$$Na + H_2O = NaOH + H.$$

Sodium + water = sodium hydroxide + hydrogen

H_2SO_4 + Zn = $ZnSO_4$ + H_2.
Sulphuric acid + zinc = zinc sulphate + hydrogen.

2 KOH + Zn = K_2O_2Zn + H_2.
Potassium hydroxide + zinc = potassium zincate + hydrogen.

3 KOH + Al = K_3O_3Al + 3 H.
Potassium hydroxide + aluminum
= potassium aluminate + hydrogen.

2 H_2O (on electrolysis) = 2 H_2 + O_2.
3 Fe + 4 H_2O = Fe_3O_4 + 4 H_2.
Mg + H_2O = MgO + H_2.

(2) Preparation of Oxygen

HgO (on heating) = Hg + O.
Mercuric oxide (on heating) = mercury + oxygen.

Ag_2O (on heating) = 2 Ag + O.
Argentic oxide (on heating) = silver + oxygen.

$KClO_3$ (on heating) = KCl + 3 O.
Potassium chlorate (on heating)
= potassium chloride + oxygen.

3 MnO_2 (on ignition) = Mn_3O_4 + O_2.
Manganese dioxide (on ignition)
= manganese proto-sesquioxide + oxygen.

KNO_3 (on heating) = KNO_2 + O.
Potassium nitrate or saltpeter (on heating)
= potassium nitrite + oxygen.

(3) Oxidations

2 H_2 + O_2 = 2 H_2O.
Mg + O = MgO.
Cu + O = CuO.
2 P + 5 O = P_2O_5,
phosphorus pentoxide.
C + O_2 = CO_2.
3 Fe + 2 O_2 = Fe_3O_4.
2 Fe + 3 O = Fe_2O_3,
ferric oxide or sesquioxide of iron
S + O_2 = SO_2.

(4) **Reductions**

$$CuO + H_2 = Cu + H_2O.$$
$$Fe_3O_4 + 4\,H_2 = 3\,Fe + 4\,H_2O.$$

(5) **Preparation of Chlorine**

$$4\,HCl + MnO_2 = MnCl_2 + 2\,H_2O + Cl_2.$$

manganous chloride.

(6) **Reactions of Chlorine**

$$H_2O + Cl_2 = 2\,HCl + O.$$
$$P + 3\,Cl = PCl_3,$$

phosphorus trichloride.

$$P + 5\,Cl = PCl_5,$$

phosphorus pentachloride.

$$Sb + 3\,Cl = SbCl_3,$$

antimony trichloride.

$$C_{10}H_{16} + 8\,Cl_2 = 16\,HCl + 10\,C.$$

turpentine.

Phenomena of the Nascent State. — When a dilute solution of sulphuric acid is acting on zinc, the hydrogen liberated will reduce many substances like potassium permanganate, potassium bichromate, or saltpeter, *if these are added directly to the mixture in the generator.* The reduction will not take place if the hydrogen is passed through solutions of these salts contained in a separate vessel. The explanation of this as commonly given is that at the moment of liberation, the hydrogen is in the so-called **nascent state**, *i.e.* in an atomic condition represented by H, whereas afterwards it passes over into the molecular condition H_2. While in the nascent state the hydrogen is more active than in the molecular state, and it consequently effects many reductions. Similarly we may have nascent oxygen O, as compared with molecular oxygen O_2. Cases of this kind will be mentioned later.

REVIEW QUESTIONS

1. What is the difference between a law and a theory, as these terms are used in science?

2. State the three fundamental laws of stoichiometry, illustrating each by means of a concrete example.

3. Upon what facts is the atomic theory of matter based?

4. What is meant by the term "combining weights"? Illustrate by means of an example.

5. What is the hypothesis of Avogadro? Upon what facts is it based?

6. Why is the symbol for hydrogen H_2, and for chlorine Cl_2?

7. Define atomic weight, also molecular weight.

8. Why is the formula for water written H_2O? State fully all the facts which this formula represents. What three important facts does every chemical formula represent?

9. What is meant by the term "specific heat"? State the law of Dulong and Petit. For what purpose is it used in chemistry?

10. A new element has a specific heat of 0.0328; what is its atomic weight?

11. What is the significance of the volume 22.38 liters? The weight of a liter of a certain gaseous substance is 2.1 grams, under standard conditions; what is its molecular weight?

12. State the law of isomorphism. Who discovered it?

13. What are the different methods used in choosing the atomic weights from the combining weights?

14. What is the valence of the first element in the compounds represented by the following formulas: CO_2; P_2O_5; NH_3; Fe_2O_3; SO_3; $NaCl$; $BaCl_2$; CuO; $BiCl_3$; SO_2; PCl_5; NO; PbO_2; Cl_2O_7.

15. How much oxygen may be prepared from 100 kilograms of silver oxide? What volume would this gas occupy at standard conditions? How much greater would its volume be at 10° C and 760 mm. pressure?

16. What chemical elements generally have names ending in *um*? Give six illustrations. Mention four cases that do not follow the rule.

17. Using the formula for water, explain what is meant by valence and structural formula.

18. Write the chemical equation expressing the action of metallic potassium upon water and explain in detail what the equation means.

19. Name two compounds illustrating the use of the endings *ous* and *ic* in chemical nomenclature.

20. Write the equation expressing the reaction by means of which Joseph Priestley first prepared oxygen. Why can not oxygen be prepared in an analogous manner by heating cupric oxide?

21. Distinguish between nascent hydrogen and molecular hydrogen. Use examples.

22. Write the equations expressing the change when each of the following is burned in oxygen: Mg, C, S, Cu, P.

23. By means of a chemical equation express the electrolytic decomposition of water.

24. Write the equation expressing the action of metallic calcium on water.

25. Write the names of the compounds represented by the following formulas: Mn_3O_4, $FeCl_2$, $FeCl_3$, BaO, BaO_2, Pb_2O_3, PbO, $NaOH$.

CHAPTER VII

OZONE, ALLOTROPY, AND HYDROGEN PEROXIDE

History, Occurrence, and Preparation of Ozone. — When a frictional electrical machine is operated, there is observed in its neighborhood a peculiar characteristic odor, which is sometimes described as similar to the odor of chlorine, burnt sulphur, or garlic. The observation that this smell is produced when electric sparks are passed through oxygen was made in 1785 by Van Marum, who had constructed an especially powerful machine. The same odor is noticed whenever electric sparks pass through the air, as, for instance, from an induction coil, or when objects are struck by lightning. In 1840 Christian Schönbein, professor at the University of Basel, showed that when water is electrolyzed the oxygen obtained always contains some of this odoriferous substance, which he named **ozone**, meaning a smell. From the fact that ozone is produced when electric sparks pass through pure, dry oxygen, it is clear that the substance consists of oxygen. By means of the silent electrical discharge ozone is produced in larger quantities. For this purpose an apparatus like that in Fig. 28 is commonly employed. The apparatus is blown of one piece of glass. The

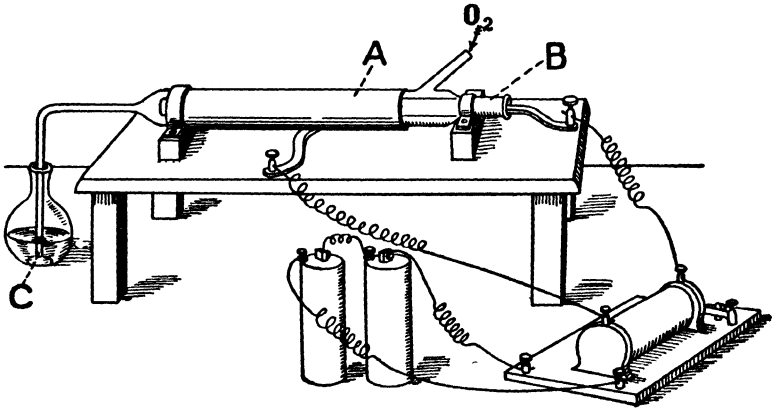


FIG. 28.

outside of the tube *A* is coated with tin foil, as is also the inside of the tube *B*, as indicated. Dry oxygen is passed through the apparatus as shown, and when the tin foil coatings are connected with the poles of an induction coil, ozone issues at *C*. In this way about 5 to 8 per cent of the oxygen is converted into ozone. By liquefying oxygen and ozone by means of liquid air, a liquid is obtained which upon slow evaporation leaves a very dark blue liquid consisting of about 86 per cent ozone and 14 per cent oxygen.

Besides being formed by means of electrical discharges and in the electrolysis of water, ozone is produced in chemical reactions, notably when moist phosphorus slowly oxidizes in the air; also generally when oxygen is rapidly evolved, as by heating potassium chlorate, or when potassium permanganate is treated with strong sulphuric acid. Further, ozone is formed in very small quantities when hydrogen burns in oxygen. By the action of fluorine on water, oxygen containing up to 15 per cent of ozone is formed.

Relation between Ozone and Oxygen, Allotropy. — As already stated, ozone is produced from oxygen. By passing ozone through a red-hot tube, it is again converted into oxygen. Under standard conditions, 22.38 liters of ozone weigh 48 grams. The molecular weight of ozone is consequently 48; and since the atomic weight of oxygen is 16, the formula of ozone is O_3. The change of oxygen to ozone is expressed by the following equation: —

$$3\ O_2\ (\text{plus energy}) = 2\ O_3.$$

The energy that must be added to oxygen to convert it into ozone may be obtained from the silent electric discharge, or from chemical changes, as we have seen. When ozone is heated, the reaction is reversed. We have here then a reversible reaction. This fact may be expressed thus: —

$$3\ O_2\ (\text{plus energy}) \rightleftarrows 2\ O_3,$$

where the arrows are used instead of the usual sign of equality.

In forming ozone, oxygen shrinks from 3 volumes to 2 volumes and simultaneously a considerable amount of energy is absorbed. Ozone is called an **allotropic form** of oxygen. The property which some elements possess of occurring in two or more forms is called **allotropy.**

Ozone is a much more powerful oxidizing agent than oxygen. Many of the reactions which take place in oxygen only at higher temperatures proceed readily in ozone at room temperatures.

Properties of Ozone. — In thick layers ozone gas has a bluish color. Inhaled in quantity, it attacks the mucous membranes and produces headache. Liquid ozone is indigo-blue in color, and boils at $-119°$ under atmospheric pressure. The liquid is strongly magnetic. On warming, it is liable to explode, due to sudden change of the substance to ordinary oxygen. According to Ladenburg, 1000 volumes of water dissolve 10 volumes of ozone. It acts slowly on water, forming oxygen and hydrogen peroxide (which see), and the solubility in water may be due to this fact.

The chief chemical property of ozone is its oxidizing power. It will bleach litmus, indigo, and other dyestuffs, the colors being destroyed by oxidation. Ozone destroys disease germs and other minute organisms, and, consequently, it is used as a germicide in sterilizing drinking water. Ozone is soluble in turpentine, also in oil of cinnamon and other similar oils. In solutions, ozone is also a powerful oxidizing agent. On account of its oxidizing power, it causes many oils to thicken and become resinous.

Ozone rapidly oxidizes such substances as silver, lead, arsenic, phosphorus, and sulphur, to their highest stages of oxidation. It is the most powerful oxidizing agent known. It acts on potassium iodide solutions, liberating iodine, thus: —

$$2\,KI + H_2O + O_3 = 2\,KOH + O_2 + I_2.$$

Iodine turns starch paste blue, and so when a strip of paper saturated with starch paste plus a solution of potassium iodide is exposed to ozone, the paper turns deep blue in color. This is a common test for ozone. However, it must be used with proper care; for, as we shall see, there are other things besides ozone that turn starch potassium iodide paper blue. The above reaction may be used in estimating the amount of ozone in a given sample of oxygen, by determining the quantity of iodine set free. Ozone is the only gaseous oxidizing agent that will blacken a bright silver foil, and consequently this test is used in detecting ozone in presence of other oxidizing gases.

History, Occurrence, and Preparation of Hydrogen Peroxide. — In 1818 Thénard prepared a compound of hydrogen and oxygen containing twice as much oxygen as there is in water. He treated barium dioxide with hydrochloric acid, thus: —

$$BaO_2 + 2\,HCl = BaCl_2 + H_2O_2.$$

Both the barium chloride and hydrogen peroxide (which is also called hydrogen dioxide or hydroperoxide) remain in solution. Hydrogen peroxide may also be prepared by adding barium dioxide to cold, dilute sulphuric acid: —

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2\ ;$$

or by passing carbon dioxide through water and gradually adding barium dioxide in small amounts: —

$$BaO_2 + CO_2 + H_2O = BaCO_3 + H_2O_2.$$

Barium sulphate and barium carbonate are insoluble in water, and hence may be removed by filtration; and thus a filtrate, which is an aqueous solution of hydrogen peroxide, may be obtained.

When ozone acts on water, hydrogen peroxide is produced: —

$$H_2O + O_3 = H_2O_2 + O_2.$$

Hydrogen peroxide occurs in very small amounts in the air, and this is probably due to the fact that ozone has been produced, which in turn has acted on the moisture in the air. It is consequently very doubtful whether ozone itself occurs in air. It should be stated here that the occurrence of hydrogen peroxide in the air has been questioned by some chemists, the claim being made that the strong oxidations observed may very well be caused by oxides of nitrogen which are present in the atmosphere.

Hydrogen peroxide may also be formed by treating cold, dilute hydrochloric acid with sodium peroxide: —

$$2\,HCl + Na_2O_2 = 2\,NaCl + H_2O_2.$$

Both the sodium chloride and hydrogen peroxide remain in solution. Instead of the peroxide of barium or sodium, that of potassium or strontium may be used. By distilling an aqueous solution of hydrogen peroxide in a partial vacuum, the water passes off first, leaving hydrogen peroxide in the retort.

On heating a 3 per cent solution of hydrogen peroxide on the water bath to temperatures below 70°, in a retort from which the air has been exhausted so as to create a partial vacuum, a 45 per cent solution may readily be obtained without loss. On continuing the distillation further, nearly pure hydrogen perox ide passes over between 84° and 85° at 68 mm. pressure.

Properties of Hydrogen Peroxide. — Pure hydrogen peroxide is a colorless, sirupy liquid, which, like water, has a bluish hue in thick layers. At 0° its specific gravity is 1.458. It boils at 69° under 26 mm. pressure, and at 84° to 85° under 68 mm. pressure. It forms colorless prismatic crystals which melt at − 2°.

Hydrogen peroxide slowly decomposes into water and oxygen on standing. In the sunlight the decomposition proceeds more rapidly. By warming hydrogen peroxide the rate of decomposition is increased; and at 100° the evolution of oxygen becomes so rapid as to cause explosion. It is, therefore, necessary to distill hydrogen peroxide in a vacuum, so that it will not need to be heated to a temperature at which violent decomposition sets in.

Solutions of hydrogen peroxide have a peculiar bitter, disagreeable taste. Concentrated solutions act on the skin. The aqueous solutions on the market usually contain about 3 per cent hydrogen peroxide, though 30 per cent solutions are also now placed on sale. The latter are kept in small bottles coated with paraffin on the inside; for in contact with glass the solution soon suffers decomposition on account of the fact that alkali is dissolved from the glass.

In contact with platinum black, manganese dioxide, or finely divided silver, gold, or carbon, hydrogen peroxide is decomposed into oxygen and water even at room temperatures and in dilute solutions. The action is more rapid at higher temperatures. All these cases are illustrations of catalytic or contact action.

Hydrogen peroxide is a strong oxidizing agent. It will act on black sulphide of lead and convert it into lead sulphate, which is a white salt: —

$$PbS + 4\ H_2O_2 = PbSO_4 + 4\ H_2O.$$

Potassium iodide in solution is oxidized thus: —

$$2\ KI + H_2O_2 = 2\ KOH + I_2.$$

For this reason, starch potassium iodide paper may be used to detect the presence of hydrogen peroxide. The action goes on much more slowly than in the case of ozone; but the addition of a little ferrous sulphate hastens the action very markedly, so that the test is really a sensitive one. In presence of ozone, which also liberates iodine from potassium iodide, this test for hydrogen peroxide can, of course, not be used. Hydrogen peroxide does not oxidize a bright silver foil as ozone does, and thus the latter may be detected in presence of the former.

In contact with blood, meat, and the mucous membranes, hydrogen peroxide decomposes. The oxygen thus liberated destroys germs by oxidizing them, hence the use of hydrogen peroxide in medicine as a gargle and an antiseptic.

When limewater is treated with hydrogen peroxide solution, a precipitate of calcium peroxide is formed: —

$$Ca(OH)_2 + H_2O_2 = CaO_2 + 2\,H_2O.$$

The action on the hydroxide of barium or strontium is similar. All of these peroxides may be regarded as hydrogen peroxide in which the hydrogen is replaced by metals.

When hydrogen peroxide solution is slightly acidified with sulphuric acid, and a few drops of potassium bichromate solution and some ether are added, and the mixture is then shaken, an indigo-blue compound is formed which dissolves in the ether and so finally collects in the light ethereal layer on standing. This reaction is used as a test for hydrogen peroxide. The nature of the blue compound is not known with certainty, though it is probably perchromic acid.

While hydrogen peroxide is an oxidizing agent, it may also at times act as a reducing agent, in which case ordinary oxygen gas is evolved. So the oxides of metals like silver, gold, and platinum suffer reduction to the metallic state when treated with hydrogen peroxide, thus: —

$$Ag_2O + H_2O_2 = 2\,Ag + H_2O + O_2.$$

We see that hydrogen peroxide in such cases loses one atom of oxygen which unites with oxygen of the metallic oxides and escapes as ordinary oxygen gas. Lead peroxide is changed to lead monoxide: —

$$PbO_2 + H_2O_2 = PbO + H_2O + O_2.$$

Added to a potassium permanganate solution acidified with sul-

phuric acid, hydrogen peroxide reduces the permanganate with liberation of oxygen and formation of a solution of potassium sulphate and manganous sulphate, which is nearly colorless: —

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2.$$

This reaction is used in the quantitative determination of the strength of hydrogen peroxide solutions; for if a certain volume of a potassium permanganate solution of known strength is just decolorized by a known volume of a hydrogen peroxide solution, the strength of the latter can readily be computed from the data given in the above equation.

It would seem rather peculiar that hydrogen peroxide, which is a good oxidizing agent, may also serve in effecting reductions. It must be borne in mind, however, that it only reduces compounds that are rich in oxygen which is readily set free. The explanation of the reduction is that when compounds like potassium permanganate, or oxides of silver, gold, lead, etc., are brought in contact with hydrogen peroxide, the tendency to form the ordinary oxygen molecule O_2, that is, the attraction of oxygen for oxygen, is so great that the compounds mutually reduce each other.

Formula of Hydrogen Peroxide. — Thénard, the discoverer of hydrogen peroxide, determined that it consists of 16 parts of oxygen to 1 part of hydrogen by weight. The simplest formula one could assign to the compound would therefore be HO, the atomic weight of oxygen being 16. However, the fact that water H_2O and oxygen are formed when hydrogen peroxide decomposes, is much better indicated by adopting the formula H_2O_2 for the latter substance. The vapor density of hydrogen peroxide cannot well be determined because the substance is so unstable, and so the weight of 22.38 liters of its vapor under standard conditions is unknown. Its molecular weight has, however, been found to be 34, from a study of the freezing point of its aqueous solution.

The fact that hydrogen peroxide decomposes into water and oxygen has led Kingsett to ascribe to it the formula $\begin{matrix} H \\ H \end{matrix}\!\!>\!O=O$, in which it will be seen that one oxygen atom is regarded as a tetrad and the other as a dyad. From a study of the index of refraction of the substance, Brühl has on the other hand suggested that both oxygen atoms are tetrads and that the formula

should be written, $H - O \equiv O - H$. As a rule chemists regard both atoms of oxygen as bivalent, writing the structural formula of hydrogen peroxide, $H - O - O - H$.

A structural formula expresses not only the qualitative and quantitative composition of a substance and its molecular weight, but it also indicates its chemical behavior. This is accomplished by arranging the relative position of the atoms in the formula so as to indicate what chemical changes the compound will undergo.

Uses of Hydrogen Peroxide. — As already stated, hydrogen peroxide is used in medicine as a germicide. As such it has the distinct advantage that, after it has acted, only water remains, which is harmless.

The usual 3 per cent solution on the market is also called **dioxogen**; it frequently is diluted further as required. It is kept in brown bottles, in a cool place, and is generally very slightly acidified, which greatly reduces the rate of its decomposition by neutralizing the alkali that is taken up from the glass of the bottle.

Hydrogen peroxide is manufactured on a large scale, and most of it is employed as a bleaching agent. Thus, delicate silks, ostrich feathers, ivory, hair, and sponges are bleached with hydrogen peroxide. It is used to change dark-colored living hair to lighter color. It is also employed similarly in changing the color of furs. In these bleaching processes, hydrogen peroxide is used because it is a mild agent, which does not injure these animal tissues as much as other bleaching agents do. Hydrogen peroxide is also used in photography to remove the last traces of sodium thiosulphate from the photographic plates, after the latter have been "fixed." In analytical chemistry it is frequently employed as an oxidizing agent.

Ozonic Acid. — Baeyer and Villiger have described an oxide of hydrogen which contains still more oxygen than hydrogen peroxide. This compound, to which the formula HO_2 or H_2O_4 has been assigned, has been called ozonic acid, because it may be regarded as formed by the addition of ozone to water: —

$$O_3 + H_2O = H_2O_4.$$

Ozonic acid has not yet been isolated, but Baeyer and Villiger regard the peroxide of potassium K_2O_4, for instance, as a salt of ozonic acid, the two potassium atoms having replaced the hydrogen atoms.

REVIEW QUESTIONS

1. Give two essentially different methods by means of which ozone may be prepared, and state the important properties of this substance.

2. Under standard conditions, how much ozone could be prepared from 2.5 liters of oxygen? What would be the weight of the ozone in grams?

3. Define "allotropy."

4. Why should the formula of ozone be written O_3?

5. What are the important properties of ozone? What use may be made of ozone?

6. What action has ozone upon potassium iodide? Upon water? Upon metallic silver? Write the appropriate chemical equation in each case.

7. How determine experimentally whether oxygen or ozone is the more active chemically?

8. Describe two methods of making hydrogen peroxide. Write the chemical equations expressing the changes that take place.

9. How prepare pure hydrogen peroxide from sodium peroxide?

10. What use is made of hydrogen peroxide? Upon what property of this compound does its use depend?

11. Mention three catalytic agents that will decompose hydrogen peroxide.

12. How distinguish between ozone and hydrogen peroxide?

13. Why is the formula of hydrogen peroxide written H_2O_2?

14. Explain the action of hydrogen peroxide upon potassium iodide-starch paper.

15. Mention some of the different structural formulas that have been proposed for hydrogen peroxide and point out the balance of the oxygen atoms in each formula.

16. Explain the use of the prefix *per* in the name hydrogen peroxide. Why may this substance also be called hydrogen dioxide?

17. Why does hydrogen peroxide attack the mucous membranes and "set the teeth on edge"?

18. How much per cent of pure hydrogen peroxide does the ordinary commercial solution of hydrogen peroxide contain? Why should such solutions be kept in a cool place and not exposed to the light?

19. Compare the colors of liquid oxygen, ozone, water, and hydrogen peroxide. Explain.

20. How much pure hydrogen peroxide may be prepared from 25 pounds of barium dioxide?

21. Give an illustration showing that hydrogen peroxide, while commonly an oxidizing agent, may yet also act as a reducing agent.

22. State briefly the history of the discovery of ozone.

23. By whom was hydrogen peroxide first prepared? What method was used in the preparation of this compound? Why is not this method used at present? Write the appropriate chemical equations.

CHAPTER VIII

THE HALOGENS

The Halogen Family. — The elements that belong to this group are fluorine, chlorine, bromine, and iodine. Of these chlorine is the most common and the most abundant in nature. Its properties have already been discussed. Fluorine, bromine, and iodine form with hydrogen the compounds hydrogen fluoride or hydrofluoric acid HF, hydrogen bromide or hydrobromic acid HBr, and hydrogen iodide or hydriodic acid HI. These compounds are analogous to hydrogen chloride or hydrochloric acid HCl. By replacing the hydrogen of these hydrohalogen acids by means of sodium, the sodium salts, sodium fluoride NaF, sodium chloride NaCl, sodium bromide NaBr, and sodium iodide NaI are formed. These salts are quite similar to one another; and as common salt is a member of the group, the elements fluorine, chlorine, bromine, and iodine have been termed the **halogens,** meaning salt formers. This must not be taken to mean that all salts contain one of these four elements, for such is not at all the case.

With the exception of fluorine, the halogens unite with oxygen and hydrogen to form certain acids. Chlorine and iodine also unite with oxygen to form oxides. Furthermore, the halogens form compounds with one another, with the metals, and with many other elements.

We shall now take up the compounds which chlorine forms with oxygen and hydrogen, after which the remaining halogens and their principal compounds will be considered.

Compounds of Chlorine with Oxygen. — There are three of these compounds, namely, chlorine monoxide Cl_2O, chlorine dioxide ClO_2, and chlorine heptoxide Cl_2O_7. These are all very unstable substances, decomposing readily into chlorine and oxygen. They are not formed by direct interaction of chlorine and oxygen.

Chlorine monoxide is formed when chlorine acts on cold mercuric oxide: —

$$2\,HgO + 2\,Cl_2 = HgO \cdot HgCl_2 + Cl_2O.$$

It is a brownish yellow gas, which may be condensed to a liquid boiling at +5°. The substance, especially when liquefied, is *highly explosive.* It detonates when heated or subjected to concussions; but in the sunlight it soon decomposes into chlorine and oxygen without explosion.

Chlorine dioxide is formed when potassium chlorate is treated with concentrated sulphuric acid. The reaction may be regarded as taking place in two steps, thus: —

$$(1)\ KClO_3 + H_2SO_4 = KHSO_4 + \underset{\text{chloric acid}}{HClO_3}.$$

$$(2)\ 3\,HClO_3 = \underset{\substack{\text{perchloric}\\\text{acid}}}{HClO_4} + H_2O + 2\,ClO_2.$$

Chlorine dioxide is also called **chlorine peroxide.** It is a yellow gas which may be condensed to a liquid, boiling at +9.9°. Solid chlorine dioxide melts at −79°. The substance is *very explosive.* Its odor resembles that of chlorine. In the sunlight it slowly decomposes into the elements. It is a powerful oxidizing agent. Sugar mixed with potassium chlorate bursts into flame when touched with a drop of concentrated sulphuric acid; for thus chlorine peroxide is liberated, which at once attacks the sugar violently. Phosphorus introduced into chlorine peroxide gas at once takes fire. When the gas is touched with a red-hot iron, it explodes.

Chlorine heptoxide is formed by the action of phosphorus pentoxide on perchloric acid. The action simply consists of the elimination of a molecule of water from two molecules of perchloric acid: —

$$2\,HClO_4 = H_2O + Cl_2O_7.$$

Chlorine heptoxide is a colorless oil which boils at 82°. On percussion it explodes with violence, also when brought in contact with a flame. It is therefore a *dangerous substance* to handle, and great care must be exercised in distilling it.

Hypochlorous Acid and Hypochlorites. — When chlorine monoxide acts on water a solution of hypochlorous acid is formed: —

$$Cl_2O + H_2O = 2\,HOCl.$$

Hypochlorous acid is known only in solution and in form of its salts.

When caustic potash solution is treated with chlorine at room temperatures, the following change occurs: —

$$2\,KOH + Cl_2 = \underset{\text{potassium hypochlorite}}{KOCl} + \underset{\text{potassium chloride}}{KCl} + H_2O.$$

A perfectly analogous change occurs when chlorine acts on calcium hydroxide, slaked lime: —

$$2\,Ca(OH)_2 + 2\,Cl_2 = \underset{\text{calcium hypochlorite}}{Ca(OCl)_2} + CaCl_2 + 2\,H_2O.$$

The product is **bleaching powder** or so-called **chloride of lime.** It consists of calcium hypochlorite $Ca(OCl)_2$ and calcium chloride $CaCl_2$. The formula of bleaching powder is, however, best expressed thus: $Ca\begin{matrix}\diagup OCl \\ \diagdown Cl\end{matrix}$, for the substance really contains no calcium chloride, since it lacks the hygroscopicity of the latter salt. Furthermore, alcohol will not extract calcium chloride from bleaching powder, though calcium chloride is soluble in alcohol.

By treating calcium hypochlorite with very dilute, cold nitric acid HNO_3, hypochlorous acid is liberated, thus: —

$$Ca(OCl)_2 + 2\,HNO_3 = Ca(NO_3)_2 + 2\,HOCl.$$

Hypochlorous acid readily loses oxygen and passes over into hydrochloric acid, especially in the sunlight: —

$$HOCl = HCl + O.$$

The nascent oxygen thus liberated readily oxidizes substances like coloring matters, and hence *hypochlorous acid is an oxidizing and bleaching agent.* Hypochlorous acid has twice the bleaching power possessed by chlorine water containing the same amount of chlorine, as is evident from the following equations: —

$$2\,HOCl = 2\,HCl + O_2.$$
$$2\,Cl_2 + 2\,H_2O = 4\,HCl + O_2.$$

Hypochlorous acid readily decomposes in sunlight into oxygen and hydrochloric acid. Concentrated solutions readily form chloric acid and hydrochloric acid: —

$$3\,HClO = 2\,HCl + HClO_3.$$

Hypochlorites are also oxidizing agents. They part with their oxygen and pass over into chlorides. Thus calcium hypochlorite slowly forms calcium chloride and oxygen: —

$$Ca(OCl)_2 = CaCl_2 + O_2.$$

Upon this fact depends the bleaching action of bleaching powder, and also its disinfecting action, for the oxygen liberated destroys organic matter. **Javelle water** is made by treating bleaching powder with sodium carbonate. By treating bleaching powder with sulphuric acid all the chlorine is liberated, thus: —

$$Ca\begin{matrix}OCl\\Cl\end{matrix} + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

The chlorine liberated then acts upon water, forming hydrochloric acid and oxygen, the latter destroying the coloring matter to be bleached. Hence, in using bleaching powder in practice it is generally treated with an acid.

Chloric Acid and Chlorates. — When a solution of potassium hypochlorite is heated, the following change occurs: —

$$3\,KClO = 2\,KCl + \underset{\text{potassium chlorate}}{KClO_3}.$$

Potassium chlorate may be formed directly by saturating a hot solution of caustic potash with chlorine, thus: —

$$6\,KOH + 3\,Cl_2 = 5\,KCl + KClO_3 + 3\,H_2O.$$

As potassium chlorate $KClO_3$ is much less soluble in water than potassium chloride KCl, the former readily crystallizes from a hot saturated solution on cooling.

By treating potassium chlorate with dilute sulphuric acid, **chloric acid**, whose composition is represented by the formula $HClO_3$, is liberated: —

$$2\,KClO_3 + H_2SO_4 = K_2SO_4 + 2\,HClO_3.$$

This reaction is perfectly analogous to that of making hydrochloric acid: —

$$2\,KCl + H_2SO_4 = K_2SO_4 + 2\,HCl.$$

Chloric acid is known only in solution and in form of its salts. Its anhydride Cl_2O_5 is not known at all. Chloric acid solutions, forming thick, colorless sirups of specific gravity 1.25, have been obtained. They contain 40 per cent of the free acid and correspond approximately to the formula, $HClO_3 + 7\,H_2O$.

Attempts to concentrate the solution further always result in decomposition of the chloric acid into chlorine, oxygen, and perchloric acid. The sirupy solution of chloric acid oxidizes linen, wood, paper, and other organic material very rapidly, with evolution of light and heat. The aqueous solutions of the acid are much more stable than those of hypochlorous acid; still, on standing perchloric acid is formed in them, especially in the sunlight. The salts of chloric acid, namely *the chlorates, are much more stable than the hypochlorites.*

Perchloric Acid and Perchlorates. — When potassium chlorate is melted, it gives off oxygen slowly and then becomes nearly solid, forming potassium chloride and potassium perchlorate: —

$$4\,KClO_3 = 3\,KClO_4 + KCl.$$

The **potassium perchlorate** $KClO_4$ is much less soluble in water than potassium chloride, hence the latter salt may readily be separated from the former. **Sodium perchlorate** $NaClO_4$ is found in small amounts in Chili saltpeter.

On heating potassium perchlorate, it gives up all of its oxygen, passing over into potassium chloride. Hence, the formation of potassium perchlorate is really an intermediate step in the making of oxygen by heating potassium chlorate.

By treating potassium perchlorate with strong sulphuric acid, **perchloric acid** is formed: —

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4.$$

Perchloric acid $HClO_4$ may also be produced by heating chloric acid, or by exposing the latter to sunlight: —

$$3\,HClO_3 = Cl_2 + 2\,O_2 + H_2O + HClO_4.$$

Perchloric acid, prepared by carefully distilling a mixture of potassium perchlorate and sulphuric acid in a partial vacuum, is a colorless, very corrosive liquid which fumes strongly in the air. It has a specific gravity of 1.782 at 15.5° and a boiling point of about 40° at 60 mm. pressure. It is the most stable of the oxy-acids of chlorine; still, it cannot be kept long even in the dark, for after a few days decomposition with violent explosion occurs. The acid is a *dangerous* product. In contact with the skin it produces wounds that are painful and very slow to heal. A few drops put on paper, wood, etc. causes these substances to burst into flames, while a drop of

the acid on charcoal produces a violent explosion. These phenomena occur because perchloric acid is very rich in oxygen, with which it parts readily, thus producing violent oxidation accompanied with sudden liberation of much heat.

The anhydride of perchloric acid is **chlorine heptoxide** Cl_2O_7, which, as has been stated, is produced by abstracting water from perchloric acid by treatment with phosphorus pentoxide.

Nomenclature and General Relations. — The following table presents the formulæ and names of the compounds of chlorine with oxygen and hydrogen : —

HCl, hydrochlor*ic* acid.	KCl, potassium chlor*ide*.
HClO, hypochlor*ous* acid.	KClO, potassium hypochlor*ite*.
($HClO_2$, chlor*ous* acid).	$KClO_2$, potassium chlor*ite*.
$HClO_3$, chlor*ic* acid.	$KClO_3$, potassium chlor*ate*.
$HClO_4$, perchlor*ic* acid.	$KClO_4$, potassium perchlor*ate*.

Chlorous acid $HClO_2$ is not known in the free state; but its salts, like **potassium chlorite** $KClO_2$, are known. The latter, for instance, is formed together with potassium chlorate when chlorine dioxide acts on caustic potash : —

$$2\,KOH + 2\,ClO_2 = KClO_2 + KClO_3 + H_2O.$$

The above table presents an interesting series of compounds. Beginning with hydrochloric acid and its salt potassium chloride, each member of the series contains one atom of oxygen more than the preceding. Hydrochloric acid is a very stable compound; but hypochlorous acid is very unstable. On the other hand, chloric acid is more stable than hypochlorous acid, and perchloric acid is the most stable of the three known oxy-acids of chlorine. The salts of these acids, obtained by replacing the hydrogen of the acid by a metal, are much more stable than the corresponding acids. Such salts form articles of commerce. Their uses will be considered more fully later.

The names given the oxy-acids of chlorine and their corresponding salts afford an excellent illustration of the system of naming a series of acids of increasing oxygen content and the salts which they form. From the table it appears that $HClO_3$ is called chlor*ic* acid and its salts chlor*ates*; the acid which is richest in oxygen, $HClO_4$, is called *per*chlor*ic* acid, and its salts *per*chlor*ates*; the acid containing less oxygen than chlor*ic* acid,

namely $HClO_2$, is termed chlor*ous* acid and its salts the chlor*ites*; whereas the acid containing still less oxygen, HClO, is called *hypo*chlor*ous* acid and its salts *hypo*chlor*ites*. Finally, HCl, which contains no oxygen at all, is termed *hydro*chlor*ic* acid, which distinguishes it sufficiently from $HClO_3$, chlor*ic* acid. This method of naming acids and their corresponding salts is generally applied in chemistry whenever a similar series of compounds is found. The *ic* acid forms the *ate* salt; the *ous* acid forms the *ite* salt; the *hypo . . ous* acid forms the *hypo . . ite* salt; and the *per . . ic* acid forms the *per . . ate* salt. Numerous other illustrations of this will be met in our further considerations.

Occurrence, Preparation, and Properties of Fluorine. — This element is widely distributed in nature. It occurs in large quantities, but always in combination with other elements. It is chiefly found combined with calcium as **fluorspar**, calcium fluoride CaF_2, which crystallizes in octahedra and in cubes like common salt. In Greenland, fluorine is found in the mineral **cryolite**, which is a fluoride of sodium and aluminum, the composition of which is expressed by the formula $(NaF)_3 . AlF_3$. In many minerals and siliceous rocks fluorine occurs in small quantities, in combination with calcium and other metals. Fluorides also are found in small quantities in sea water, in many mineral waters, in the ashes of plants, and in the teeth and the bones of animals. Fluorspar has been known for a very long time. It melts at red heat, and has been used as a flux in metallurgical processes as early as the fifteenth century. It used to be called fluate of lime. The name "fluorine" comes from the use of fluorspar as a flux.

Fluorine was not isolated till 1886, when Henri Moissan prepared it by passing the electric current through dry, liquid hydrofluoric acid HF, in which potassium hydrogen fluoride KHF_2 had been dissolved, in order to have the liquid conduct electricity. The solution was placed in a tube made of platinum (Fig. 29), the stoppers being made of fluorspar. The electrodes were made of an alloy of platinum and iridium. The apparatus was kept at $-23°$ C., and the fluorine was collected in a platinum tube, the ends of which were closed with transparent plates of fluorspar. The difficulty in isolating fluorine lies in the fact that the element combines so readily with other elements. Moissan found later that perfectly pure fluorine attacks glass

but very slowly indeed, so that the gas may be collected in glass vessels. It has also been demonstrated that a copper vessel may be used instead of one of platinum in preparing fluorine.

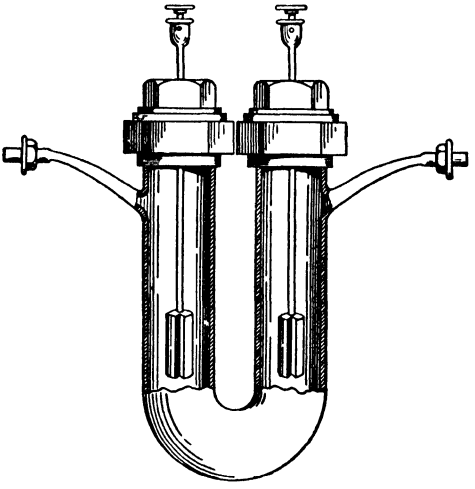


FIG. 29.

Fluorine is a gas of a light, greenish yellow color and a strong pungent odor. It may be condensed to a liquid which boils at $-187°$. By chilling the liquid with liquid hydrogen, it freezes, the white crystals formed melting at $-223°$. Fluorine gas is 19 times as heavy as hydrogen. Its molecular weight is therefore 38; and since its atomic weight is 19.0, the formula of fluorine is F_2. The atomic weight of fluorine has been determined from the analysis of calcium fluoride.

Fluorine is the most active of all the elements. It acts on water, yielding ozone and hydrofluoric acid:—

$$3\,H_2O + 3\,F_2 = 6\,HF + O_3.$$

It unites with hydrogen with great violence in the dark at ordinary temperatures, and even at $-253°$ solid fluorine still acts with explosive violence on liquid hydrogen, according to Dewar and Moissan. Most of the non-metallic elements unite directly with fluorine at ordinary temperatures with evolution of heat and light. Iron, lead, barium, strontium, calcium, sodium, and potassium are acted upon by fluorine at ordinary temperatures; magnesium, aluminum, manganese, nickel, and silver burn in fluorine when slightly heated. At ordinary temperatures gold and platinum are not attacked, but between 300° and 400° they are converted into fluorides. Copper is acted upon at ordinary temperatures, a coating of cuprous fluoride being formed at once on the metal, which is thus protected from further action. Oxygen, chlorine, nitrogen, and

argon do not unite with fluorine. Organic substances generally burn in fluorine gas. Hydrochloric acid gas is decomposed by fluorine with explosive violence: —

$$2\,HCl + F_2 = 2\,HF + Cl_2.$$

Dry glass is but very slowly attacked by fluorine, but in presence of hydrofluoric acid or water, even in traces, glass is rapidly destroyed.

Hydrofluoric Acid. When calcium fluoride is treated with sulphuric acid, hydrofluoric acid is formed: —

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF.$$

The experiment is carried on in a platinum or lead dish, for hydrofluoric acid acts upon glass or porcelain. The process of making the acid is perfectly analogous to that of preparing hydrochloric acid. To obtain hydrofluoric acid which is anhydrous, *i.e.* free from water, potassium hydrogen fluoride KHF_2 is heated to redness in a platinum retort: —

$$KHF_2 = KF + HF.$$

Hydrofluoric acid is a liquid whose boiling point is + 19.4°. Solid hydrofluoric acid melts at − 92.3°. When perfectly dry, the liquid does not act upon glass. In presence of moisture, however, glass is rapidly attacked, fluorides and water being formed. Glass consists essentially of the silicates of sodium and calcium, Na_2SiO_3 and $CaSiO_3$. When hydrofluoric acid acts upon these, the following changes occur: —

$$CaSiO_3 + 6\,HF = CaF_2 + SiF_4 + 3\,H_2O.$$
$$Na_2SiO_3 + 6\,HF = 2\,NaF + SiF_4 + 3\,H_2O.$$

The compound silicon tetrafluoride SiF_4 is a gas, and so escapes. Calcium fluoride is soluble in acids, so that when glass is attacked by hydrofluoric acid, it is dissolved. Use is made of this fact in the chemical analysis of glass and other silicates, also in etching glass. In the latter process the glass is first coated with paraffin; the design is traced in the paraffin coating so as to expose the portions of the glass to be etched, and the whole is then treated either with the fumes of hydrofluoric acid or with an aqueous solution of the latter. When the paraffin is finally removed, the design is found etched into the sur-

face of the glass. This process is used in marking graduations on glass utensils, thermometers, etc.

Because hydrofluoric acid attacks glass, it is kept in rubber or wax bottles. It is very soluble in water, and fumes in contact with moist air. The concentrated solution boils at 120°, and contains about 36 to 38 per cent of the anhydrous acid.

Hydrofluoric acid is a dangerous substance, for it is very poisonous. When inhaled it produces death. In contact with the skin it produces swellings, pains, and wounds that are very slow to heal.

At 100° hydrogen fluoride is about ten times as heavy as hydrogen; this leads to the molecular formula HF. But at 25° the vapor of hydrofluoric acid is nearly 20 times as heavy as hydrogen, which leads to the formula H_2F_2. The acid is prone to form acid salts like KHF_2 and $NaHF_2$. The other hydrohalogens do not form analogous compounds.

Occurrence, Preparation, and Properties of Bromine. — Like chlorine, bromine does not occur in nature except in combination with other elements. Bromine is generally found in nature with chlorine in salt deposits. And just as chlorine occurs mainly in form of sodium chloride, so bromine occurs chiefly as sodium bromide. Bromine is widely distributed in nature, but it is not found anywhere in very large quantities. In sea water, sodium bromide and magnesium bromide are found. Together these constitute from 0.3 to 1.3 per cent of the residue obtained by evaporating the water. In the Stassfurt salt beds, bromine occurs as magnesium bromide. The salt wells of West Virginia, Ohio, and Michigan furnish most of the bromine used in the United States. Here the element occurs as sodium bromide together with common salt. On evaporating the brine the sodium chloride is first deposited, it being less soluble than sodium bromide. From the mother liquor sodium bromide, together with some common salt, is obtained by further evaporation. In the year 1910 the United States produced 245,437 pounds of bromine valued at $41,684.

Bromine was discovered in 1826 by Balard, who prepared it from the residue obtained by evaporating sea water.

The method of preparing bromine is the same as that of preparing chlorine, thus: —

$$2\,NaBr + 3\,H_2SO_4 + MnO_2 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + Br_2.$$

Chlorine will readily replace bromine, and so this method may be employed in making bromine: —

$$2\,NaBr + Cl_2 = 2\,NaCl + Br_2.$$
$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

This method is used in manufacturing bromine in Michigan and at Stassfurt.

Bromine is the only non-metallic element which is a liquid at ordinary temperatures. It is dark reddish brown in color, boils at 59°, and has a specific gravity of 3.188 at 0°. At −7.5° it freezes to a dark brown solid, and at −98° it crystallizes from carbon disulphide in carmine red needles. At room temperatures bromine vaporizes readily. It irritates the eyes and the mucous membranes of the mouth and throat and has an extremely disagreeable odor; whence its name bromine, meaning a stench. In contact with the skin it produces wounds that are painful and difficult to heal.

Bromine dissolves in water. The solution has the color of bromine and is known as **bromine water**. At room temperature 20° the saturated solution contains about 3 per cent bromine. On cooling the solution to about 0° a hydrate of the composition $Br_2 + 10\,H_2O$ separates out. This, however, readily decomposes when warmed to room temperature.

In its chemical behavior, bromine closely resembles chlorine. With metals and a large number of other elements it unites directly, forming bromides. Thus arsenic and antimony will burn in bromine, which also reacts vigorously with phosphorus and sulphur. On the other hand, it does not unite with carbon or oxygen directly. It acts violently on potassium; but dry sodium may even be heated with bromine up to 200° before appreciable action begins. Bromine turns starch paste yellow. It bleaches like chlorine, only much more slowly. *The bleaching action depends upon the fact that bromine, like chlorine, acts upon water, liberating oxygen, which attacks organic coloring matters*, thus: —

$$H_2O + Br_2 = 2\,HBr + O.$$

The atomic weight of bromine is 79.92, and as its vapor is about 79.5 times heavier than hydrogen, its molecular weight is 159.84, and its molecular formula is Br_2.

Hydrobromic Acid. — Hydrogen bromide, or hydrobromic acid HBr, may be formed by direct union of hydrogen with bromine, which occurs when hydrogen charged with bromine vapor is ignited. By treating sodium bromide with sulphuric acid hydrogen bromide is formed, just as hydrogen chloride forms when common salt is similarly treated, thus: —

$$NaBr + H_2SO_4 = NaHSO_4 + HBr.$$

However, in this case a portion of the hydrobromic acid liberated at once reacts with some of the sulphuric acid, forming bromine, water, and sulphur dioxide. That is to say, some of the hydrobromic acid reduces sulphuric acid: —

$$H_2SO_4 + 2\,HBr = SO_2 + 2\,H_2O + Br_2.$$

Thus, pure hydrobromic acid cannot be obtained by treating sodium bromide with sulphuric acid, for the product contains free bromine and also sulphur dioxide.

Pure hydrogen bromide is formed when phosphorus tribromide PBr_3 or phosphorus pentabromide PBr_5 is acted upon by water, thus: —

$$PBr_3 + 3\,H_2O = \underset{\text{phosphorous acid}}{H_3PO_3} + 3\,HBr.$$

$$PBr_5 + 4\,H_2O = \underset{\text{phosphoric acid}}{H_3PO_4} + 5\,HBr.$$

Phosphorous and phosphoric acids are not volatile, but hydrobromic acid is, and so the latter can readily be separated from the former.

The apparatus used for making hydrobromic acid is shown in Fig. 30. The flask *F* contains red phosphorus covered with a little water. Bromine is gradually added by opening the cock *C*. Phosphorus bromide is formed, which is at once decomposed by the water, yielding hydrobromic acid. The latter generally contains some bromine vapor, which is removed by allowing the gas to pass over pumice covered with moist red phosphorus in the U-tube *A*.

Hydrobromic acid is a colorless gas of strong pungent odor. It may be condensed to a liquid which boils at − 64.9° under 738.2 mm. pressure. It forms colorless crystals which melt at − 88°. It fumes strongly in the air, and is very soluble in

water, one volume of the latter absorbing about 600 volumes of hydrobromic acid gas at 10°.

Hydrobromic acid is a strong acid which readily attacks many metals, forming bromides of the metals and liberating hydrogen, thus: —

$$Mg + 2\,HBr = MgBr_2 + H_2.$$
$$Zn + 2\,HBr = ZnBr_2 + H_2.$$

In general, the chemical behavior is like that of hydrochloric acid. Like the chlorides of the metals, the bromides are generally soluble in water; and just as the chloride of silver AgCl

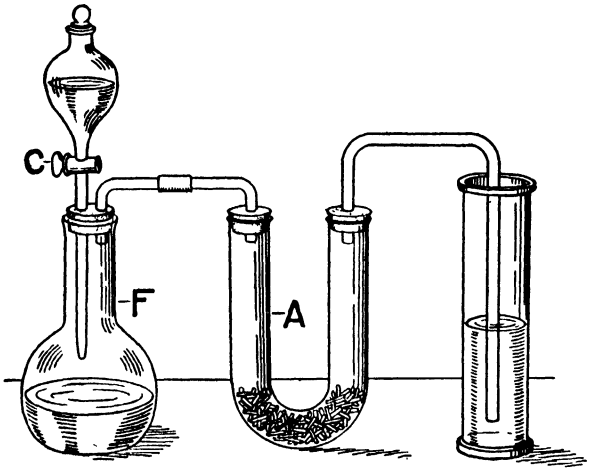


FIG. 30.

is insoluble, so the bromide of silver AgBr is also insoluble. Further, the bromide of lead $PbBr_2$ and mercurous bromide HgBr are difficultly soluble like the corresponding chlorides.

When hydrobromic acid is treated with chlorine, hydrochloric acid and bromine are produced: —

$$2\,HBr + Cl_2 = 2\,HCl + Br_2.$$

On boiling, a strong aqueous solution of hydrobromic acid becomes weaker, and a weak solution becomes stronger, till finally a solution containing from 47.4 to 47.8 per cent of hydrobromic acid is formed. This solution then distills over unchanged in concentration at 752 to 762 mm. pressure. However, by distilling it at other pressures its strength is changed.

Thus at 16 mm. pressure the acid that distills over contains 51.6 per cent HBr.

Hydrobromic acid is 40.45 times heavier than hydrogen. Its molecular weight is therefore 80.9. By weight it contains 1.008 grams of hydrogen to every 79.92 grams of bromine. From these data, its formula is HBr. When dry hydrobromic acid gas is treated with metallic sodium in an apparatus like that used in investigating the composition of HCl (Fig. 23), it is found that the hydrogen liberated occupies one half of the volume of the hydrobromic acid taken.

At very high temperatures hydrobromic acid gas decomposes into hydrogen and bromine. This reaction, which is a reversible one, like the decomposition of hydrochloric acid gas and of water in the gaseous state at very high temperatures, is another typical case of dissociation, and may be represented thus: —

$$2\,HBr \rightleftarrows H_2 + Br_2.$$

The term **dissociation** is only applied to reversible reactions in which a compound is decomposed into products which may again unite to form the original compound as the pressure, temperature, or amount of material contained in unit of volume is varied. We shall have occasion to refer to other instances of dissociation.

Oxy-acids of Bromine. — There are no oxides of bromine known, and but two oxy-acids have thus far been prepared. They are hypobromous acid HBrO and bromic acid $HBrO_3$, the latter being known in aqueous solution only.

Hypobromous acid and its salts, the **hypobromites**, are prepared in a manner analogous to the preparation of hypochlorous acid and hypochlorites. Thus, by action of bromine water on mercuric oxide, hypobromous acid HBrO results, just as hypochlorous acid is formed when chlorine water acts on mercuric oxide. The changes are expressed as follows: —

$$2\,Br_2 + H_2O + HgO = HgBr_2 + 2\,HBrO.$$
$$2\,Cl_2 + H_2O + HgO = HgCl_2 + 2\,HClO.$$

While hypochlorous acid is known only in aqueous solutions, hypobromous acid may be isolated by distillation in a partial vacuum at 40°. The solution of the acid in water is straw-yellow in color. The acid readily decomposes into hydrobromic

acid and oxygen, and is, therefore, like hypochlorous acid, a strong oxidizing and bleaching agent.

When bromine acts on a *cold* solution of caustic alkali, *hypobromites* are formed. The process is analogous to the formation of hypochlorites, thus: —

$$2\,KOH + Br_2 = KBr + KBrO + H_2O.$$

Hypobromites, like hypochlorites, are unstable compounds, readily giving up oxygen. The hypobromite solutions yield **bromates** readily, especially at higher temperatures: —

$$3\,KBrO = 2\,KBr + KBrO_3;$$

or in *warm* caustic potash solution, bromine at once forms potassium *bromate*, thus: —

$$3\,Br_2 + 6\,KOH = 5\,KBr + 3\,H_2O + KBrO_3.$$

Bromic Acid and Bromates. — When silver bromate $AgBrO_3$ is treated with bromine and water, bromic acid is formed: —

$$5\,AgBrO_3 + 3\,Br_2 + 3\,H_2O = 5\,AgBr + 6\,HBrO_3.$$

It is also formed when dilute sulphuric acid acts on barium bromate: —

$$Ba(BrO_3)_2 + H_2SO_4 = BaSO_4 + 2\,HBrO_3;$$

or when chlorine is passed into bromine water, thus: —

$$Br_2 + 6\,H_2O + 5\,Cl_2 = 10\,HCl + 2\,HBrO_3.$$

Bromic acid is very similar to chloric acid in its behavior. At 100° the aqueous solution decomposes, yielding oxygen and bromine. The pure anhydrous acid has not been prepared.

On heating potassium bromate, it yields oxygen and potassium bromide, without, however, first forming a potassium perbromate. In this respect the behavior of potassium bromate $KBrO_3$ differs from that of potassium chlorate.

By melting potassium bromide with potassium chlorate potassium bromate results: —

$$KClO_3 + KBr = KBrO_3 + KCl.$$

We thus see that under these conditions the bromate is more stable than the chlorate, and the chloride more stable than the bromide.

Uses of Bromine and its Compounds. — Bromine is used in the manufacture of dyestuffs from coal-tar products. In medicine potassium bromide is used as a sedative. In photography silver bromide is used in the sensitized plates.

History and Occurrence of Iodine. — This element is a solid at room temperatures. It was discovered in 1812 by Courtois, who evolved it from the ashes of seaweeds. It forms beautiful violet vapors, whence its name iodine, meaning violet-colored. Indeed it was the color of the vapor that led to the discovery of iodine. The substance was then examined by Sir Humphry Davy and by Gay-Lussac; the latter in 1815 established its elementary character.

Like bromine, iodine always occurs in nature associated with chlorine. It has been reported by Wanklyn that the water from the spring, Woodhall Spa, near Lincoln, Nebraska, contains iodine in minute quantities; but with this singular exception, iodine has always been found in combination with other elements, chiefly with sodium, potassium, magnesium, and calcium in form of iodides and iodates. In sea water it occurs in extremely minute quantity. Seaweeds, particularly those growing in deeper waters, like the genera Fucus and Laminaria, assimilate iodine and store it up in their bodies. The ashes of such seaweeds are termed kelp in Scotland and varech in Normandy, and from these iodine is prepared. However, the chief source of iodine at present is the crude Chili saltpeter, or caliche $NaNO_3$, in which iodine occurs mainly as sodium iodate $NaIO_3$. The amount of iodine in caliche is, however, only about 0.2 per cent. Besides occurring in seaweeds, iodine is found in many sponges, oysters, and other sea animals, in cod-liver oil, in some fresh-water plants, in coal, and in the thyroid glands of animals. In combination with silver, copper, and lead it occurs as iodides, though these minerals are rare. Many mineral springs contain minute amounts of iodine, and in deposits of common salt the element generally occurs in small quantity. Thus it is evident that iodine is quite widely distributed in nature, though it is nowhere present in large amounts.

Preparation of Iodine. — From the ashes of seaweeds, iodine is liberated by treatment with sulphuric acid and manganese dioxide, or by passing chlorine through the solution, which con-

tains the iodine mainly in the form of sodium iodide. The equations expressing the changes that occur are as follows: —

(1) $2\,NaI + 3\,H_2SO_4 + MnO_2 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + I_2$

(2) $2\,NaI + Cl_2 = 2\,NaCl + I_2$.

It will be observed that equation (1) is perfectly analogous to the process of making chlorine or bromine from chlorides or bromides by treatment with sulphuric acid and manganese dioxide. Further, equation (2) is analogous to the process of making bromine from a bromide by treatment with chlorine. On the coasts of France and Scotland the seaweeds are gathered, dried, and burned, the latter process being carried on in closed retorts so that no iodine is lost by volatilization. The charcoal remaining after the ash has been leached out of it is similar to animal charcoal. It readily absorbs odors and is used as a deodorant. The iodine is then liberated from the solution by means of one of the processes just mentioned. It is purified by volatilizing it and condensing the vapor, which forms crystals. The process of vaporizing a solid without melting it and condensing the vapor to the solid state is called **sublimation**. To get pure iodine the latter is mixed with potassium iodide, and the mixture is heated so as to volatilize the iodine, which is condensed on cool surfaces in form of crystals. In this way bromine and chlorine remain behind, in combination with potassium. Figure 31 shows a simple laboratory apparatus for subliming iodine, and Fig. 32 represents an arrangement for resubliming raw iodine on a commercial scale.

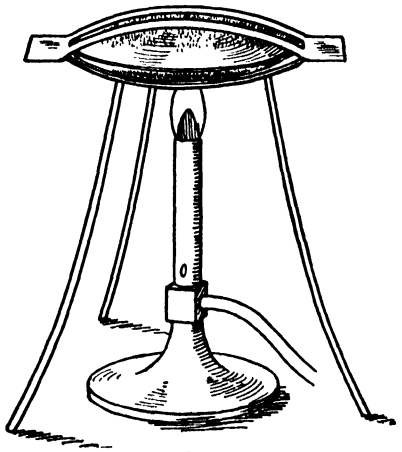


FIG. 31.

From Chili saltpeter, in which iodine occurs as sodium iodate together with smaller amounts of sodium iodide and magnesium iodide, iodine is prepared by treatment with sodium bisulphite. The reaction which takes place is as follows: —

$$2\,NaIO_3 + 5\,NaHSO_3 = 2\,Na_2SO_4 + 3\,NaHSO_4 + H_2O + I_2.$$

The iodine is thus obtained in precipitated form from the aqueous solution. It is allowed to settle and is then collected and purified by sublimation. The quantity of iodine produced annually from Chili saltpeter is about 300 tons, which is somewhat more than half of the total production. Of recent years, the process of obtaining iodine from seaweeds has been improved, the best method consisting of lixiviating the seaweeds without previous charring. In this way much less iodine is lost, and the remains of the seaweeds are worked up into *algin*, which is like gelatine. Thus the method of preparing iodine from seaweeds has again become profitable.

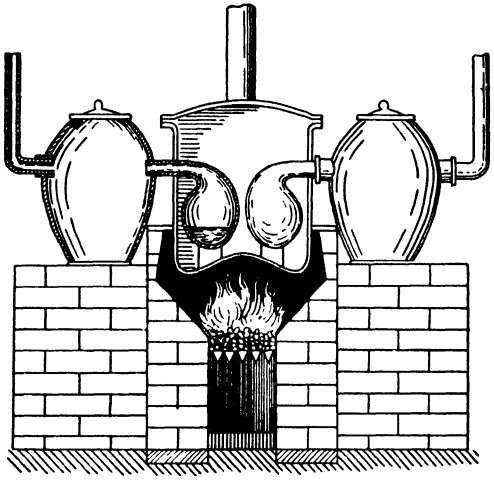


FIG. 32.

Properties of Iodine. — Iodine is a grayish black, lustrous solid which crystallizes in plates that belong to the rhombic system. From solutions in alcohol or hydriodic acid beautiful crystals may be obtained. Iodine really has a metallic luster. It is brittle and may be pulverized readily. Its specific gravity is 4.95 at 17°. It melts at 116.1°, forming a reddish brown liquid which boils at 184°. Iodine volatilizes perceptibly, though slowly, at room temperatures. Its vapors are violet-colored, but when dense they appear very dark and opaque. Its odor reminds one of that of chlorine and bromine, but it is much less intense. It colors the skin brown and exerts an irritating and corrosive action upon it.

In water it is but very slightly soluble, about 1 part in 5000. However, water containing potassium iodide or hydriodic acid readily dissolves iodine. These solutions are brown, as is also the solution of iodine in alcohol, which is called **tincture of**

Iodine. Iodine furthermore dissolves in hydrocarbon oils, chloroform, and carbon disulphide. With the latter it forms beautiful violet solutions, which fact is frequently used in detecting iodine in chemical analysis. We have already learned that iodine turns starch paste blue. This is used as a test for iodine and also for starch in analytical chemistry.

Uses of Iodine. — The solution of iodine in alcohol, tincture of iodine, is used as a counter irritant in medicine. Iodine is also administered internally in form of potassium iodide as a specific in certain diseases, particularly those which, like goiter, are caused by disturbances in the thyroid gland. The latter normally contains iodine in form of an organic compound known as thyroiodine. This also occurs in the thyroid glands of animals, particularly in sheep, from which source it is mainly obtained. It is administered as a specific for goiter and myxœdema.

Iodine is also used in the manufacture of iodoform, iodocrol, and other iodine preparations. These are used principally as antiseptics in healing wounds. In synthetic chemistry, hydriodic acid and compounds of iodine with carbon and hydrogen are frequently employed.

Hydriodic Acid. — There is but one compound of hydrogen and iodine known; namely, hydriodic acid or hydrogen iodide. Its composition and vapor density are represented by the formula HI. It may be prepared by passing a mixture of hydrogen and iodine vapor through a red-hot tube containing platinum in a finely divided state, thus: —

$$H_2 + I_2 \rightleftarrows 2\,HI.$$

The reaction is, however, incomplete since it is a reversible one, hydriodic acid decomposing readily into iodine and hydrogen.

By treating potassium iodide with sulphuric acid, we cannot obtain hydriodic acid; for the latter reduces sulphuric to sulphurous acid far more readily than does hydrobromic acid: —

$$2\,KI + 3\,H_2SO_4 = 2\,KHSO_4 + SO_2 + 2\,H_2O + 2\,I.$$

However, by treating potassium iodide with hot, concentrated phosphoric acid, hydriodic acid may be obtained, thus: —

$$KI + H_3PO_4 = KH_2PO_4 + HI.$$

The acid is best prepared by decomposition of phosphorus iodide by water: —

$$PI_3 + 3\,H_2O = H_3PO_3 + 3\,HI;$$

or by simply having red phosphorus and iodine act on each other in presence of water. In this way phosphorus iodide is formed and then decomposed into phosphorous acid and hydrogen iodide: —

$$P + 3\,I + 3\,H_2O = H_3PO_3 + 3\,HI.$$

Hydrogen iodide may also be obtained by the action of iodine on hydrogen sulphide H_2S (which see), or by the action of hydrogen sulphide upon cuprous iodide suspended in water, thus: —

$$H_2S + I_2 = 2\,HI + S.$$
$$H_2S + 2\,CuI = 2\,HI + Cu_2S.$$

These methods are quite similar to those by means of which pure hydrobromic acid can be obtained. Hydrochloric acid may also be prepared by similar methods; but it is not at all necessary to resort to these in this case, since this acid is much more stable than hydrobromic or hydriodic acid. It does not reduce sulphuric acid, and can therefore readily be prepared by the action of the latter on common salt.

At room temperatures hydrogen iodide is a colorless gas, which, like hydrochloric and hydrobromic acids, fumes strongly in the air and is very soluble in water. At 60°, 485 volumes of hydriodic acid gas are absorbed by 1 volume of water. At 0° a solution of specific gravity 2.0 may be obtained which contains about 90 per cent hydrogen iodide. On distillation, a solution of hydrogen iodide behaves like the corresponding solution of hydrogen bromide and hydrogen chloride. On boiling, a concentrated solution becomes weaker, and a weak solution becomes more concentrated, till finally a liquid is obtained which contains 57 per cent HI. This boils at 127° at 774 mm. and distills over without change of composition. On changing the pressure, however, the composition of the distillate is changed. The distillation of the hydriodic acid must be conducted in a current of hydrogen to prevent decomposition of the acid.

Pure hydriodic acid may be condensed to a colorless liquid which boils at − 34.1°. Solid hydriodic acid forms colorless crystals which melt at − 50.8°. The vapor of hydriodic acid

is 62.92 times heavier than hydrogen, whence its molecular weight is 126.84, which corresponds fairly well to the formula HI; for the atomic weight of iodine is 126.92, and the calculated molecular weight for the formula HI is 127.92.

Hydriodic acid forms **iodides** and hydrogen when treated with many metals. *These salts are as a rule soluble in water, the exceptions being the iodides of silver, mercury, and lead.* Hydriodic acid is a powerful reducing agent, which comes from the fact that it readily gives up its hydrogen to oxidizing agents. The decomposition of hydriodic acid proceeds more rapidly in the light and at higher temperatures. Its reducing power is frequently used in chemistry, especially in the investigation of the compounds of carbon.

Oxide of Iodine. — But one oxide of iodine is known. Its composition is expressed by the formula I_2O_5. It is the anhydride of iodic acid, and is prepared by heating the latter to 170°, thus: —

$$2\,HIO_3 = H_2O + I_2O_5.$$

When the oxide is dissolved in water, the acid is regenerated. Iodine pentoxide is a white crystalline solid, which decomposes into its elements at 300°; thus *it is much more stable than the oxides of chlorine.*

Oxy-acids of Iodine. — There are three oxy-acids of iodine known, namely hypoiodous acid HIO, iodic acid HIO_3, and periodic acid HIO_4.

A dilute solution of **hypoiodous acid** may be prepared by shaking together mercuric oxide, iodine, and water: —

$$HgO + 2\,I_2 + H_2O = 2\,HIO + HgI_2.$$

The method is thus similar to the preparation of HClO and HBrO. When iodine is introduced into *cold* caustic alkali solutions, a colorless liquid having bleaching power results, due to the formation of **hypoiodites**, thus: —

$$2\,NaOH + I_2 = NaIO + NaI + H_2O.$$

Hypoiodites are, however, extremely unstable, readily passing over into iodates, especially on warming, thus: —

$$3\,NaIO = 2\,NaI + NaIO_3.$$

Iodic acid HIO_3 is perfectly analogous to chloric and bromic

acids. It is, however, much more stable than the latter. It may be formed by treating barium iodate with sulphuric acid: —

$$Ba(IO_3)_2 + H_2SO_4 = BaSO_4 + 2\,HIO_3;$$

or by oxidation of iodine either by means of chlorine or nitric acid, thus: —

$$I + 3\,H_2O + 5\,Cl = 5\,HCl + HIO_3$$
$$3\,I + 5\,\underset{\text{nitric acid}}{HNO_3} = 5\,\underset{\text{nitric oxide}}{NO} + H_2O + 3\,HIO_3.$$

Iodic acid readily gives up oxygen and is consequently a good oxidizing agent. Thus in contact with hydriodic acid, both acids are decomposed, yielding water and iodine: —

$$HIO_3 + 5\,HI = 3\,H_2O + 3\,I_2.$$

The salts of iodic acid are called the **iodates**. The potassium and sodium salts readily dissolve in water; but, in general, the salts of other metals are sparingly soluble. On being heated, the iodates behave like the bromates. The iodates of sodium and potassium yield iodides and oxygen, whereas other iodates decompose into oxides of the metal, iodine, and oxygen. The iodates of potassium and sodium readily unite with one or two additional molecules of iodic acid, forming acid salts. Thus, $KIO_3 \cdot HIO_3$ and $KIO_3 \cdot 2\,HIO_3$ are known. The chlorates and bromates do not thus add on chloric and bromic acid.

Periodic acid is formed by the action of iodine upon an aqueous solution of perchloric acid: —

$$2\,HClO_4 + 4\,H_2O + I_2 = Cl_2 + 2\,(HIO_4 \cdot 2\,H_2O).$$

Periodic acid has the composition corresponding to the formula $HIO_4 \cdot 2\,H_2O$, or as it is often written, H_5IO_6. The acid of the formula HIO_4 has never been obtained. Periodic acid forms colorless, transparent, deliquescent, prismatic crystals that melt at 133°, while at 140° they are entirely decomposed, forming water, oxygen, and iodine pentoxide, thus: —

$$2\,H_5IO_6 = 5\,H_2O + O_2 + I_2O_5.$$

Periodic acid is a strong oxidizing agent. **Periodates** are generally difficultly soluble in water. Sodium periodate may readily be prepared by the interaction of chlorine, sodium hydroxide, and sodium iodate, thus: —

$$Cl_2 + 3\,NaOH + NaIO_3 = 2\,NaCl + Na_2H_3IO_6.$$

By heating barium iodate, the periodate of barium may be obtained, thus: —

$$5\,Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4\,I_2 + 9\,O_2.$$

It will thus be seen that while periodic acid and the periodates are analogous to perchloric acid and the perchlorates, the fact that periodic acid has the composition $HIO_4 \cdot 2\,H_2O$ or H_5IO_6 leads to a more complicated series of salts than we have in case of the perchlorates.

Compounds of the Halogens with Each Other. — By passing chlorine over iodine, a dark reddish brown liquid not unlike bromine in appearance is formed. It is very volatile and has an exceedingly pungent odor. It is about 3 times as heavy as water and boils at about 101°, during which process it suffers partial decomposition. Its composition corresponds to the formula ICl; it is **iodine monochloride**. Two modifications of this compound have been described, the one melting at 24.7°, and the other at 13.9°. Iodine monochloride does not turn starch paste blue. By contact with water it is decomposed: —

$$3\,H_2O + 5\,ICl = HIO_3 + 5\,HCl + 2\,I_2.$$

When iodine is treated with chlorine in excess, or when iodine monochloride is further treated with chlorine, yellow, needle-like crystals are formed having the composition ICl_3. They are **iodine trichloride**. They may be purified by sublimation at ordinary temperatures. On heating, they decompose into chlorine and iodine monochloride, but on cooling the trichloride forms again, thus: —

$$ICl_3 \rightleftarrows ICl + Cl_2.$$

Water dissolves iodine trichloride. The solution has great germicidal power and is consequently used as an antiseptic.

With bromine, iodine forms a crystalline compound, **iodine monobromide**, of the composition IBr. It has chemical properties similar to those of iodine monochloride. It melts at 36°.

A compound of iodine with fluorine, **iodine pentafluoride** IF_5, is also known. It is formed by direct union of the elements. It is a colorless liquid which boils at 97° and solidifies at 8°. On heating it to 400°, it suffers decomposition. Water decomposes it into hydrofluoric and iodic acids.

General Relations of the Halogens to One Another. — Fluorine, chlorine, bromine, and iodine increase in atomic weight in the order named. With increasing atomic weight their melting points and boiling points rise, their specific gravities increase, and their color becomes more intense. Thus, with increasing atomic weight, we have here an increase in the degree of condensation of matter, as it were.

While the physical properties thus show a regular change with increasing atomic weight, the chemical properties also exhibit regularity of change. So the affinity for hydrogen is greatest in the case of fluorine, and least in the case of iodine. The general chemical activity of the halogens diminishes as the atomic weight increases. So fluorine is by far the most active element of the group, and iodine the least active. However, for oxygen iodine has a much greater affinity than fluorine, which unites with oxygen neither directly nor indirectly. Indeed, in case of the oxygen compounds of the halogens the stability increases with the atomic weight of the halogen, being greatest in the iodine compounds.

It is interesting to note that the atomic weight of bromine, 79.92, is approximately equal to one half the sum of the atomic weights of chlorine, 35.46, and iodine, 126.92. We shall meet more such groups of three elements in which a similar relation holds. The consideration of the relations between the atomic weights of the elements and their physical and chemical properties has led to a classification of the elements known as the periodic system, which will be considered when more of the elements have been studied.

REVIEW QUESTIONS

1. Name the halogens. Why are they so called? Why are they grouped together?

2. How do the properties of the halogens vary with their atomic weights?

3. What is the weight of 22.38 liters of each of the halogens in the gaseous state under standard conditions?

4. What is the action of chlorine upon a cold solution of potassium hydroxide? Upon a hot concentrated solution of the latter? Write the appropriate equations. Write similar equations expressing the action of bromine and iodine respectively on cold and hot solutions of sodium hydroxide.

5. What is bleaching powder? How is it prepared? Write the equation. Upon what properties of bleaching powder do its uses depend?

6. Measured under standard conditions, how many liters of hydrobromic acid gas could be prepared from 8 liters of hydrogen? How much would the hydrobromic acid gas weigh?

7. Give two *general* methods for preparing chlorine, bromine and iodine. What difficulty would be met in preparing fluorine by these methods?

8. Write the equation expressing the action of manganese dioxide on a mixture of common salt and sulphuric acid. What actions would take place if potassium bromide and sodium iodide, respectively, were substituted for the common salt? Write the equation in each case.

9. Name three products that are formed when chlorine acts upon water. How do the other halogens act upon water?

10. Compare the action of the four halogens upon hydrogen. Write the equations.

11. How is hydrochloric acid commonly prepared? Why cannot hydrobromic and hydriodic acids be prepared similarly? How can these three hydrohalogen acids be prepared from the phosphorus halides? Write the appropriate equation in each case.

12. Complete the equation in each of the following cases, if an action occurs: $Cl_2 + NaBr$; $Br_2 + NaCl$; $Cl_2 + NaI$; $Br_2 + NaI$; $I_2 + KBr$; $I_2 + CaCl_2$; $NaCl + F_2$.

13. In which cases may the halogens replace one another in chemical compounds?

14. Given the formulas of the following oxides: PbO_2, Fe_2O_3, Ag_2O, CuO, CrO_3, write the formulas of the corresponding chlorides and fluorides.

15. Given the formulas of the following chlorides: $NaCl$, $CrCl_3$, $CaCl_2$, $SnCl_4$, PCl_5, write the formulas of the corresponding oxides.

16. What is an oxygen acid? Give the names and formulas of all of the oxygen acids of chlorine, and the corresponding sodium salts. Do the same for bromine and iodine.

17. Give the names of the following compounds: KIO_4, $Ca(ClO_2)_2$, HIO_2, $KBrO_3$, $NaClO$, $Ca \cdot Cl \cdot ClO$.

18. Write the equation expressing the action of hydrochloric acid upon hypochlorous acid.

19. What is the chief use of hydrofluoric acid? Illustrate the action by means of an equation.

20. What use is made of bromine in the arts? How is iodine used? In what liquids is the latter soluble? How may bromine and iodine be distinguished from each other?

21. What interesting relation exists between the atomic weights of chlorine, bromine, and iodine?

22. What is thyroiodine?

23. Write the equation expressing the action of each of the following upon hydrogen sulphide: chlorine, bromine, iodine.

24. What is iodine trichloride? How may it be formed? Write the equation.

25. Give an illustration showing that hydriodic acid is a powerful reducing agent. Write the equation.

CHAPTER IX

ACIDS, BASES, SALTS, HYDROLYSIS, MASS ACTION, AND CHEMICAL EQUILIBRIUM

Acids. — In connection with the study of oxygen it was found that this element readily unites with non-metals like phosphorus, sulphur, and carbon, forming oxides which, when dissolved in water, have a sour taste and redden blue litmus. These oxides are consequently called acidic oxides or *acid-forming oxides*, for with water they form acids. Thus when sulphur burns in oxygen **sulphur dioxide** results: —

$$S + O_2 = SO_2.$$

When conducted into water, sulphur dioxide unites with the water, forming **sulphurous acid** H_2SO_3, thus: —

$$SO_2 + H_2O = H_2SO_3.$$

It is possible to form a similar acid of higher oxygen content. By passing sulphur dioxide mixed with oxygen over red-hot, finely divided platinum, a higher oxide of sulphur, namely **sulphur trioxide** SO_3, is formed. This is a white crystalline solid which greedily unites with water, forming **sulphuric acid** H_2SO_4. The changes may be expressed as follows: —

$$2\,SO_2 + O_2 = 2\,SO_3.$$
$$SO_3 + H_2O = H_2SO_4.$$

Similarly, when phosphorus is burned in oxygen **phosphorus pentoxide** P_2O_5 is formed, which readily unites with water, forming **phosphoric acid** H_3PO_4: —

$$P_2O_5 + 3\,H_2O = 2\,H_3PO_4.$$

Again, when carbon is burned in oxygen, **carbon dioxide** CO_2 is produced, which, when dissolved in water, forms **carbonic acid** H_2CO_3, thus: —

$$CO_2 + H_2O = H_2CO_3.$$

Carbonic acid H_2CO_3 has not been isolated; it exists merely in solution. The combination of water and carbon dioxide is very

weak, and carbonic acid is but slightly sour to the taste, reddens blue litmus slowly, and acts in all respects much more feebly than the other acids just mentioned. It is a good example of a *weak acid.*

It will be recalled that the fact that oxides like the above yield sour or acidic substances originally led to the idea that it is the oxygen that imparts these acidic characteristics to the compounds. Indeed, oxygen received its name in accordance with this notion. However, we have seen that the halogens form a series of compounds with hydrogen, namely, HF, HCl, HBr, and HI, which are all pronounced acids, in that they are sour to the taste, redden litmus, and attack metals like magnesium, zinc, and iron, evolving hydrogen and yielding compounds consisting of the halogen and the metal employed. *These latter products are salts of the metal.*

When chlorine was discovered, it was looked upon as an oxide (as oxidized hydrochloric acid); for it was well known that chlorine is an acid-forming substance, and consequently it was thought that it must contain oxygen, which was regarded as the essential element in every acid. In fact, it was not till iodine was discovered that the correct view of chlorine as an element was really established. For this reason the discovery of iodine and the proof that it is elementary in character was of great importance in the development of the idea of the real nature of an acid. Thus, from the study of the hydrohalogens, which are all pronounced acids, came the true notion that hydrogen, and not oxygen, is the essential constituent of every acid. *An acid is a compound containing hydrogen which may be replaced by a metal, the product formed being a salt.* Acids commonly have sour taste and redden blue litmus; but we shall learn of acids that are so weak that they do neither of these things; yet they are nevertheless acids, because they contain hydrogen which may be replaced by a metal, the product formed being a salt. While it is thus true that there are very pronounced acids that contain no oxygen, still it must be stated that after all by far the great majority of acids do contain oxygen, and often it is by the addition of the latter element that the acidic character is produced.

Since phosphoric acid H_3PO_4, sulphuric acid H_2SO_4, sulphurous acid H_2SO_3, and carbonic acid H_2CO_3, may be formed by

the addition of water to the oxides P_2O_5, SO_3, SO_2, and CO_2, respectively, in accordance with the equations already given above, these oxides are called the *anhydrides* of the respective acids.

When an acid acts on a metal like zinc or magnesium, hydrogen is evolved and a salt is formed, thus: —

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
$$Mg + 2\,HCl = MgCl_2 + H_2.$$

A salt is thus one of the products of the interaction of an acid and a metal. It is possible to form salts by other means, however, as will be shown below.

Bases. — We have seen in connection with the study of hydrogen that when this element is liberated by the action of sodium or potassium on water, caustic soda or caustic potash results, thus: —

$$H_2O + Na = NaOH + H.$$
$$H_2O + K = KOH + H.$$

The solutions of sodium hydroxide and potassium hydroxide are alkaline in character. They turn red litmus blue, and when treated with an acid they become neutral; that is, they do not affect either red or blue litmus. When these hydroxides are treated with an acid, they are said to be *neutralized*. In this process the acid is, of course, also neutralized. *The interaction of an alkaline hydroxide with an acid is a mutual act, resulting in the neutralization of both compounds.* On evaporating the neutral solution it is found that a *salt* has been formed. The reaction or neutralizing sodium hydroxide with hydrochloric acid may be expressed thus: —

$$NaOH + HCl = NaCl + H_2O.$$

When, for example, potassium hydroxide is neutralized with sulphuric acid, the following change takes place: —

$$2\,KOH + H_2SO_4 = K_2SO_4 + 2\,H_2O$$

Hydroxides of metals which are thus capable of reacting with acids, forming salts and water, are called *basic hydroxides* or *bases*. Hence *a base is an hydroxide or oxide of a metal which will react with an acid, forming* (1) *a neutral substance called a salt, and* (2) *water.*

Elements which are thus capable of uniting with the hydroxyl radical OH to form bases are called *base-forming elements*, while those that form acids by union with hydrogen are called *acid-forming elements*. Hydroxides of some of the elements, however, are capable of acting as bases toward more acidic hydroxides, and as acids toward hydroxides that are more basic than themselves. This will be more evident as we proceed in our considerations.

Salts. — From what has been stated in connection with the consideration of acids and bases, the nature of salts is already sufficiently characterized. Thus, *a salt is a neutral compound resulting as a product of the interaction of an acid with a base;* or *a salt is a neutral compound which is formed when the hydrogen of an acid is replaced by a metal.* So it appears that **a salt may be formed in the following ways:** —

(1) *By the neutralization of an acid with a base*, as, for example, sodium sulphate Na_2SO_4 is formed when sodium hydroxide and sulphuric acid act on each other: —

$$2\,NaOH + H_2SO_4 = Na_2SO_4 + 2\,H_2O.$$

(2) *By the action of a metal on an acid*, thus: —

$$2\,Na + H_2SO_4 = Na_2SO_4 + H_2.$$

(3) It is possible, however, to form a salt *by the direct action of two oxides, a base-forming oxide or basic oxide, and an acid-forming oxide or acidic oxide, on each other*, thus: —

$$Na_2O + SO_3 = Na_2SO_4.$$

(4) It is also possible to form a salt *by direct union of a base-forming element with an acid-forming element*, thus: —

$$Na + Cl = NaCl.$$

In all cases, however, one may think of the salt as derived from some acid whose hydrogen has been replaced by the metal. So, though in (3) the sulphate of sodium was made by the union of sodium oxide and sulphur trioxide, that is sulphuric anhydride, one may think of the product Na_2SO_4 as derived from H_2SO_4 in which the hydrogen is replaced by sodium. Likewise, *all sulphates may be regarded as similarly derived from sulphuric acid.* The latter may in turn be looked upon as *hydrogen sulphate, i.e.* a salt in which hydrogen is the basic

element; indeed, *any acid may be regarded as a salt of hydrogen.* Thus, hydrochloric acid HCl is the chloride of hydrogen. Sodium chloride NaCl, whether made by the direct union of the elements as in (4) above, or by the action of sodium hydroxide upon hydrogen chloride, may yet be regarded as derived from HCl in which the hydrogen is replaced by sodium.

Similarly, all fluorides may be regarded as derived from HF, the hydrogen of which has been replaced by the metal. All iodides may similarly be considered as derived from HI, all chlorates from $HClO_3$, *etc.*

Older View of the Process of Salt Formation. — Salts were formerly considered as the result of the union of a basic oxide with an acidic oxide. Thus, sodium sulphate was regarded as sodium oxide Na_2O plus sulphur trioxide SO_3, and the formula of the salt was written $Na_2O \cdot SO_3$. Similarly, calcium carbonate was regarded as made up of calcium oxide CaO, plus carbon dioxide CO_2, and the formula of calcium carbonate was consequently $CaO \cdot CO_2$. Again, ferrous sulphate was considered as ferrous oxide FeO plus sulphur trioxide, thus: $FeO \cdot SO_3$. This was the *dualistic* way of writing which was in vogue during the former half of the last century, and it is not to be denied that it had many advantages. So these formulæ indicated at once that the salts can be formed by direct union of the acidic and basic oxides; and since it is true that many of these salts when strongly heated decompose into the basic and acidic oxides, the formulæ also in a simple way represented this fact. For instance, on heating, calcium carbonate yields calcium oxide and carbon dioxide: —

$$CaCO_3 = CaO + CO_2;$$

and ferrous sulphate decomposes thus: —

$$FeSO_4 = FeO + SO_3.$$

According to the older view the process of solution of a metal like zinc or iron in sulphuric acid consisted of two steps. First, when the zinc was introduced into dilute sulphuric acid, the metal was oxidized to zinc oxide ZnO, hydrogen being simultaneously liberated from the water; and second, zinc oxide would then combine with the sulphur trioxide, forming zinc sulphate $ZnO \cdot SO_3$. Sulphuric acid was regarded as SO_3 dissolved in water. This dualistic way of writing the formulæ

of salts was strongly defended by Berzelius, and it was only through the development of the study of the compounds of carbon and of electrochemistry that the present method of expressing the formulæ was finally adopted. In the study of some of the complicated silicates, however, the old way of writing is still frequently employed with distinct advantages, as will be seen when the compounds of silicon are discussed. The dualistic formulæ of Berzelius were, moreover, also based upon electrochemical ideas.

Acid- and Base-forming Elements. — In general, the acid-forming elements are the non-metals, and the base-forming elements are the metals. Oxygen, sulphur, nitrogen, phosphorus, carbon, the halogens, etc., are acid-forming elements; and potassium, sodium, magnesium, zinc, lead, copper, etc., are base-forming elements. However, as stated above, an acidic element may act as a basic element toward a still more acidic element; and a basic element may act as an acidic element toward a still more basic element. Of this we have already had illustrations. Thus while zinc acts as a base in zinc sulphate $ZnSO_4$, in which compound sulphur and oxygen form the acid radical SO_4, in potassium zincate K_2ZnO_2, formed thus, —

$$Zn(OH)_2 + 2\,KOH = K_2ZnO_2 + 2\,H_2O,$$

zinc is a part of the acid radical ZnO_2. So toward the acid group SO_4 zinc acts as a base, while toward the strongly basic potassium the zinc forms a part of the acidic group ZnO_2. Again, in sodium iodide NaI, sodium is the basic and iodine the acidic element; whereas in iodine chloride ICl, the iodine plays the rôle of base toward the more acidic chlorine. Further, in phosphorus trichloride PCl_3, phosphorus is the basic and chlorine the acidic element, whereas in phosphates, like sodium metaphosphate $NaPO_3$, phosphorus plays the rôle of an acidic element. Additional examples will readily occur to the reader, and many others will be met in our further study.

The distinction between acid- and base-forming elements is thus not a sharp one; nevertheless, from what has been stated, the difference between acids and bases can generally be made without difficulty.

Other Views of Solutions of Acids, Bases, and Salts. — In recent years the attempt has been made to define acids, bases, and salts

on the basis of the behavior of their solutions toward the electric current. In this attempt the boiling and freezing points of dilute solutions have also been a prime consideration. This study has further led to another way of regarding the act of neutralization and the resulting salt solutions. A consideration of these views of acids, bases, and salts in solution will be taken up later in connection with the subjects of solutions and electrolysis.

Basicity of Acids; Acid Salts. — *An acid which contains one replaceable hydrogen atom in its molecule is called a monobasic acid; one that contains two replaceable hydrogen atoms is called a dibasic acid;* etc. *There are also tribasic, tetrabasic, and pentabasic acids.* For example, HCl, HBr, HI, HClO, HBrO, HIO, $HClO_3$, $HBrO_3$, HIO_3, $HClO_4$, HNO_3 (nitric acid), are all **monobasic acids.** With a univalent basic element like potassium or sodium, for instance, each of these monobasic acids forms but one salt, thus: —

$$KCl,\ NaI,\ KBrO,\ KClO_4,\ NaNO_3.$$

Sulphuric acid H_2SO_4 and carbonic acid H_2CO_3 are **dibasic acids**, since they contain two atoms of replaceable hydrogen per molecule. *In the neutralization of a dibasic acid the operation may take place in two steps,* thus: —

$$(1)\ H_2SO_4 + NaOH = NaHSO_4 + H_2O.$$
$$(2)\ NaHSO_4 + NaOH = Na_2SO_4 + H_2O.$$
$$(1)\ H_2CO_3 + KOH = KHCO_3 + H_2O.$$
$$(2)\ KHCO_3 + KOH = K_2CO_3 + H_2O.$$

The salt $NaHSO_4$ still contains replaceable hydrogen, *i.e.* acidic hydrogen. It is consequently an **acid salt,** as contrasted with Na_2SO_4, in which all the hydrogen has been replaced. The latter salt is a **neutral** or **normal salt.** Acid sodium sulphate $NaHSO_4$ is also called *sodium bisulphate,* for it contains twice as much acid radical per same amount of sodium as does the normal salt Na_2SO_4, which is also called *bisodium sulphate,* as well as simply sodium sulphate. Similarly, $KHCO_3$ is potassium bicarbonate, and K_2CO_3 is bipotassium carbonate, or simply potassium carbonate.

Thus *an acid salt is one which still contains hydrogen that is replaceable by a metal.*

The ability of an acid to form acid salts shows that the acid is not monobasic. Thus, for instance, the fact that hydrofluoric acid forms acid salts like KHF_2 and $NaHF_2$ would argue in favor of the view that the acid is dibasic in character and has the formula H_2F_2, rather than the simple formula HF.

In phosphoric acid H_3PO_4 and periodic acid H_5IO_6 we have an example of a tribasic and a pentabasic acid, respectively. The hydrogen atoms of these acids can be replaced step by step, thus forming a series of salts which grow less and less acid in character. For instance, in case of phosphoric acid, we may form the three salts KH_2PO_4, K_2HPO_4, and K_3PO_4, which are called primary, secondary, and tertiary potassium phosphate, respectively. We may also call these salts monopotassium phosphate, dipotassium phosphate, and tripotassium phosphate. The commonest salt of the three is dipotassium phosphate, and so it is generally referred to simply as potassium phosphate. In the case of the pentabasic periodic acid, we have a still greater range of possibility of formation of acid salts; indeed, *the greater the number of replaceable hydrogen atoms the molecule of an acid contains*, i.e. *the greater its so-called* **basicity**, *the larger is the number of acid salts that it is able to form.*

Acidity of Bases. — A base like KOH or NaOH, which is an hydroxide of a univalent metal, is called a *monoacid base*, for it is capable of reacting with an acid, and thus forming *one* molecule of water and replacing *one* atom of acidic hydrogen. A base like $Ca(OH)_2$ is called a *diacid base*, for it is capable of reacting with an acid, forming *two* molecules of water and a salt in which the bivalent metal replaces *two* atoms of acidic hydrogen. Similarly, we may have *triacid*, *tetraacid*, and *pentaacid bases* like antimonous hydroxide $Sb(OH)_3$, stannic hydroxide $Sn(OH)_4$, and antimonic hydroxide $Sb(OH)_5$. *The so-called acidity of a base consequently is determined by the valence of the metal of the base; or what really comes to the same thing, by the number of basic hydroxyl groups the molecule of the base contains.*

Basic Salts. — Just as in the case of acids that contain more than one hydrogen atom to the molecule it is possible to secure acid salts by replacing these hydrogen atoms step by step, so in the case of bases that contain more than one basic OH group it is possible to neutralize those groups step by step by means of an acid, thus forming a series of **basic salts**. For example,

(1) $Sb(OH)_3 + HCl = Sb(OH)_2Cl + H_2O$.
(2) $Sb(OH)_2Cl + HCl = Sb(OH)Cl_2 + H_2O$.
(3) $Sb(OH)Cl_2 + HCl = SbCl_3 + H_2O$.

Thus $Sb(OH)_2Cl$ and $Sb(OH)Cl_2$ are *basic salts*, for they still contain an excess of base that is not yet neutralized. The compound $Sb(OH)_2Cl$ readily splits off water, thus: —

$$Sb(OH)_2Cl = SbOCl + H_2O.$$

The salt SbOCl is called antimony *oxychloride;* it is also clearly a basic salt, for it is still capable of further neutralization with an acid. So with hydrochloric acid it undergoes the following change: —

$$SbOCl + 2\ HCl = SbCl_3 + H_2O.$$

A basic salt is one that contains an excess of base, which may still be neutralized with an acid. Basic salts are frequently met with, and they often split off water, as was exemplified above.

Normal Salts. — *Normal salts are those that contain neither hydrogen that is replaceable by a metal nor an excess of base that may still be neutralized by an acid.* Thus NaCl, K_2SO_4, $CaCO_3$, are normal salts of hydrochloric, sulphuric, and carbonic acids, respectively. From what has been said it is evident that a monobasic acid can form only normal salts with monoacid bases; whereas with polyacid bases it may form basic salts as well as normal salts. Again, polybasic acids may form either normal salts, acid salts, or basic salts with polyacid bases; whereas with monoacid bases they can form only acid salts and normal salts.

Acidimetry and Alkalimetry. — The fact that it always takes a definite amount of acid and a definite amount of base to exactly neutralize each other is used in the quantitative estimation of acids and markedly alkaline bases in processes that are called **acidimetry** and **alkalimetry**. A given volume of a solution of an acid of known strength will always neutralize a perfectly definite volume of a given solution of an alkali. If we place the acid of known strength in the burette *A* (Fig. 33) and an alkaline solution of unknown strength, *e.g.* of sodium hydroxide, in the burette *B*, then run out say 20 cc. into the dish *D* and find that it is necessary to add 23.6 cc. of the acid in *A* to just make the solution in the dish *D* neutral to litmus,

it is possible to compute the strength of the sodium hydroxide solution from the data at hand. *Any solution of known strength is called a* **standard solution.** In working with acid solutions of known strength normal solutions are frequently used. *A* **normal solution** *of an acid is one which contains* 1.008 *grams of replaceable hydrogen per liter of solution.* Thus a normal solution of hydrochloric acid would contain 36.468 grams of pure HCl per liter, for in this amount there are 1.008 grams of replaceable hydrogen. In the case of hydrobromic acid, a liter of normal solution would contain 80.928 grams of HBr; in the case of sulphuric acid a liter of normal solution would contain 49.043 grams of H_2SO_4, etc. Sometimes solutions of one half, one tenth, or one twentieth, etc., of the strength of normal solutions are employed; these contain the corresponding amounts of replaceable hydrogen per liter. Solutions of an acid may be prepared which contain some multiple of 1.008 grams of replaceable hydrogen or some aliquot part thereof per liter. These are then called twice normal, normal, half normal, fiftieth normal, etc., as the case may be.

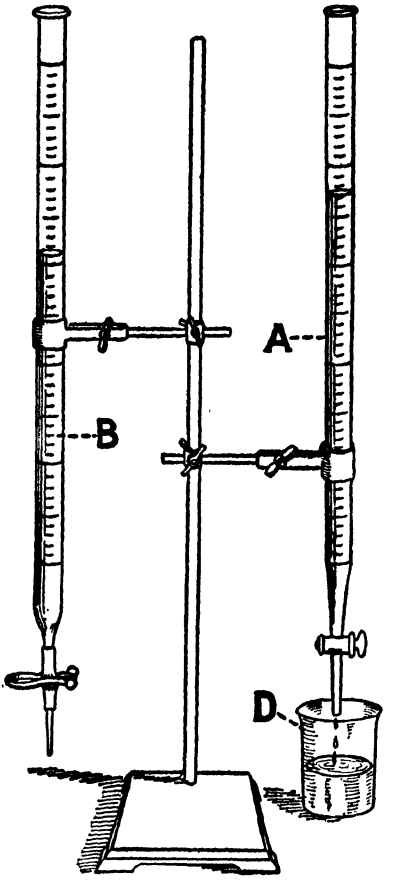


FIG. 33.

A normal solution of an alkali is one that will just neutralize a normal solution of an acid volume for volume; consequently a normal solution of an alkali is a solution that contains the chemical equivalent of 1.008 *grams of replaceable hydrogen per liter.* Alkaline solutions may be made up as normal solutions or as some multiple or fractional part of normal, just as in the case

of the acid solutions. So, for instance, a normal solution of sodium hydroxide NaOH contains 40.008 grams of pure NaOH per liter, and a tenth normal solution contains one tenth as much per liter.

The process of exactly neutralizing an acid solution with an alkaline solution to ascertain the strength of one of them in terms of the other, as illustrated in connection with Fig. 33, is called **titration.** If, in the instance cited above, the acid solution was normal, then the 20 cc. of NaOH solution required would just be equal to 23.6 cc. of normal solution. In other words, the NaOH solution would be $\frac{23.6}{20}$ normal, and contain $\frac{23.6}{20} \times 40.00$ grams of pure NaOH, or 47.20 grams per liter.

Indicators. —**Litmus** may serve to indicate the acidity or alkalinity of a solution. There are, however, many other coloring matters that change their hue on being treated with an acid and an alkali in succession. Such substances may consequently also serve as **indicators.** So **phenolphthalein** is colorless in acid solution, pink in a faintly alkaline solution, and a beautiful purplish red in strongly alkaline solution. **Methyl orange** is red when acid, straw yellow when alkaline, and orange colored when neutral. **Congo red** is red when alkaline and blue when acid; that is, it acts in just the opposite way that litmus does. **Turmeric** paper, that is paper soaked in a decoction of turmeric root, is yellow when neutral or acid, but turns brown when moistened with an alkaline solution. There are still other indicators in use, but those mentioned are the ones commonly employed in the laboratory.

Hydrolysis. — When phosphorus trichloride is brought into contact with water, violent action ensues, heat is liberated, and phosphorous and hydrochloric acids are formed, thus: —

$$PCl_3 + 3\ H_2O = P(OH)_3 + 3\ HCl.$$

The action is complete and **irreversible.** No such change takes place, for example, when sodium chloride NaCl is treated with water. The solution in this case remains quite neutral, and the salt may be recovered by evaporating off the water. In phosphorus trichloride we have a compound which in contact with water readily passes over into the much more stable com-

pounds hydrochloric and phosphorous acids. In the formation of hydrochloric acid, the great affinity of hydrogen for chlorine comes into play, and in the formation of phosphorous acid the strong affinity of phosphorus for oxygen exerts itself. We thus see that all three chlorine atoms in PCl_3 are exchanged for OH groups taken from three water molecules, the remaining hydrogen atoms of which unite with the chlorine atoms to form hydrochloric acid. *When a substance is thus decomposed by water, the process is termed hydrolytic decomposition, or* **hydrolysis.** Very many salts suffer hydrolysis in water to a slight extent, others are not decomposed by water, and still others are completely hydrolyzed. Thus we have seen that PCl_3, which is a salt of an extremely weak basic element, phosphorus, with a very strong acidic element, chlorine, is *completely decomposed by hydrolysis.* On the other hand, sodium chloride, a salt of the strongly basic sodium with the strongly acidic chlorine, is *not hydrolyzed.* In general, *salts of weak bases with strong acids are more or less hydrolyzed when brought into contact with water. The same is true of salts of strong bases with very weak acids.* So cupric sulphate $CuSO_4$, ferric chloride $FeCl_3$, and in general *all the ordinary salts of the heavy metals, are somewhat hydrolytically decomposed when dissolved in water.* This is made evident, for instance, by the fact that all these solutions react *acid* toward litmus. On the other hand, salts like sodium carbonate Na_2CO_3 and borax $Na_2B_4O_7$, which contain a very weak acid radical united to the strongly basic sodium, are also hydrolyzed to some extent. This is evidenced by the fact that their solutions react *alkaline* toward litmus. Even sodium bicarbonate $NaHCO_3$ is thus hydrolyzed, and its solutions react alkaline toward litmus, though the salt still contains hydrogen that is replaceable by a metal and consequently is an acid salt. Thus it is that the normal salts need not necessarily yield solutions that are neutral toward indicators, for many of them are hydrolyzed. Indeed, *neutrality toward indicators is met only in dealing with solutions of normal salts of strong acids with strong bases.* Thus, the chlorides, sulphates, nitrates, and bromides of sodium, potassium, calcium, and magnesium in solution are neutral toward indicators ; whereas the corresponding salts of iron, copper, lead, and mercury have acid reactions in solution, and the carbonates, silicates, and borates of sodium and potassium yield alkaline so-

lutions. From this it is evident that the processes of acidimetry and alkalimetry described above can be used only in estimating the strength of solutions of fairly pronounced acids and alkalies.

If now we take cupric chloride $CuCl_2$ and dissolve it in water, we find that the solution is distinctly acid toward litmus and other indicators, showing that the salt has suffered decomposition to a certain degree. The hydrolysis which has taken place has resulted in the liberation of a slight amount of hydrochloric acid. One may indicate the change, at least in part, thus: —

$$CuCl_2 + H_2O \rightleftarrows Cu(OH)Cl + HCl;$$

meaning that only a small percentage of the salt is thus hydrolyzed in solutions that contain say ten per cent or more of the salt.

Such solutions remain clear, the basic cupric chloride forming with the cupric chloride $CuCl_2$ a compound which consists of a soluble, though slightly basic cupric chloride. On dilution of the solution of cupric chloride, the hydrolysis proceeds further and a basic cupric chloride finally forms, which is richer in base and poorer in chlorine than that in the stronger solutions. This basic salt is difficultly soluble and gradually separates out in form of a precipitate. The more dilute the solution, then, the more does the reaction proceed in the direction indicated by the upper arrow in the equation. On the other hand, on concentrating the solution the reaction proceeds from right to left; *i.e.* it reverses. We have here then a case of **reversible hydrolysis.**

Mass Action; Chemical Equilibrium. — Thus we see, in the instance just mentioned, that the more water there is added to the cupric chloride solution, the greater is the extent of the hydrolysis. The water consequently influences the process to proceed from left to right (see the equation); but it is to be borne in mind that it is the mass of water present *relative* to the amount of cupric chloride in the solution that really determines the direction of the reaction.

The amount of matter contained in unit of volume is commonly called the **concentration.** In the case of a solution, the concentration is the amount of dissolved substance contained in unit of volume of the solution. Very commonly the concentration

of a solution is expressed by stating the number of gram-molecules contained in one liter of the solution. *By a gram-molecule is meant the molecular weight in grams.* Thus a gram-molecule of hydrochloric acid is 36.46 grams HCl; a gram-molecule of potassium iodide, 166.02 grams KI.

We may state the facts elucidated in the case of the hydrolysis of cupric chloride by saying that the extent of the hydrolysis is determined by the relative concentrations of the cupric chloride and the water in the solution; *i.e.* by the relative masses of the substances that are acting on each other. The amount of undecomposed cupric chloride, water, basic cupric chloride, and hydrochloric acid which the solution contains at any particular temperature and concentration of the cupric chloride solution is perfectly definite; and the amounts of these four ingredients are said to be in chemical equilibrium with one another. The equilibrium of this system may be disturbed by changing the concentration of any one of the four ingredients that make up the solution. Thus to abstract water from the solution causes the action to proceed in the direction of the lower arrow, —

$$CuCl_2 + H_2O \rightleftarrows Cu(OH)Cl + HCl;$$

while to add water causes the action to go in the direction of the upper arrow. To abstract cupric chloride from the system causes the equilibrium to be displaced in the direction of the lower arrow, for this practically amounts to the same thing as adding more water relatively. Addition of cupric chloride causes the opposite effect. Addition of hydrochloric acid to the system causes the action to proceed in the direction of the lower arrow; abstracting hydrochloric acid causes the equilibrium to be displaced in the direction of the upper arrow. Addition of basic cupric chloride to the system causes the equilibrium to be changed in the direction of the lower arrow, while removal of basic cupric chloride from the system causes the reaction to proceed in the direction of the upper arrow. It is obvious that if either the hydrochloric acid or the basic cupric chloride were taken from the system as fast as formed, the reaction would go to completeness from left to right and with increased rapidity.

What has been thus presented is really a special case of a

general law, termed the **law of mass action**, which may be stated thus : —

The speed or rate of any chemical change is proportional to the active mass, that is, the molecular concentration of each substance engaged in the reaction. This is universal and holds for all chemical changes, whether they are reversible or not. In case of reversible reactions, the law holds for the change from right to left as well as from left to right, and hence the final chemical equilibrium reached is also determined by the law of mass action. One can best comprehend this by thinking of the equilibrium as reached when the rate of speed of the forward action just equals that of the reverse action. Chemical equilibrium is commonly regarded as dynamic rather than static in character.

Additional Illustrations of Chemical Equilibrium and the Operation of the Law of Mass Action. — In the first chapter it was stated that the factors which determine whether a chemical change will go on or not are : (1) the right substances must be brought into contact, *i.e.* chemical attraction or chemical affinity must exist between the substances that are to react ; (2) the temperature must be properly chosen ; (3) the pressure is of consequence, particularly when a gas enters into the change ; (4) the concentrations of the active substances must be considered. All of these factors determine not only whether the change will proceed at all or not, but they also influence the rate with which the action proceeds and consequently affect the final equilibrium reached. Now it is clear that it is with factor (4), above mentioned, that the law of mass action is concerned.

There are many reactions which are, so far as we know, irreversible ; that is, they go to completion in one direction. We have already seen that the hydrolysis of phosphorus chloride is of this class. The combustion of calcium, magnesium, or sodium in oxygen, the decomposition of potassium chlorate into potassium chloride and oxygen, the neutralization of potassium hydroxide by hydrochloric acid, the burning of sugar to water and carbon dioxide, are further examples of this kind. In these reactions, the chemical affinity factor, namely (1) above, is really the determining one ; *i.e.* its influence overshadows all the other factors very greatly, and so the action goes on in one

direction to completion and is irreversible. The cases of irreversible reactions are after all then fairly clearly distinguished, for as a rule they belong to one of two categories; namely: (1) they represent the formation of very stable compounds directly from the elements, in which processes powerful affinities come into play; or (2) they represent the decomposition of relatively unstable or complicated compounds into simpler and much stabler ones.

The burning of barium to barium oxide is a typical illustration of the first class; the decomposition of sugar or nitroglycerine by heat illustrates the second class. In speaking of irreversible reactions, it must be borne in mind that the term does not mean that the original substances taken cannot be got back by roundabout means. So while the burning of magnesium to magnesium oxide is an irreversible reaction, it is yet possible to get back the metallic magnesium and also the oxygen that it contains. In this sense, of course, all chemical reactions could be reversed, for matter cannot be destroyed, but simply transformed. *What we mean by an* **irreversible reaction**, *in the sense in which the term is here used, is a reaction that cannot be reversed entirely or in part by simply altering the temperature, pressure, or the concentration of the substances concerned in the reaction.*

In the irreversible reactions the factors of temperature, pressure, and concentration cannot reverse the process. But *in many chemical changes the affinities that come into play in fixing the direction in which the change will go on are so well balanced that changes of temperature, pressure, or concentration suffice as determining factors in altering the direction the reaction takes. Such reactions are consequently* **reversible**. This class of reactions is very large indeed. It is therefore evident that at constant temperature and pressure the effect of concentration is of vast importance in case of reversible reactions, for in these it determines the direction of the change and consequently the final equilibrium. On the other hand, in the irreversible reactions the concentration changes can only affect the rate of the reaction. Thus, in the burning of magnesium ribbon the final product is MgO, and whether the action proceeds in oxygen at atmospheric pressure, or in compressed oxygen, only affects the rate of the combustion, not the character or the

amount of the final product. But when, for instance, chlorine acts on water in diffused light, we have a case of a reversible reaction, thus: —

$$H_2O + Cl_2 \rightleftarrows HOCl + HCl.$$

All four ingredients are finally in equilibrium at any given temperature and pressure. By increasing either the relative amount of water or chlorine the change progresses somewhat more from left to right; the reverse happens by increasing the relative concentration of either the hydrochloric acid or hypochlorous acid. By diminishing the concentration of either the water or chlorine or both, the reaction proceeds from right to left. Decreasing the concentration of either the hypochlorous acid or hydrochloric acid or both causes the change to proceed from left to right. If we were to abstract say the hypochlorous acid as fast as it forms, the reaction would complete itself from left to right. Now, in the sunlight hypochlorous acid undergoes decomposition, thus: —

$$2\,HOCl = O_2 + 2\,HCl.$$

Therefore as the oxygen escapes and only hydrochloric acid remains in the solution, we have (when chlorine acts on water in sunlight) a reaction which goes on to completion. This reaction is complete because of the removal of one of the ingredients; namely, the hypochlorous acid.

Again, when sulphuric acid acts on common salt in moderately dilute solution, 10 to 20 per cent for instance, an equilibrium is established which may be expressed thus : —

$$NaCl + H_2SO_4 \rightleftarrows NaHSO_4 + HCl.$$

The action is reversible, for it is possible to displace the equilibrium in the one direction or the other by changing the concentration of the substances that enter into the change. Now, when concentrated sulphuric acid is poured on sodium chloride and the mass becomes warm, the reaction will complete itself from left to right; for the hydrochloric acid is volatile, and under the conditions of the experiment it can escape and so get out of the field of action. This does not necessarily mean that the sulphuric acid is stronger than the hydrochloric acid and so drives the latter out, as was formerly supposed. It will

be observed that the determining factor is rather the volatility of the hydrochloric acid, which takes it out of the reacting mass. Indeed, it is possible to displace the hydrochloric acid from common salt by boiling it with strong solutions of much weaker acids than hydrochloric acid, provided that the acid so employed is non-volatile. So, for example, it is possible to evolve hydrochloric acid from salt by employing boric acid, which, as we shall learn, is a very weak yet practically non-volatile acid.

Whenever liquids act on liquids, or solids act on liquids, forming a product which is gaseous and so escapes, the reaction proceeds practically to completion. The same is true whenever in such cases a solid forms which is insoluble, *i.e.* is practically not acted upon, and so is thrown out of the field of action. Thus, for instance, when sodium sulphate acts on barium chloride we have the following change taking place : —

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2\,NaCl.$$

This goes practically to completion because the barium sulphate formed is very difficultly soluble, and nearly all of it drops out of the field of action as a precipitate.

In the case of gases we frequently have instances of reversible changes. At red heat, water vapor partially decomposes into hydrogen and oxygen; at still higher temperatures, the reaction progresses further in the sense mentioned, whereas on cooling it again is reversed. The process of thus decomposing a substance on heating it is called **dissociation.** It was studied particularly by Henri Saint Claire Deville. We shall consider cases of the dissociation of gases more carefully later.

Strength of Acids and Bases. — The relative strengths of acids has been a favorite subject of study with chemists. By having, let us say, tenth normal solutions of hydrochloric, sulphuric, and acetic acids each separately act on a piece of zinc (the pieces being arranged so as to expose the same area of zinc to each acid) and estimating the volume of hydrogen liberated by each acid per minute, it is possible to compare the relative strengths of the acids. The apparatus for this purpose might be arranged as in Fig. 14. In each tube is placed a piece of zinc of the same size and shape. The whole apparatus is then filled with water, the same quantity being used in each case.

The acids are then introduced in chemically equivalent amounts from above by means of the stopcocks, care being taken to admit no air through the cocks. The volumes of hydrogen evolved per minute may then readily be read. We should thus be estimating the strengths of these acids by their rate of action upon zinc. It is, of course, possible to use other characteristic activities of acids as a basis of estimating their strength. Similarly, strengths of alkalies might be compared by measuring the rate with which they transform a fat into soap (which see).

REVIEW QUESTIONS

1. What is formed when each of the following compounds acts upon water: SO_2, P_2O_5, K_2O, CO_2, CaO, Na_2O? Write the equation in each case and state what conclusion may be drawn as to the nature of (*a*) the metallic oxides, (*b*) the non-metallic oxides.

2. Define: acid, base, salt, neutralization, normal salt, acid salt, basic salt, anhydride, and give an example of each.

3. Mention four *general* methods of preparing a salt. Give an equation for the preparation of calcium chloride by each method.

4. How many grams H_2SO_4 will neutralize 250 grams KOH?

5. Define: normal solution, indicator, hydrolysis. Give illustrations.

6. Explain the fact that a solution of $NaHSO_4$ reacts acid toward litmus while a solution of $NaHCO_3$ reacts alkaline.

7. State how an aqueous solution of each of the following reacts towards litmus and explain the action: $AlCl_3$, K_2CO_3, $FeCl_3$, KNO_3, NH_4Cl, $CuSO_4$, NaCl, $Na_2B_4O_7$. In general what normal salts react neutral toward litmus? What normal salts react alkaline? What normal salts show an acid reaction?

8. Given the following normal salts: $Bi(NO_3)_3$; $SbCl_3$; $FeCl_3$; write the formulas of two basic salts which each could form.

9. Write the formulas for the anhydrides of the oxy-acids of chlorine.

10. What is meant by the term "reversible reaction"? Illustrate.

11. In the following reaction, state what would be the effect of increasing (*a*) the amount of water, and (*b*) the amount of nitric acid in the solution: —

$$Bi(NO_3)_3 + 2\ H_2O \rightleftarrows Bi(OH)_2NO_3 + 2\ HNO_3.$$

12. If dry common salt is treated with hot, concentrated sulphuric acid, it is completely converted into hydrochloric acid and sodium sulphate; but, if a twenty per cent solution of common salt is treated with sulphuric acid, the reaction is incomplete. Explain these facts from the standpoint of chemical equilibrium.

13. How compare the strengths of hydrochloric, sulphuric, and acetic acids?

CHAPTER X

NITROGEN, THE ATMOSPHERE, AND THE ELEMENTS OF THE HELIUM GROUP

History and Occurrence of Nitrogen. — In 1772 Dr. Rutherford, professor of botany at Edinburgh, found that when animals are confined in an air-tight space, the air they breathe becomes incapable of supporting combustion or respiration. After treating such air with caustic potash solution to absorb the carbon dioxide, then called "fixed air," he showed that the remaining gas supported neither life nor combustion. A lighted candle thrust into the gas, for instance, was immediately extinguished. He called this residual gas "mephitic air." Priestley burned carbon in a confined volume of air, and then treated the latter with limewater; thus the carbon dioxide formed during the combustion was absorbed, and a residual gas was obtained, which he called "phlogisticated air." He found that one fifth of the volume of atmospheric air can thus be converted into "fixed air" and absorbed by caustic lime. But he did not regard the "phlogisticated" air he had prepared as a constituent of the atmosphere. It was Scheele (1777) who first showed that there are two different gases in the air. Lavoisier was the first to consider mephitic or phlogisticated air as an element. He called it *azote*, because of its inability to support life. The name **nitrogen** was given to the gas by Chaptal, because it forms an essential constituent of niter or saltpeter. Cavendish showed that nitrogen obtained from air is essentially a simple body which is somewhat lighter than ordinary air; and, indeed, till 1894 the residual gas thus prepared was regarded as pure nitrogen. Sir William Ramsay and Lord Rayleigh showed that the gas remaining after the oxygen and carbon dioxide have been removed from the air consists of 98.814 per cent nitrogen and 1.186 per cent other gases, which, unlike nitrogen, will not unite with oxygen or with red-hot magnesium. This notable observation led to the discovery of the new elements of the helium group.

About 80 per cent of the volume of atmospheric air consists of nitrogen in the free state. In combination with carbon, hydrogen, and oxygen, nitrogen forms an essential constituent of the bodies of all plants and animals. It is found especially in the blood, muscles, nerves, seeds, and, in general, in all tissues that are concerned in movement or reproduction. When plants and animals die and their bodies decay, their nitrogen content passes over into simpler compounds, namely, ammonia, nitrites, and nitrates (which see). Thus it is that in all soils nitrogen is present in the form of nitrates and ammonium salts. It also occurs in all refuse matter of plant or animal origin, like barn-yard manure, guano, sewage, etc. In coal, which represents the remains of plants of the carboniferous age, nitrogen is found in combination with hydrogen, carbon, and oxygen. In minute quantities, nitrogen also occurs in granitic rocks, in meteoric iron, and in steel. In Chili saltpeter, consisting chiefly of sodium nitrate, nitrogen occurs in large quantities.

Preparation and Properties of Nitrogen. — Nitrogen which is approximately 99 per cent pure may be prepared from the air by removing the oxygen from the latter. This is generally accomplished by heating in the air some elementary substance which will readily combine with oxygen, forming an oxide that is either a non-volatile solid or that can readily be removed by absorption in some liquid. Thus, when phosphorus is burned in a little dish resting on water under a bell jar (Fig. 34), phosphorus pentoxide is formed, which is a solid that is readily absorbed by water, forming phosphoric acid: —

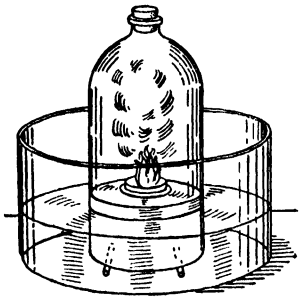


FIG. 34.

$$P_4 + 5\,O_2 = 2\,P_2O_5, \text{ and}$$
$$3\,H_2O + P_2O_5 = 2\,H_3PO_4.$$

Again, air may be passed over red-hot copper, when the latter unites with the oxygen, forming cupric oxide CuO, which is non-volatile, thus leaving the nitrogen. The oxygen may also be removed from the air by shaking the latter with an alkaline solution of pyrogallic acid, which readily absorbs oxygen, and

which is frequently used for this reason in gas analysis. Left in contact with moist yellow phosphorus, the air is also deprived of its oxygen even at room temperatures. This fact is often used in determining the amount of oxygen in a given sample of gas. By cooling air to $-182°$ the oxygen liquefies, leaving the nitrogen in form of a gas.

Pure nitrogen cannot very well be prepared from atmospheric air, for the gases of the helium group, with which it is always contaminated, are chemically very inert, and hence difficult to remove. Pure nitrogen is prepared from compounds in which it occurs. Thus, by treating ammonia NH_3 with chlorine, nitrogen and hydrochloric acid are formed, the latter uniting with some of the ammonia (which should be present in excess) to form ammonium chloride, which dissolves in water. The reactions may be expressed thus: —

$$2\,NH_3 + 3\,Cl_2 = 6\,HCl + N_2.$$
$$NH_3 + HCl = NH_4Cl.$$

The simplest way of preparing pure nitrogen consists of heating ammonium nitrite NH_4NO_2, either in pure form or in strong aqueous solution. The compound when thus treated decomposes into water and nitrogen: —

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

Frequently ammonium nitrite is not at hand, and a mixture of sodium nitrite and either ammonium chloride or ammonium sulphate is employed. By the interaction of the sodium nitrite and the ammonium salt employed, ammonium nitrite is formed, which on heating decomposes into water and nitrogen. When, for instance, sodium nitrite and ammonium sulphate are employed, the reaction is as follows: —

$$2\,NaNO_2 + (NH_4)_2SO_4 = Na_2SO_4 + 4\,H_2O + 2\,N_2.$$

By heating ammonium bichromate $(NH_4)_2Cr_2O_7$, or a mixture of ammonium chloride and potassium bichromate, nitrogen is formed, thus: —

$$K_2Cr_2O_7 + 2\,NH_4Cl = 2\,KCl + (NH_4)_2Cr_2O_7,$$

and

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4\,H_2O + N_2;$$

or, by combining the two equations, —

$$K_2Cr_2O_7 + 2\,NH_4Cl = 2\,KCl + Cr_2O_3 + 4\,H_2O + N_2.$$

When oxides of nitrogen are passed over red-hot copper, cupric oxide and nitrogen are formed, for example: —

$$2\,NO + 2\,Cu = 2\,CuO + N_2.$$

When urea $CO(NH_2)_2$ is oxidized by means of hypochlorous or hypobromous acids or their salts, nitrogen is formed. So, for instance, with potassium hypobromite the reaction is: —

$$CO(NH_2)_2 + 3\,KBrO = 2\,H_2O + 3\,KBr + CO_2 + N_2.$$

The potassium hypobromite solution as usually prepared contains an excess of caustic potash, which at once absorbs the carbon dioxide, forming potassium carbonate, which dissolves in water: —

$$2\,KOH + CO_2 = K_2CO_3 + H_2O.$$

In estimating the quantity of urea in urine, which often needs to be done in medical practice, these reactions are used.

Nitrogen is a colorless, odorless, tasteless gas, which is 0.9672 time as heavy as air. It may be liquefied and solidified. Liquid nitrogen is colorless, and boils at $-195.5°$ at atmospheric pressure. The critical temperature is $-146°$, at which it requires a pressure of 35 atmospheres to liquefy the gas. Liquid nitrogen has the specific gravity 0.80 at its boiling point. Solid nitrogen is a white, crystalline substance melting at $-214°$; its specific gravity is 1.0265 at $-252.5°$. Nitrogen is less soluble in water than oxygen. At 10°, 1000 cc. of water dissolve 16.1 cc. of nitrogen, while at 0°, 20.34 cc. are absorbed.

At ordinary temperatures, nitrogen is a very inert element chemically. At higher temperatures it unites with lithium, boron, silicon, magnesium, barium, strontium, or calcium to form **nitrides.** Lithium burns readily in nitrogen, and even unites slowly with that gas at ordinary temperatures, forming the nitride Li_3N. Magnesium at red heat absorbs nitrogen greedily, forming Mg_3N_2. In general, nitrogen is trivalent in the nitrides. When nitrogen and oxygen are mixed and subjected to the action of the electric spark (Fig. 35), nitrogen and oxygen unite to form an oxide of a brown color. Its formula is NO_2; at room temperatures it is N_2O_4. Hydrogen and nitrogen when mixed and similarly sparked yield small amounts of ammonia, which is a nitride of hydrogen having the composition NH_3.

Due to electrical disturbances in the atmosphere, especially during thunder storms when lightning flashes from cloud to cloud or to earth, small amounts of ammonia and oxides of nitrogen are formed.

The atomic weight of nitrogen is 14.01; and since at 0° and 760 mm. pressure 22.38 liters of nitrogen weigh 27.98 grams, the molecule contains 2 atoms and the molecular formula is N_2. This is also in harmony with the composition of ammonia and of the oxides of nitrogen by volume, as will appear later. In compounds nitrogen is either trivalent or pentavalent. Its atomic weight was determined by Stas, who ascertained the proportion by weight in which nitrogen exists in silver nitrate and in ammonium chloride.

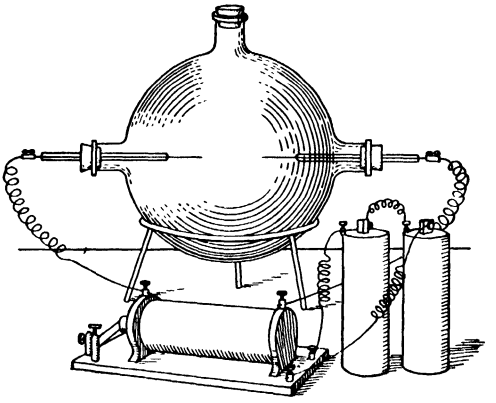


FIG. 35.

The Air. — As already stated above, the air consists of about one fifth oxygen and four fifths nitrogen by volume. That these gases are not chemically bound to each other but simply mixed is evident from the following facts: (1) When the air is cooled, the oxygen condenses to a liquid first, leaving the nitrogen in form of a gas; or when liquid air is boiled, the nitrogen distills off first, leaving nearly pure liquid oxygen behind. (2) The composition of the air, though nearly constant, varies somewhat at different times and places, the oxygen content commonly varying from 20.9 to 21.0 per cent. (3) Water will dissolve air to some extent. When the water is then deprived of this air by boiling, the air expelled from the water is richer in oxygen and poorer in nitrogen than ordinary air. Thus in air expelled from water the oxygen content is 35.1 per cent and the nitrogen is 64.9 per cent; whereas in ordinary air the corresponding figures are 20.96 and 79.04 per cent, respectively. (4) Air made by mixing four volumes of nitrogen and one of oxygen behaves like ordinary air. During

the preparation of the mixture there is neither a change of volume nor of temperature.

The amount of oxygen and nitrogen in the air may be determined by passing air freed from carbon dioxide and moisture over red-hot copper and collecting and weighing the nitrogen, which is not absorbed by the copper. The oxygen is determined by the increase of weight of the copper, which has united with the oxygen of the air passed over it. This is the method employed by Dumas and Boussingault in 1841. Another method consists of mixing a carefully measured volume of air with a known excess of hydrogen and exploding the mixture by means of an electric spark. In this way the oxygen completely unites with hydrogen to form water whose volume is extremely small relatively. And so from the diminution of the gaseous volume after the explosion and the known relation of the volumes of hydrogen and oxygen in water, the amount of oxygen in the air may readily be computed.

As a result of the average of numerous analyses of air, it has been found that *the atmosphere consists essentially of* 21 *volumes of oxygen to* 79 *volumes of nitrogen, or of* 23.2 *per cent oxygen and* 76.8 *per cent nitrogen by weight.* Usually the composition of different samples of air varies from these figures by only one-tenth of a per cent. A liter of air at 0° and 760 mm. pressure weighs 1.2933 grams. That the ratio of oxygen to nitrogen in air is so nearly constant is due to the fact that while animals are continually using up oxygen in respiration, plants are on the other hand giving off oxygen to the air. Furthermore, the atmosphere is so vast that the ordinary processes of combustion make scarcely a preceptible impression upon its oxygen content.

Besides oxygen and nitrogen, the air always contains water vapor, ammonia, hydrogen, nitric acid, carbon dioxide, dust particles of organic as well as inorganic nature, and various bacteria and other microbes. All of these constituents are, however, quite variable in amount. In the neighborhood of cities, sulphur dioxide and hydrocarbon gases have also been found in the air. The amount of water vapor in the air varies greatly with the locality and the temperature. Air saturated with moisture at 0° contains 4.87 grams of water vapor per cubic meter, while at 20° it contains 17.157 grams. As stated in connection with the consideration of water, the air is usually

saturated to only about two thirds of its capacity. The amount of moisture in the air is best found by passing a given volume of it through sulphuric acid and phosphorus pentoxide and determining the increase in weight of these drying agents.

In normal country air or air over the sea, there are about 3 volumes of carbon dioxide in every 10,000 volumes. In city air, the carbon dioxide content is often from 6 to 7 volumes per 10,000. In closed rooms where the air is contaminated by respiration and combustion of illuminating gas or oil, the carbon dioxide content may run as high as 6 to 8 times the latter amount. Air containing more than 7 volumes of carbon dioxide is considered harmful for continuous breathing. The carbon dioxide in the air is determined by passing a known volume of the latter through baryta water and weighing the barium carbonate formed. The reaction that takes place is:

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

City air contains more carbon dioxide than country air, mainly because of large amounts of fuel consumed in cities, and because in the country the carbon dioxide is taken from the air to a considerable extent by plants.

Ammonia occurs in the air in very minute and variable amounts hardly exceeding from 0.5 to 1 gram per 10,000 grams of air. It arises as a decomposition product of organic matter and is not present in the air in the free state, but is commonly combined with nitrous and nitric acids as nitrites and nitrates. The latter acids are formed, as already mentioned, when lightning discharges in the air. The ammonium salts are washed from the atmosphere during rains. Thus they get into the soil and serve as an important nitrogen supply for plants. The latter get their nitrogen from this source or from manures. Leguminous plants, like peas, beans, and the various varieties of clover, are able to get their nitrogen supply from little nodules which are produced on their roots by certain species of bacteria, which get nitrogen directly from the atmosphere that circulates in the porous soil. These nodules may contain up to five per cent of nitrogen. Many plants are incapable of assimilating nitrogen in form of ammonia. The latter must first be oxidized. This is brought about by bacterial action in the soil. The amount of nitric acid in the air is small and very variable.

Rain water has been observed to contain 0.14 part of nitrogen as nitrates per million parts of water on the average in some localities.

As has already been stated, it is doubtful whether ozone is normally present in the air. The effects observed on starch potassium iodide paper may well be due to hydrogen peroxide or higher oxides of nitrogen.

The hydrogen content of the air varies considerably. Rayleigh found it to be 0.003 per cent by volume. Dewar isolated 0.001 per cent hydrogen from liquid air; while Gautier claims to have found as much as 0.02 per cent. The hydrogen gets into the atmosphere from volcanic gases, and as a product of bacterial action. During the process of the decay of animal and vegetable matter there are also still other gases produced, which enter the atmosphere. These are, however, soon oxidized, especially in the presence of sunlight.

The particles of solid matter in the air frequently carry bacteria. As a rule the bacteria found in the air are harmless, though pathogenic organisms do get into the air, especially in the sick room and in crowded cities. Dry weather and winds increase the amount of dust in the air, and also the number of organisms that cling to dust particles. The spores of molds and microbes producing fermentation and putrefaction are practically always present in the air. By filtering the latter through plugs of cotton, dust and microbes may be removed from the air. Normal air contains but 4 or 5 microörganisms per liter. The waters of rivers and inland lakes contain from 5,000 to 20,000 organisms per cubic centimeter, whereas the soil contains about 5 times the latter number per cubic centimeter. Thus, it is clear that the air is relatively free from organisms. The latter get into the air chiefly from the dry soil, or dry objects, as dust is carried from them by currents of air. Dust particles act as nuclei for the condensation of moisture in the formation of fogs.

The air that is exhaled by animals and human beings contains, besides carbon dioxide, organic material; and it is chiefly the latter which gives rise to headache and general depression that one experiences in crowded rooms. The decomposition products of this organic matter give rise to unpleasant odors which are frequently met in crowded, poorly ventilated rooms.

Liquid air is now produced on a commercial scale. The methods employed are founded upon the principle that by subjecting a gas to very high pressure and then allowing it to escape through a small orifice, the remaining gas is cooled, due to the heat absorbed in expansion. Thus, air compressed to about 200 atmospheres (*i.e.* 3000 pounds to the square inch) is cooled to room temperature by means of cold water, and this air is then allowed to escape from the long tube in which it is contained, through an orifice the size of which is controlled by means of a needle valve. The air thus enters another chamber which surrounds the first tube. The outflow is regulated so that in this second chamber the pressure of the air is about 20 atmospheres. In thus coursing from the first chamber into the second against a pressure of 20 atmospheres work is done, and the heat required to do this work is taken from the tube containing the highly compressed air. The apparatus is carefully insulated from the surroundings by means of wool. After thus continuing to feed the apparatus compressed air for a few hours, the temperature in the inner tube becomes so low that the air liquefies and can then be drawn off. It is turbid in appearance, due to the solid particles of carbon dioxide and water that it contains. These may be filtered off. The filtrate is a clear liquid of bluish hue. Liquid air rapidly changes its composition, since nitrogen evaporates faster than oxygen. Liquid air boils at about $-190°$. The boiling point of nitrogen is $-190.5°$ and that of oxygen is $-182.5°$. After a time, nearly all the nitrogen has evaporated, leaving practically only oxygen behind. The latter is put on the market in steel cylinders as compressed oxygen.

The Elements of the Helium Group. — It was found by Lord Rayleigh that a liter of nitrogen prepared from air weighs 1.2572 grams and that the same volume of nitrogen prepared from chemical compounds weighs 1.2521 grams. This led Rayleigh and Ramsay to investigate the composition of air more carefully, with the result that they discovered in it the new element argon in 1894. **Argon** may be prepared by passing air over heated copper to take out the oxygen, and then over hot magnesium or lithium to absorb the nitrogen. Or air may be mixed with an excess of oxygen and subjected to the action of the electric spark, the gas being kept over caustic potash solution to absorb the oxides of

nitrogen formed. In the latter method, the excess of oxygen may finally be absorbed by passing the gas over heated copper or by treatment with an alkaline solution of pyrogallic acid. About 0.9 per cent of the air, by volume, consists of argon. The gas has properties similar to those of nitrogen; but argon has thus far not been obtained in combination with other elements. It is very inert, chemically, whence its name argon, meaning inactive. The boiling point of argon is $-186°$ and the melting point $-189°$. It is more soluble in water than nitrogen. At room temperatures about 40 cc. of argon are dissolved by 1 liter of water. The gas has consequently been found in all natural waters. Argon is 19.95 times as heavy as hydrogen; its molecular weight is consequently 39.9. As it combines with no other elements whatever, its atomic weight cannot be ascertained by the usual means. The molecular heat of gases containing two atoms to the molecule is approximately 5 Cal.; in the case of mercury vapor, which contains but one atom in the molecule, the molecular heat is but 2.5 Cal. Now it has been found that to heat 39.9 grams of argon one degree requires 2.5 Cal., consequently argon, like mercury, contains but one atom in its molecule. The molecular weight and atomic weight of argon are consequently the same, namely 39.9. That argon is a simple substance is supported by the fact that it has a constant boiling point, and that by shaking the gas with water the dissolved portion is identical with the undissolved portion. Argon is extraordinarily stable, and since it has not been decomposed into anything simpler, it must be regarded as an element.

Helium, **neon**, **krypton**, and **xenon**, four additional new elements, were later also discovered in the air by Ramsay and Travers.

Helium was known to exist in the sun, whence its name. In 1895 Ramsay prepared helium by heating the mineral cleveite with sulphuric acid. The element exhibits a characteristic yellow line in its spectrum. This line had previously been observed in the spectrum of the sun by Lockyer, who ascribed it to an element which he called helium, then unknown on the earth. Helium does not unite with any other element. Its molecular weight is 3.99 and its atomic weight is the same. About 1.4 cc. of helium are dissolved by 100 cc. of water at room temperature. Helium was liquefied in 1908 by Professor

Kammerlingh Onnes of the University of Leiden. Its boiling point is $-268.7°$, and its specific gravity in the liquid state is 0.15. This gas is the most difficult one to liquefy, and for several years it had resisted all attempts to condense it to a liquid. We may now say that all known gases have been liquefied. In the air helium occurs to the extent of 1 to 2 volumes per million volumes.

Ramsay found neon, krypton, and xenon in the argon prepared from air. Helium and neon are dissolved in the liquid argon, from which they are expelled, together with argon, as the temperature rises. The residue Ramsay subjected to further fractional distillation, and so separated krypton and xenon from each other. By cooling a mixture of neon and helium with liquid hydrogen, neon solidifies, while the helium remains in the gaseous state. Neon, krypton, and xenon are inert gases that combine with no other elements; they are mono-atomic. Their atomic weights as determined from their densities are: —

Neon . . .	20.2
Krypton . . .	82.92
Xenon . . .	130.2

Their boiling points are as follows: —

Neon . . .	$-243°$ (approximately)
Krypton . . .	$-152°$
Xenon . . .	$-109°$

Krypton melts at $-169°$ and xenon at $-140°$.

The following table gives the amounts of the gases of the helium group contained in one cubic meter, *i.e.* 1000 liters, of air: —

Helium . .	0.0015	liter . .	=	0.00027	gram
Neon . .	0.015	liter . .	=	0.01339	gram
Argon . .	9.4	liters . .	=	16.76	grams
Krypton . .	0.00005	liter . .	=	0.00018	gram
Xenon . .	0.000006	liter . .	=	0.00003	gram

REVIEW QUESTIONS

1. Compare oxygen and nitrogen as to (*a*) their occurrence in nature, (*b*) their physical properties, (*c*) their chemical properties.

2. Give four reasons for regarding the air as a mixture and not a chemical compound.

3. Make a list of all of the gases that normally occur in the air, stating their amounts in per cent by volume.

4. State of what use each of the constituents of the air is in plant and animal life.

5. How do plants obtain their supply of nitrogen? What is a leguminous plant? How do such plants aid in the assimilation of nitrogen?

6. Outline the essential features of a process of preparing argon from the air.

7. What property do the rare gases of the atmosphere have in common?

CHAPTER XI

COMPOUNDS OF NITROGEN WITH HYDROGEN AND WITH THE HALOGENS

History and Occurrence of Ammonia. — Ammonia is by far the most important compound of nitrogen with hydrogen. Up to 1774 it was known only in its aqueous solution, which Glauber called "spiritus volatilis salis armoniaci," and which was later named **spirits of hartshorn** and **spirits of sal ammoniac.** Ammonia was prepared by treating sal ammoniac, that is, ammonium chloride, with lime or some other alkali, whence the name spirits of sal ammoniac. It may also be obtained by heating hoofs and horns of animals out of contact with the air, whence the term spirits of hartshorn. The process of thus heating substances out of contact of the air in a retort and decomposing them into other products is called **destructive distillation.** Priestley discovered ammonia gas in 1774 by evolving it from lime and ammonium chloride and collecting it over mercury. He called it "alkaline air"; for the gas turns red litmus blue and acts in other ways like a strong alkali. As stated in connection with nitrogen, ammonia occurs in small amounts in the atmosphere in form of ammonium salts, particularly as ammonium carbonate. It is a product of the decomposition of all vegetable and animal matter, and hence is found in all natural waters and soils. In the form of salts, mainly nitrate and nitrite, it occurs in rain water. Its occurrence in soils is important, for it is a fertilizer. In the neighborhood of volcanoes, particularly those of Tuscany, ammonia occurs in the form of sulphate and chloride of ammonium. Ammonium chloride used to be prepared in Egypt in the oasis near the temple of Jupiter Ammon, from the soot obtained by heating camel's dung which was used as fuel; thus the salt received its name sal ammoniac, from which comes the term ammonia.

Preparation and Properties of Ammonia. — When a mixture of nitrogen and hydrogen is subjected to the silent electrical

discharge as in making ozone, small amounts of ammonia are formed by direct union of the elements, thus: —

$$N_2 + 3\,H_2 = 2\,NH_3.$$

The common method of preparing ammonia is by heating ammonium chloride with slaked lime: —

$$2\,NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\,H_2O + 2\,NH_3.$$

Any other ammonium salt may be used instead of the chloride, and other alkalies, like sodium or potassium hydroxide, may serve in place of lime, which, however, is the cheapest.

By the reduction of nitrates and nitrites with nascent hydrogen, ammonia may be produced, thus: —

$$KNO_3 + 8\,H = KOH + 2\,H_2O + NH_3.$$
$$KNO_2 + 6\,H = KOH + H_2O + NH_3.$$

By the dry distillation of nitrogenous animal and vegetable material ammonia is formed. So by heating coal (which represents the remains of vegetation of the carboniferous age) out of contact with air, as is done in the manufacture of illuminating gas from coal, ammonia is produced. The coal gas formed is passed through water, which readily dissolves the ammonia, and it is from these ammoniacal liquors of the gas works that the ammonia of commerce is almost entirely obtained at present. From these liquors the gas is expelled by heating with slaked lime. The ammonia so liberated is passed into sulphuric acid, and the sulphate of ammonium thus formed is purified by recrystallization. From this pure salt, pure ammonia and other ammonium products are in turn prepared.

By heating organic nitrogenous products with strong alkalies, ammonia is produced. This is frequently used in ascertaining the amount of nitrogen in organic substances, particularly as they occur in fertilizers, sewage, drinking water, etc. In this process a strong solution of caustic potash and potassium permanganate is frequently employed. The latter substance is a powerful oxidizing agent and so aids in the destruction of the organic material. Animal matter when heated with fuming sulphuric acid is decomposed, the nitrogen being converted into ammonia, which unites with the sulphuric acid, forming ammonium sulphate. This process (known as Kjeldahl's

method) is of importance in the chemical analysis of nitrogenous organic substances.

Ammonia is a colorless gas of a strong, peculiar, penetrating odor. It is 0.59 time as heavy as air. It may be condensed to a liquid which boils at $-32.5°$. It has also been obtained in form of white crystals that melt at $-78°$. The specific gravity of liquid ammonia, taken under pressure at 0°, is 0.6233. In water the gas is extremely soluble At 0°, 1 volume of water absorbs 1148 volumes of ammonia, while at 16° and 50°, only 764 volumes and 306 volumes, respectively, are absorbed. On boiling an aqueous solution of ammonia, the gas is completely expelled, which fact is frequently used in laboratories for preparing ammonia gas. On account of its solubility in water, ammonia gas is collected over mercury, or simply by displacement of air, the vessel in which gas is to be collected being supported with the bottom upward, for the gas is but little more than half as heavy as air.

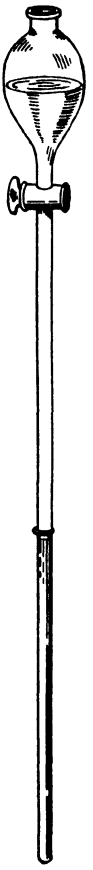


FIG. 36.

The weight of a liter of ammonia gas at 0° and 760 mm. is 0.7635 gram, and since the gas consists of 82.27 per cent nitrogen and 17.73 per cent hydrogen by weight, its formula is NH_3. By electrolyzing an aqueous ammonia solution, to which some common salt has been added to make the solution conduct better, *three volumes of hydrogen are obtained to one volume of nitrogen.* The apparatus used for this purpose is the same as that shown in Fig. 2.

Again, when a given volume of ammonia gas (Fig. 36) is treated with a concentrated solution of potassium hypobromite, nitrogen is formed which occupies half the volume of the original ammonia. Care must be taken not to admit air into the tube during the experiment. We thus see that 2 *volumes of ammonia yield* 1 *volume of nitrogen, while by electrolysis* 3 *volumes of hydrogen and* 1 *volume of nitrogen were obtained from ammonia.* Consequently, these volume relations may be expressed thus: —

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

We have here another excellent confirmation of the law of Gay-Lussac of the combination of gases by volume. By

Avogadro's hypothesis, equal volumes of gases contain an equal number of molecules, hence: —

3 molecules hydrogen + 1 molecule nitrogen = 2 molecules ammonia

or $3\,H_2 + N_2 = 2\,NH_3$.

While it is true that a mixture of 3 volumes of hydrogen and 1 volume of nitrogen when subjected to the electric spark yields small amounts of ammonia, it is also the case that when the latter gas is thus treated it is partly decomposed into nitrogen and hydrogen. The reaction is thus a reversible one: —

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3.$$

If none of the gases are removed, an equilibrium is finally slowly reached, which is the same in each case, the gases consisting of 2 per cent ammonia and 98 per cent of uncombined nitrogen and hydrogen. So if ammonia gas contained in the closed limb of the apparatus shown in Fig. 37 is treated with the electric spark, the volume of hydrogen plus nitrogen formed will be nearly twice that of the original volume of ammonia. If, however, the ammonia is removed (absorbed by sulphuric acid, for example) as fast as it is formed, the reaction completes itself from left to right as would be expected, according to the law of mass action.

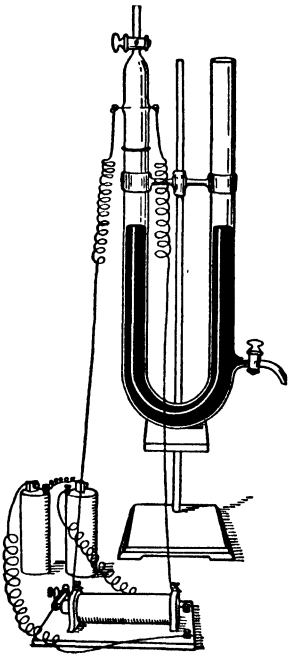


Fig. 37.

When ammonia is oxidized, as, for instance, by passing it over hot copper oxide, the latter is reduced and the only products formed are water and nitrogen, thus showing that the gas is composed of hydrogen and nitrogen. By thus oxidizing a definite volume of ammonia and weighing the water and nitrogen formed, the percentage composition of ammonia has been determined. The results of such analyses have already been given above. On account of its hydrogen content ammonia will burn. The action proceeds in oxygen, but not in air. Thus, when

in a flask (Fig. 38) strong ammonia water is heated till ammonia is copiously evolved, and oxygen is then conducted into the gas, the mixture when lighted will burn at the mouth of the flask. The products are mainly water and nitrogen, though nitrous and nitric acids are also formed to a slight extent. These acids unite with the excess of ammonia to form ammonium nitrite and nitrate. The latter salts are more copiously formed when a heated spiral of platinum wire (Fig. 39) is hung into a mixture of oxygen and ammonia gases. The platinum continues to glow, and white fumes form which consist of the salts mentioned. The platinum here acts as a catalytic agent.

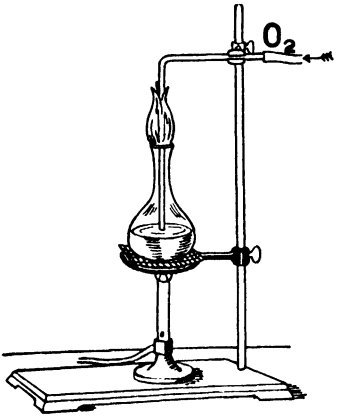


FIG. 38.

Ammonia water is lighter than water. The saturated solution at 14° C. contains 36 per cent NH_3 and has a specific gravity of 0.8844. It is sold as a *concentrated ammonia*, and may be diluted to any other strength desired.

Ammonia unites directly with acids, forming salts, thus: —

$$NH_3 + HCl = NH_4Cl.$$
$$2\,NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$
$$NH_3 + HNO_3 = NH_4NO_3.$$

We may regard these salts as derived from the acids by the replacement of each hydrogen atom by the group NH_4. So we may also consider that the group NH_4 plays the rôle of an atom of a univalent metal, like Na or K. For this reason, NH_4 is called **ammonium**, the ending *um* being used to indicate that chemically it is analogous to a metal. When ammonia dis-

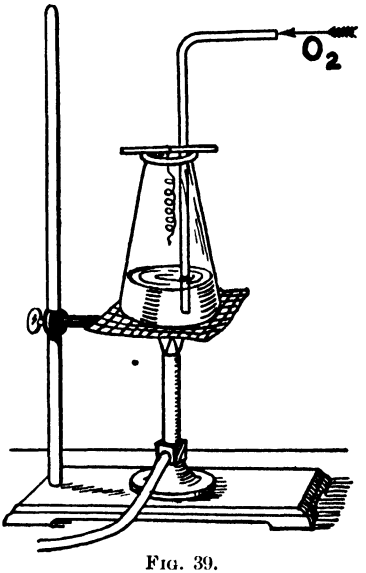


FIG. 39.

solves in water, much heat is evolved, and we may consider that the addition product formed is NH_4OH, thus: —

$$NH_3 + H_2O = NH_4OH.$$

The latter has not been isolated; but the aqueous solutions act as though this substance were contained in them. So, for example, when ammonia water is neutralized by hydrochloric or sulphuric acid, the action may be expressed thus: —

$$NH_4OH + HCl = NH_4Cl + H_2O.$$
$$2\ NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2\ H_2O.$$

At dull red heat all ammonium salts are volatilized. This is a very important fact in chemical analysis. In many cases the salts are simply broken up into ammonia and the free acid, thus: —

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

In such instances, which are typical cases of dissociation, the actions are reversible, the products again uniting as the temperature is lowered. The vapor of ammonium chloride contains all three products named in the above equation; which was demonstrated by Henri Saint Claire Deville, who separated hydrochloric acid and ammonia from these vapors by diffusion, making use of the fact that ammonia, the lighter gas, diffuses more rapidly than hydrochloric acid.

By means of chlorine, ammonia is decomposed: —

$$2\ NH_3 + 3\ Cl_2 = 6\ HCl + N_2.$$

When excess of ammonia is present, the latter at once unites with the hydrochloric acid formed and produces ammonium chloride.

Ammonia acts on many metals. Thus, sodium and potassium when heated act on ammonia as follows: —

$$2\ Na + 2\ NH_3 = 2\ NaNH_2 + H_2.$$
$$2\ K + 2\ NH_3 = 2\ KNH_2 + H_2.$$

The compounds formed are **sodium amide** and **potassium amide.** They are decomposed by water into ammonia and the hydroxide of the metal, so, for instance: —

$$KNH_2 + H_2O = KOH + NH_3.$$

The nitrides of lithium NLi_3 and of magnesium N_2Mg_3 may be regarded as ammonia in which the hydrogen atoms are replaced by the respective metals. These nitrides may be formed by igniting the metals in ammonia. On treating the nitrides with water, ammonia and the metallic hydroxides are formed, thus: —

$$NLi_3 + 3\ H_2O = 3\ LiOH + NH_3.$$
$$N_2Mg_3 + 6\ H_2O = 3\ Mg(OH)_2 + 2\,NH_3.$$

The fact that ammonia water will dissolve metals like zinc, copper, and silver and also their oxides, is used in cleaning tarnished metallic articles, for the action of ammonia is not as drastic as that of an acid, and, furthermore, the ammonia readily evaporates after use.

Liquid ammonia is a great solvent. In this respect it is similar to water, for it dissolves many salts, forming with some of them addition products that are analogous to hydrates that water forms with salts. Thus, with water copper sulphate forms the compound $CuSO_4 \cdot 5\ H_2O$, in which the water is spoken of as *water of crystallization*. Similarly with dry ammonia copper sulphate forms the compound $CuSO_4 \cdot 5\ NH_3$, in which the ammonia may be called *ammonia of crystallization*. The properties of liquid ammonia solutions have been investigated by E. C. Franklin in recent years.

Liquid ammonia is much like water in that it has a high specific heat, 1.02 between 0° and 20°, and a high latent heat of vaporization. It takes 316 cal. to vaporize 1 gram of liquid ammonia at 0°. This fact is used in the *artificial ice machines*, in which liquid ammonia is evaporated in tubes which are surrounded with concentrated calcium chloride solution. The evaporation of the ammonia requires heat, which is abstracted from the brine; and this cold brine is then distributed by means of a system of tubes to the places where refrigeration is required. The ammonia is again liquefied by compression with a powerful pump, and so it can be used over and over again in a closed system of tubes. The calcium chloride brine also circulates in a closed system of tubes, the brine after becoming warmed being returned and again chilled. That a considerable lowering of temperature can be produced by the evaporation of ammonia may be shown by a simple experiment. When a con-

centrated aqueous solution is placed in a flask standing upon a board that is wet with a few cubic centimeters of water, and a strong current of air is passed into the solution by means of a pair of bellows, the evaporation of the ammonia proceeds so rapidly that in a few minutes the cold produced is sufficient to freeze the flask to the board.

In ammonia NH_3 nitrogen is trivalent, whereas in ammonium salts the element is quinquivalent. Indeed, in most of its compounds nitrogen may be considered as having a valence of either three or five.

Ammonium salts are readily detected by the fact that ammonia is evolved when they are treated with caustic alkali. The ammonia gas is easily distinguished by its odor and by the fact that it turns red litmus paper blue. When present in very small quantities, as in drinking water, ammonium salts are detected by means of a solution of mercuric iodide HgI_2 in potassium iodide. This solution is made strongly alkaline by addition of caustic potash and is then known as *Nessler's reagent.* When added to a very dilute solution of an ammonium salt a yellow color is produced. In stronger solutions of ammonium salts a dark brown color or a precipitate is formed. Nessler's reagent is of great importance in analyzing potable waters, sewage, and the like.

Hydrazine. — The composition of hydrazine or diamide is expressed by the formula $H_2N\text{–}NH_2$. This compound was discovered by Curtius in 1887. It may be made by the oxidation of urea, thus: —

$$NH_2\text{–}CO\text{–}NH_2 + O = H_2N\text{–}NH_2 + CO_2;$$

or by the reduction of hyponitrous acid, thus: —

$$H\text{–}O\text{–}N\text{–}N\text{–}O\text{–}H + 6\ H = H_2N\text{–}NH_2 + 2\ H_2O.$$

It forms white crystals melting at $-1°$. Liquid hydrazine boils at 113°. Its specific gravity at 15° is 1.013. It is miscible with water in all proportions and forms a hydrate $H_2N\text{–}NH_3(OH)$, which melts at $-40°$ and boils at 120°. Its

specific gravity is 1.03. Like ammonia, hydrazine is a strong base. Its solutions have a corrosive action on cork and rubber, and even on glass, especially at higher temperatures. With acids hydrazine forms salts. The action is similar to the formation of ammonium salts. A large number of compounds derived from hydrazine by replacing one or more of its hydrogens by hydrocarbon radicals are known in organic chemistry. One of these, namely, phenyl hydrazine $(C_6H_5)HN\text{–}NH_2$, has been of special importance in the synthesis and investigation of sugars.

Hydroxylamine. — This compound, which was discovered by Lossen in 1865, and prepared in the pure state by Lobry de Bruyn in 1891, may be formed by the action of nascent hydrogen either on nitric acid or nitric oxide, thus: —

$$HNO_3 + 6\,H = 2\,H_2O + NH_2(OH).$$
$$NO + 3\,H = NH_2(OH).$$

It may be considered as ammonia NH_3 in which one hydrogen atom has been replaced by the OH group. The group NH_2 is called the amido or amine group, whence the name hydroxylamine. It consists of white hygroscopic needles that melt at 33°. The boiling point is 58° at 22 mm. and 70° at 60 mm. pressure. In water hydroxylamine dissolves readily. It has basic properties, showing alkaline reaction toward indicators, and forming crystalline salts with acids, thus: —

$$NH_2OH + HCl = NH_3(OH)Cl.$$
$$2\,NH_2OH + H_2SO_4 = (NH_3OH)_2SO_4.$$

These salts may be regarded as ammonium salts in which one hydrogen has been replaced by OH. Hydroxylamine is, however, a much weaker base than ammonia or hydrazine. On heating hydroxylamine or its compounds, decomposition sets in, which, on account of sudden evolution of gas, may take place with explosive violence. The reducing power of hydroxylamine is characteristic. By treating a hot alkaline solution of a cupric salt with hydroxylamine, red cuprous oxide is at once formed, thus: —

$$4\,CuO + 2\,NH_2(OH) = N_2O + 3\,H_2O + 2\,Cu_2O.$$

The reaction will take place even when hydroxylamine is present merely as 1 part in 100,000.

Hydroxylamine readily decomposes into ammonia, nitrogen, and water, thus: —

$$3\,NH_2OH = NH_3 + N_2 + 3\,H_2O.$$

In organic chemistry hydroxylamine is of importance, because with aldehydes and ketones (which see) it forms compounds known as oximes.

Hydrazoic Acid. — This compound has the composition expressed by the formula N_3H. It is also called **hydronitric acid**, **triazoic acid**, or **azoimide**. It was discovered by Curtius in 1890. It may be made by passing nitrous oxide over sodium amide at 200°, and then treating the resulting sodium hydrazoate with dilute sulphuric acid. The reactions are as follows: —

$$NaNH_2 + N_2O = H_2O + NaN_3.$$
$$2\,NaN_3 + H_2SO_4 = Na_2SO_4 + 2\,HN_3.$$

By carefully distilling the aqueous solution produced, a solution of the free acid in water may be obtained. The pure acid boils at 37°. It is a colorless liquid with a disagreeable, penetrating odor. When inhaled, it irritates the mucous membranes. It explodes with violence, forming nitrogen and hydrogen with liberation of much heat, thus: —

$$2\,N_3H = 3\,N_2 + H_2.$$

It is a monobasic acid, and in this respect it is similar to the hydrohalogen acids. Its salts are also unstable and liable to explode with violence. It is of interest to note that the one hydride of nitrogen NH_3 is alkaline and the other N_3H is acid. The two will combine to form a salt, thus: —

$$NH_3 + (N_3)H = NH_4(N_3).$$

The empirical formula of $NH_4(N_3)$, ammonium hydrazoate, is N_4H_4.

Compounds of Nitrogen with the Halogens. — With the halogens nitrogen forms extremely unstable compounds.

Nitrogen trichloride NCl_3 is formed by the action of chlorine upon ammonium chloride, thus: —

$$NH_4Cl + 3\,Cl_2 = 4\,HCl + NCl_3.$$

The compound may be prepared by the electrolysis of an aqueous solution of ammonium chloride, the chlorine liberated acting

on the solution according to the above equation. Nitrogen trichloride is a thin, yellowish, oily liquid of specific gravity 1.65. *It is an extremely dangerous substance to deal with*, for it explodes with great violence when heated or brought into contact with substances like turpentine or phosphorus, or when exposed to sunlight. Often the explosion occurs spontaneously, which makes the danger of working with it very great indeed. It has a pungent odor, and its fumes irritate the mucous membranes. It is soluble in hydrocarbons and carbon disulphide, the solutions thus formed being yellow in color and comparatively harmless. At 71° nitrogen trichloride boils and may be distilled, though the danger incurred in the operation is extremely great. By concentrated hydrochloric acid or aqueous ammonia solution, nitrogen trichloride may be decomposed, thus: —

$$NCl_3 + 4\,HCl = NH_4Cl + 3\,Cl_2.$$
$$NCl_3 + 4\,NH_4OH = 3\,NH_4Cl + 4\,H_2O + N_2.$$

Nitrogen trichloride was discovered by Dulong in 1811. In working with the substance he was so unfortunate as to lose an eye and three fingers in consequence of an explosion.

Nitrogen tribromide is a red, oily, *highly explosive substance* formed by the action of potassium bromide on nitrogen chloride. The substance is believed to have the composition represented by the formula NBr_3.

Nitrogen iodide is formed when iodine is treated with a concentrated aqueous ammonia solution, or when an alcoholic solution of iodine is mixed with strong aqueous ammonia. The compound is a brown powder having the composition $N_2H_3I_3$, probably $I_3N = NH_3$. It is not explosive when wet; but *when dry it is very explosive*, a touch with a feather sufficing to cause it to explode with detonation.

By treatment of silver hydrazoate AgN_3 with a solution of iodine in ether, **triazoiodide** IN_3 may be formed: —

$$AgN_3 + I_2 = AgI + IN_3.$$

It is a yellow powder of a very penetrating odor, and is *extremely explosive.*

REVIEW QUESTIONS

1. What is the composition of ammonia? State its chief physical and chemical properties.

2. Write the equation expressing the action of slaked lime upon ammonium chloride. This action will proceed to completion, whereas if a dilute solution of ammonium chloride is treated with lime, the action does not proceed to completion. Explain these facts. In general, how may ammonia be liberated from any ammonium salt?

3. From what source are the ammonium salts of commerce obtained? Explain fully.

4. What gases are produced when ammonia is decomposed by electrolysis? What are the respective volumes of these gases? What law does this illustrate?

5. Under what conditions will nitrogen and hydrogen unite directly to form ammonia? Write the equation and discuss it from the standpoint of chemical equilibrium.

6. What use is made of ammonia and of ammonium compounds?

7. In testing a drinking water why does a chemist always test for the presence of ammonium compounds?

8. Mention three halides of nitrogen. How may they be prepared? What is their chief characteristic?

CHAPTER XII

OXY-ACIDS AND OXIDES OF NITROGEN

THREE oxy-acids and five oxides of nitrogen are known. These are nitric acid HNO_3, nitrous acid HNO_2, hyponitrous acid $H_2N_2O_2$, nitrogen pentoxide or nitric anhydride N_2O_5, nitrogen peroxide NO_2 or N_2O_4, nitrogen trioxide or nitrous anhydride N_2O_3, nitric oxide NO, and nitrous oxide N_2O. In the consideration of these compounds nitric acid will be taken up first, for from it the other oxy-acids and oxides named are generally prepared.

History, Occurrence, and Preparation of Nitric Acid. — Nitric acid was known to the alchemists under the name of *aqua fortis.* Up to the seventeenth century the acid was prepared by heating a mixture of saltpeter, copper sulphate, and alum according to directions given by the alchemist Geber, who probably lived in the ninth and tenth centuries. In this process copper sulphate and alum yield sulphuric acid, which unites with the potassium of the saltpeter, thus setting nitric acid free. Prepared by this method, the acid was impure. In 1650 Glauber prepared nitric acid by treating saltpeter with sulphuric acid, and this method is in vogue to the present day. Though Lavoisier studied nitric acid and showed that it contained oxygen, he did not ascertain the real nature of the acid. In 1784 Cavendish demonstrated the nature of the acid by preparing it by passing an electric spark through air. In this way nitrogen peroxide is formed, which in contact with water yields nitric acid (see below).

It has already been stated that nitric acid and nitrates occur in small amounts in the atmosphere. In the soil and in natural waters nitrates occur as the final product of the decomposition and oxidation of animal and vegetable matter. The chief source of nitric acid is Chili saltpeter or sodium nitrate. Nitric acid gets its name from the fact that it is commonly prepared from niter, saltpeter.

By treating a nitrate like potassium or sodium nitrate with concentrated sulphuric acid, nitric acid is liberated, thus: —

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

In the laboratory the sodium nitrate is generally placed in a glass retort (Fig. 40), sulphuric acid is added, and the mixture

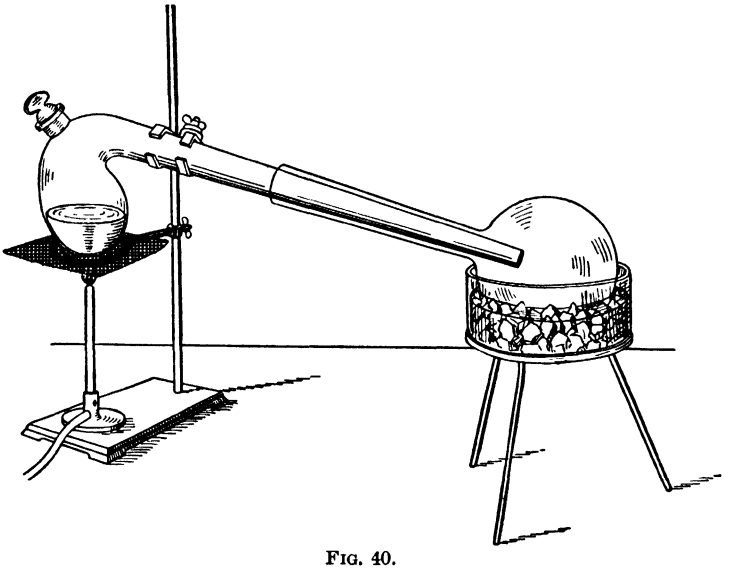


FIG. 40.

gently heated, when nitric acid distills over. On a commercial scale Chili saltpeter is treated with sulphuric acid in a cast-iron retort, and the nitric acid formed is condensed in bottles of stoneware that contain a little water, the last bottle being connected with a tower filled with coke over which water trickles so as to dissolve the acid vapors that still remain uncondensed. Of late stoneware pipes are frequently employed instead of the bottles. In this way an aqueous solution is obtained which contains about sixty per cent nitric acid and has a specific gravity of 1.37. By using dry sodium nitrate and concentrated sulphuric acid, the nitric acid obtained has a specific gravity of 1.53 and is practically free from water. On heating the pure acid, as in the process of distillation, it decomposes in part, thus: —

$$4\ HNO_3 = 2\ H_2O + 4\ NO_2 + O_2.$$

The nitrogen dioxide forms reddish brown fumes that dissolve in the nitric acid. This solution, which fumes strongly in the

air, is termed **red fuming nitric acid.** Its specific gravity is about 1.54.

When the electric spark passes through air, brown fumes are formed which are nitrogen dioxide. These in contact with water form nitric acid, thus: —

$$3\ NO_2 + H_2O = 2\ HNO_3 + NO.$$

This may readily be shown by means of the apparatus in Fig. 35. Sparks from an induction coil are passed through the air between the platinum points in the glass globe. After a time the gas in the globe appears brownish in color. On shaking the gas with water, and testing with blue litmus paper, the presence of acid is demonstrated. Many attempts have been made to use this process for the profitable production of nitric acid on a commercial scale. These have been unsuccessful till recently, for the amount of nitric acid produced was too small as compared with the electric power that had to be expended, even when water power was available for running dynamos. Of late, however, the process has been perfected by subjecting the electric arc formed to the action of a powerful electro-magnetic field. In this way arcs produced by means of large alternating current dynamos are obtained in form of disks over six feet in diameter, through which air is passed. Thus in this process, which is used in Norway and is known as the **Birkelund and Eyde process,** nitric oxide NO is formed at the very high temperature of the arc. It is the high temperature secured by means of the electric arc, and not an electrical effect, that causes the oxygen and nitrogen to unite. When the nitric oxide is then treated with air and water in a tower filled with moist coke, nitrogen dioxide and nitric acid form, thus: —

$$2\ NO + O_2 \rightleftarrows 2\ NO_2.$$
$$H_2O + 3\ NO_2 \rightleftarrows NO + 2\ HNO_3.$$

All of the reactions involved in the process are reversible, so that in order to have them go to completion from left to right as far as possible, the products formed are rapidly removed by condensation and solution. The dilute nitric acid thus obtained is neutralized with lime, and the calcium nitrate formed is sold as a fertilizer. This process of making nitric acid is of special importance, because the large demands made upon the deposits

of Chili saltpeter annually will ere long exhaust this source of supply, though new deposits have been found of recent years in the same region. About one and a half million tons of Chili saltpeter have been used annually in recent years. The salt is used as a fertilizer to a large extent, but it is also employed in making nitric acid, which is used in the manufacture of explosives, dyestuffs, medicinal chemicals, nitrates of metals, etc. Upwards of 100,000 tons of nitric acid are used annually in the chemical industries of the world.

Properties of Nitric Acid. — Pure nitric acid is a colorless liquid which boils at 86° with partial decomposition, as stated above. It is a monobasic acid whose composition is expressed by the formula HNO_3. On distilling the acid under diminished pressure, this decomposition may be avoided, and this is actually done in the manufacture of pure nitric acid. On cooling, nitric acid forms colorless crystals that melt at 42°. The acid that is sold in the market as concentrated nitric acid is a 68 per cent solution. It has a constant boiling point, which is 120.5°, and a specific gravity of 1.414 at 15°. The composition of this constant boiling solution changes when it is distilled under diminished pressure (compare hydrochloric acid); the solution is consequently not regarded as a chemical compound.

Nitric acid is a powerful acid which fumes in the air. In aqueous solutions it is much more stable than when pure. The concentrated acid is rather an unstable substance. It is slowly decomposed in sunlight to a slight extent, the yellow color developed being due to the formation of nitrogen dioxide, which remains in solution. At about 280° nitric acid decomposes, practically completely, into nitrogen dioxide, water, and oxygen. Concentrated nitric acid has a very corrosive action on the skin, producing painful wounds that are slow to heal. More dilute solutions color the skin yellow, due to the formation of nitro products. The effect upon wool, linen, silk, and other organic substances is similar.

When nitric acid is neutralized with bases, **nitrates** are formed. These salts are all readily soluble in water. *Nitric acid does not attack gold or platinum. When it attacks other metals, they are either oxidized, as is the case with tin, or converted into nitrates, as is more frequently the case.* So zinc, copper, iron, magnesium, when treated with nitric acid, are converted

into the corresponding nitrates. There is, however, no concomitant evolution of hydrogen, as when these metals are attacked with hydrochloric acid, for instance; for the hydrogen at once attacks the nitric acid, reducing it commonly to nitric oxide NO and water. With metals like zinc, iron, and magnesium, the temperature and concentration of the acid and resulting solutions may be regulated so as to secure a very gradual reduction of the nitric acid, the products being successively nitrogen dioxide NO_2, nitrous acid HNO_2, nitric oxide NO, nitrous oxide N_2O, nitrogen N_2, hydroxylamine NH_2OH, and ammonia NH_3. As nitrogen dioxide and nitrous acids are readily reduced to nitric oxide, the latter is generally formed when nitric acid acts on a metal, thus: —

$$3\,Zn + 8\,HNO_3 = 3\,Zn(NO_3)_2 + 4\,H_2O + 2\,NO.$$

Nitric acid is a powerful oxidizing agent and will convert many of the non-metals into their highest oxidation products with ease. Thus, when heated with nitric acid, phosphorus is oxidized to phosphoric acid, sulphur to sulphuric acid, carbon to carbon dioxide. A glowing stick of charcoal thrust into concentrated nitric acid continues to burn brightly.

While neither nitric nor hydrochloric acid alone attacks gold or platinum, these metals are readily dissolved in a mixture of nitric and hydrochloric acids. This mixture, since it dissolves gold, the "king of metals," is called **aqua regia.** The action depends upon the fact that nitric acid oxidizes hydrochloric acid, one of the products formed being chlorine, which attacks gold. Aqua regia was known even in the days of alchemy, for Geber dissolved gold in a solution of ammonium chloride in nitric acid. The action of concentrated nitric and hydrochloric acids on each other may be represented thus: —

$$3\,HCl + HNO_3 = 2\,H_2O + NOCl + Cl_2.$$

The compound NOCl is called **nitrosyl chloride.** It occurs here as one of the products of the reaction, but it does not attack gold.

Nitrogen Pentoxide. — When nitric acid is treated with phosphorus pentoxide, nitrogen pentoxide or nitric acid anhydride is formed. The action consists of the subtraction of water from nitric acid: —

$$2\,HNO_3 + P_2O_5 = 2\,HPO_3 + N_2O_5.$$

In this process, pure nitric acid is carefully mixed with about an equal weight of phosphorus pentoxide in the cold, and the sirupy mass obtained is carefully distilled. Nitric anhydride may also be formed from silver nitrate and chlorine, thus: —

$$4\,AgNO_3 + 2\,Cl_2 = 4\,AgCl + 2\,N_2O_5 + O_2.$$

It was by this method that the substance was discovered by Deville in 1849. Nitrogen pentoxide consists of colorless prismatic crystals that melt at 30°, forming a dark yellow liquid. The latter boils at 50° with concomitant partial decomposition. It is very unstable, readily giving off a portion of its oxygen, thus: —

$$2\,N_2O_5 = 4\,NO_2 + O_2.$$

The decomposition goes on slowly, though spontaneously, at ordinary temperatures. When rapidly heated, the decomposition proceeds with explosive violence. The substance cannot be kept long in any case. Dissolved in water, nitric anhydride N_2O_5 yields nitric acid.

Nitric Oxide. — Nitric oxide NO, discovered by Priestley in 1772, is formed by the action of copper, silver, mercury, and many other metals upon a solution of nitric acid of about 30 to 35 per cent: —

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO.$$

The temperature should be kept low during the reaction, as otherwise nitrous oxide N_2O and nitrogen are apt to form. Nitric oxide is also conveniently produced by the action of ferrous chloride or sulphate on nitric acid in presence of hydrochloric or sulphuric acid, thus: —

$$HNO_3 + 3\,FeCl_2 + 3\,HCl = 2\,H_2O + 3\,FeCl_3 + NO.$$

$$2\,HNO_3 + 6\,FeSO_4 + 3\,H_2SO_4 = 4\,H_2O + 3\,Fe_2(SO_4)_3 + 2\,NO.$$

The gas is colorless, but on coming in contact with the oxygen of the air it immediately turns brown, due to the formation of nitrogen dioxide: —

$$2\,NO + O_2 = 2\,NO_2.$$

It is consequently necessary to expel the air from the apparatus before collecting the gas, which may be done over water since the latter dissolves nitric oxide but slightly.

Nitric oxide is a colorless, neutral gas which is 1.039 times

as heavy as air. Its critical temperature is $-94°$, and its critical pressure 71.2 atmospheres. Under atmospheric pressure the liquid, which is colorless, boils at $-150°$. When solidified, nitric oxide forms colorless crystals that melt at $-167°$. At 0° one volume of water absorbs 0.075 volume of the gas, and at 20°, 0.05 volume.

Nitric oxide is the most stable of the oxides of nitrogen. A lighted candle or burning sulphur will be extinguished when introduced into the gas. On the other hand, burning magnesium or phosphorus will continue to burn in the gas with great brilliancy.

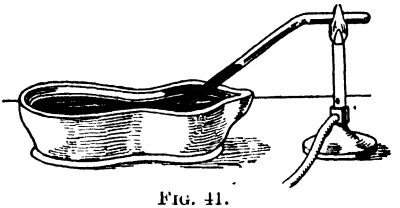


FIG. 41.

On heating metallic sodium or iron in nitric oxide (Fig. 41), *these metals are oxidized, and the nitrogen which remains occupies just one half of the volume of the nitric oxide*, thus : —

$$\underset{\text{(solid)}}{4\,Na} + \underset{\text{(2 volumes)}}{2\,NO} = \underset{\text{(solid)}}{2\,Na_2O} + \underset{\text{(1 volume)}}{N_2}.$$

$$\underset{\text{(solid)}}{3\,Fe} + \underset{\text{(4 volumes)}}{4\,NO} = \underset{\text{(solid)}}{Fe_3O_4} + \underset{\text{(2 volumes)}}{2\,N_2}.$$

Knowing the specific gravities of nitric oxide and nitrogen, and the fact that 2 volumes of nitric acid yield 1 volume of nitrogen, it follows that in nitric oxide 14 grams of nitrogen are combined with every 16 grams of oxygen. As nitric oxide is 15 times heavier than hydrogen, its molecular weight is 30. The formula of nitric oxide is therefore NO.

Nitric oxide may be used to detect the presence of free oxygen in a mixture of gases on account of its ability to form brown fumes NO_2 with oxygen. In solutions of ferrous salts nitric oxide dissolves readily, forming a dark brown liquid. From these solutions the gas is expelled by heating. It is probable that the solutions contain the unstable compound $FeSO_4 \cdot NO$. This reaction is a delicate **test for nitrates**, for, as we have seen, ferrous salts in presence of free acid readily reduce nitrates to NO, which then gives the brown color with the excess of the ferrous salt.

Nitrogen Dioxide and Tetroxide. — Nitrogen dioxide is produced by heating nitrates of the heavy metals : —

$$2\,Pb(NO_3)_2 = 2\,PbO + O_2 + 4\,NO_2.$$
$$2\,Cu(NO_3)_2 = 2\,CuO + O_2 + 4\,NO_2.$$

When oxygen acts on nitric oxide, nitrogen dioxide is formed: —

$$2\,NO + O_2 = 2\,NO_2.$$

When the electric spark is passed through a mixture of oxygen and nitrogen, nitrogen dioxide forms: —

$$2\,O_2 + N_2 = 2\,NO_2.$$

As stated under nitric acid, this reaction takes place slowly and is ordinarily very incomplete. Concentrated nitric acid oxidizes nitric oxide to nitrogen dioxide, consequently the latter is formed when metals like copper or tin are acted upon by strong nitric acid even out of contact with the air.

At ordinary temperatures, nitrogen dioxide is a gas of a dark reddish brown color. When chilled with a freezing mixture, consisting of ice and common salt, the dark brown nitrogen dioxide becomes much lighter in color and condenses to a pale yellow liquid. At $-30°$ this liquid congeals, yielding colorless crystals that melt at $-10°$, thus forming a colorless liquid which is fairly stable even at 0°. On gently warming this liquid, it assumes a greenish yellow hue. At about 10° it is yellow in color, at 15° it is orange colored, and at higher temperatures it becomes still darker, till at 26°, its boiling point, the color becomes a dark reddish brown. On lowering the temperature, these changes occur in the reverse order. At 2° the vapor is 38 times as heavy as hydrogen, while at 140° the vapor is only 23 times as heavy as hydrogen. At 26°, therefore, the molecular weight would be 76, and at 140°, 46. Now the formula NO_2 corresponds to a molecular weight of 46, consequently at 140° the gas is NO_2. But the double formula N_2O_4 corresponds to a molecular weight of 92, so that at 26° the gas has more nearly the formula N_2O_4. The vapor density decreases gradually as the temperature is raised, and all these facts are best explained by assuming that at low temperatures the molecules are N_2O_4, which are colorless, and that these decompose gradually, with rise of temperature, into brown molecules of NO_2, thus: —

$$\underset{\text{(1 vol.)}}{N_2O_4} \rightleftarrows \underset{\text{(2 vols.)}}{2\,NO_2}.$$

At 26°, therefore, the dissociation will have progressed to the extent of about 34 per cent, as may be computed from the densities above given; while at 140° the dissociation is practically complete.

When nitrogen dioxide acts on water in the cold, nitrous and nitric acids result, as already mentioned in connection with nitric acid.

On passing nitrogen dioxide through a red-hot tube, it is decomposed into oxygen and nitric oxide. The action is reversible, thus: —

$$2\ NO_2 \rightleftarrows 2\ NO + O_2.$$

Nitrogen dioxide is a poisonous gas having a corrosive action on the mucous membranes. It is also a strong oxidizing agent, and consequently will support the combustion of many substances.

Nitrous Acid. — When potassium nitrate is heated, it loses a portion of its oxygen and is converted into potassium nitrite, thus: —

$$2\ KNO_3 = 2\ KNO_2 + O_2.$$

The nitrite may also be formed by heating saltpeter with lead or copper, thus: —

$$KNO_3 + Pb = PbO + KNO_2.$$
$$KNO_3 + Cu = CuO + KNO_2.$$

Potassium nitrite KNO_2 is a salt of nitrous acid HNO_2. The latter has never been prepared except in dilute solutions at low temperatures. On attempting to isolate nitrous acid from a nitrite by treating with sulphuric acid, the following reaction occurs: —

$$2\ KNO_2 + H_2SO_4 = K_2SO_4 + H_2O + NO + NO_2.$$

It is possible that at first HNO_2 is set free, which undergoes decomposition into nitrogen trioxide, that is, nitrous acid anhydride N_2O_3, and water, thus: —

$$2\ HNO_2 = H_2O + N_2O_3.$$

The latter then decomposes into nitric oxide NO and nitrogen dioxide NO_2, thus: —

$$N_2O_3 = NO + NO_2.$$

By dissolving nitrogen trioxide (see below) in water at 0° a blue solution is obtained which is commonly regarded as a solution of nitrous acid HNO_2. This solution readily evolves nitric oxide with concomitant formation of nitric acid, thus: —

$$3\ HNO_2 = H_2O + 2\ NO + HNO_3.$$

Thus it is evident that *nitrous acid is very unstable.* Its salts, however, are fairly stable. They may be formed by neutralizing aqueous solutions of nitrous acid with bases, or by reducing nitrates. In rain water and frequently in contaminated drinking water, nitrites are present.

Nitrous acid may act as a reducing agent, for it will take up oxygen and form nitric acid. Thus it will reduce a potassium permanganate solution as follows: —

$$2\ KMnO_4 + 3.H_2SO_4 + 5\ HNO_2 = K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5\ HNO_3.$$

On the other hand, *toward substances that will take up oxygen, nitrous acid plays the rôle of an oxidizing agent.* So with hydriodic acid, the following reaction occurs: —

$$2\ HNO_2 + 2\ HI = 2\ NO + 2\ H_2O + I_2.$$

Nitrous acid is of importance in the study of carbon compounds, and in the preparation of aniline dyes. Nitrites are readily distinguished from nitrates, for nitrites evolve the characteristic brown nitrogen dioxide fumes when acidified with sulphuric acid. Furthermore, a dilute solution of a nitrite acidulated with sulphuric acid will turn starch potassium iodide paper blue; compare the last equation above.

Nitrogen Trioxide. — Nitrogen trioxide or nitrous anhydride N_2O_3 readily decomposes into NO and NO_2. When equal volumes of the latter gases are mixed and cooled to $-21°$ in a tube, nitrous anhydride, a deep blue liquid, is formed. It slowly decomposes even at $-21°$, but at its boiling point the decomposition is more rapid. The dissociation may be indicated thus: —

$$N_2O_3 \rightleftarrows NO + NO_2.$$

Hyponitrous Acid. — By reducing sodium or potassium nitrate or nitrite with nascent hydrogen formed by the action of

sodium amalgam on the aqueous solution, a salt of hyponitrous acid may be obtained thus: —

$$2\ KNO_2 + 4\ H = K_2N_2O_2 + 2\ H_2O.$$

When the potassium hyponitrite is treated with sulphuric acid, the hyponitrous acid liberated is decomposed into nitrous oxide and water, thus: —

$$K_2N_2O_2 + H_2SO_4 = K_2SO_4 + H_2O + N_2O.$$

The reaction is not reversible, and so hyponitrous acid cannot be obtained by dissolving N_2O in water. Free hyponitrous acid may be obtained by first making the silver salt $Ag_2N_2O_2$ and decomposing this by means of hydrochloric acid, thus forming insoluble silver chloride AgCl and the free acid. The latter may also be obtained by the oxidation of hydroxylamine NH_2OH by means of nitrous acid, thus: —

$$NH_2OH + HNO_2 = H_2N_2O_2 + H_2O.$$

The anhydrous acid forms transparent crystalline plates which are *highly explosive.* On exploding, the acid decomposes into water, nitrogen and oxygen; while on slow decomposition at room temperatures in aqueous solution nitrous oxide and water are formed. The aqueous solution, however, is more stable.

Nitrous Oxide. — On heating ammonium nitrate, nitrous oxide N_2O and water are produced, thus: —

$$NH_4NO_3 = 2\ H_2O + N_2O.$$

A mixture of ammonium chloride and saltpeter may be substituted for the ammonium nitrate, for thus potassium chloride and ammonium nitrate are formed, and the latter then decomposes on heating as represented above.

Nitrous oxide is a colorless, neutral gas which is 1.52 times as heavy as air. It has a sweetish odor and taste, and when inhaled it produces peculiar symptoms that frequently are accompanied by fits of hysterical laughing; whence its name, **laughing gas.** On continued inhalation, it produces insensibility, and hence the gas has been used as an anæsthetic in dental operations. The gas cannot take the place of oxygen in respiration, however, and if inhaled for a long time death results.

Nitrous oxide is much more soluble in cold than in warm water; so at 0°, 1.30 volumes are absorbed by 1 volume of water, while at 25° only 0.59 volume is absorbed. For this reason the gas is collected over warm water.

Nitrous oxide boils at $-89.5°$. The solid melts at $-102.7°$.

It may be obtained in the market in compressed form in steel cylinders. A glowing splinter burns in nitrous oxide as in pure oxygen. Similarly phosphorus and sulphur burn in nitrous oxide as in oxygen, the products in all cases being oxides and free nitrogen. Nitrous oxide is, however, readily distinguished from oxygen by the fact that nitric oxide and oxygen form red fumes NO_2, which does not take place when nitrous oxide and nitric oxide are mixed.

When mixed with an equal volume of hydrogen, nitrous oxide explodes on ignition with an electric spark, and the volume of nitrogen formed is equal to that of the original hydrogen, thus: —

$$\underset{\text{(1 volume)}}{H_2} + \underset{\text{(1 volume)}}{N_2O} = \underset{\text{(liquid)}}{H_2O} + \underset{\text{(1 volume)}}{N_2}.$$

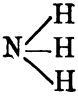
On heating nitrous oxide with sodium (Fig. 41), the following reaction takes place: —

$$\underset{\text{(solid)}}{2\,Na} + \underset{\text{(1 volume)}}{N_2O} = \underset{\text{(solid)}}{Na_2O} + \underset{\text{(1 volume)}}{N_2}.$$

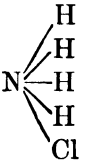
The volume of nitrogen formed equals that of the nitrous oxide. From this fact and the specific gravities of the gases involved, it follows that the formula of nitrous oxide is N_2O.

While nitrous oxide is a good oxidizing agent, exhibiting many of the properties of oxygen, it is not as energetic as the latter. So metals will not rust in contact with moist N_2O as in contact with moist oxygen. A feebly burning piece of sulphur or phosphorus will be extinguished in nitrous oxide, though when these substances are burning strongly, they continue to burn brilliantly in the gas.

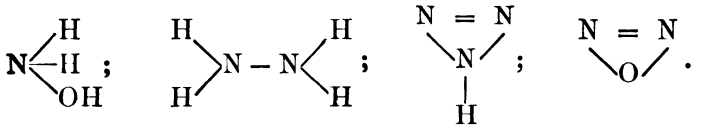
General Considerations. In ammonia, nitrogen has a valence of three, thus: —



In ammonium salts it has a valence of five, thus: —



In hydroxylamine, in hydrazine, in hydrazoic acid, and in nitrous oxide, nitrogen is trivalent, thus: —

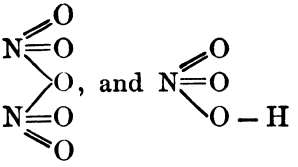


(hydroxylamine) (hydrazine) (hydrazoic acid) (nitrous oxide)

At first sight one might be inclined to the view that nitrogen is univalent in N_2O, and that this compound is analogous to water, the two hydrogen atoms of which are replaced by nitrogen atoms. However, the ease with which nitrous oxide parts with its oxygen and forms free nitrogen speaks for the above formula. If in nitrous oxide the oxygen is replaced by the bivalent group $=NH$, called the imide group, hydrazoic acid results.

In the salts of hydroxylamine and of hydrazine, nitrogen is quinquivalent as in the ammonium salts.

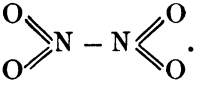
In nitrogen pentoxide and nitric acid nitrogen has a valence of five, thus: —



In nitrogen dioxide, nitrogen is tetravalent, thus: —

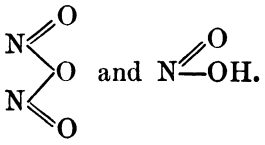
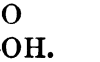
$$O = N = O.$$

In nitrogen tetroxide, formed by chilling nitrogen dioxide, nitrogen has been regarded as quinquivalent, thus: —



This formula is not generally accepted, however.

In nitrogen trioxide and nitrous acid nitrogen is trivalent, thus: —

 and  .

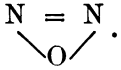
In nitric oxide, nitrogen is bivalent, thus: —

$$N = O.$$

Finally in hyponitrous acid $(N\text{–}O\text{–}H)_2$, as in N_2O, nitrogen has at times been considered as univalent. However, the compound NOH is not known. Attempts to isolate it have always yielded $(NOH)_2$, the constitution of which is best represented by regarding nitrogen as trivalent, thus: —

$$HO - N = N - OH.$$

From this compound, water readily splits off, forming nitrous oxide thus: —

 .

The valence of nitrogen thus exhibits a relatively great range of variation in different compounds.

We may regard all the oxides and oxy-acids of nitrogen as derived from hypothetical hydroxides by successive elimination of water, as the following table shows, in which all the compounds except those in the first column are known: —

$2\,N(OH)_5$ minus $4\,H_2O = 2\,HNO_3$;	$2\,HNO_3$ minus $H_2O = N_2O_5$.
$2\,N(OH)_4$ minus $4\,H_2O = N_2O_4$;	N_2O_4 yields $2\,NO_2$.
$2\,N(OH)_3$ minus $2\,H_2O = 2\,HNO_2$;	$2\,HNO_2$ minus $H_2O = N_2O_3$.
$2\,N(OH)_2$ minus $2\,H_2O = 2\,NO$;	. . . . .
$2\,NOH$ . . . . . $N_2O_2H_2$;	$N_2O_2H_2$ minus $H_2O = N_2O$.

There is also a striking similarity between the oxy-acids of nitrogen and their salts on the one hand, and the oxy-acids of the halogens and their salts on the other hand. This similarity, which is evident from the following table, is not a mere similarity of formulæ, for the compounds themselves exhibit analogies in their crystal forms, solubility in water, and general

stability on heating and on treatment with reagents. Only known compounds are included in the table.

N_2O . . . $H_2N_2O_2$ . . . $Na_2N_2O_2$	Cl_2O . . . $HClO$ . . . $NaClO$.
NO	. . . . .
N_2O_3 . . . HNO_2 . . . . $NaNO_2$	. . . . . $NaClO_2$.
NO_2	ClO_2 . . . . .
N_2O_5 . . . HNO_3 . . . . $NaNO_3$	I_2O_5 . . . $HClO_3$ . . . $NaClO_3$.
. . . . .	Cl_2O_7 . . $HClO_4$ . . . $NaClO_4$.

REVIEW QUESTIONS

1. Make a list of the oxy-acids of nitrogen, giving their formulas, also of their anhydrides. What other oxides of nitrogen are there, and what is the valence of nitrogen in each of the nitrogen compounds you have listed?

2. Write the equation for the preparation of nitric acid from Chili saltpeter and compare it with the equation for the preparation of hydrochloric acid from common salt.

3. If solid saltpeter is treated with hot, concentrated nitric acid, the change proceeds to completion; why is this not true when a twenty per cent solution of saltpeter is treated with sulphuric acid?

4. How much nitric acid could be prepared from 100 tons of $NaNO_3$?

5. What are the two main properties of nitric acid? Illustrate each by means of an example, writing the appropriate chemical equation.

6. How may nitric acid be prepared from the air and water? Equations.

7. Make a list of the uses of nitric acid.

8. Why is hydrogen not liberated when nitric acid acts on metals? Write the equation showing the action of nitric acid on copper.

9. How could one form ammonia from nitric acid? What intermediate products might be prepared in this process?

10. What principle of chemical equilibrium is illustrated in making hydrochloric acid, nitric acid, and ammonia?

11. What is aqua regia? Write the equation. 'Upon what property of nitric acid does its efficiency in aqua regia depend? What is the active agent in aqua regia?

12. What is meant by "fixation of atmospheric nitrogen"? How may this be accomplished? Why is it of importance commercially?

13. How distinguish between oxygen and laughing gas? Between the latter and nitric oxide?

14. Show the resemblance of the structural formulas of bromic acid and nitric acid, also of potassium nitrite and potassium chlorite. What is the valence of nitrogen and of the halogen in each of these cases?

CHAPTER XIII

SULPHUR, SELENIUM, AND TELLURIUM

Occurrence and Preparation of Sulphur. — Sulphur has been known since ancient times, for it occurs in nature in the uncombined state, especially in the vicinity of active or extinct volcanoes. Thus in Italy, Sicily, Spain, Poland, Egypt, Iceland, California, the Yellowstone Park, China, and India, sulphur is found native. As a result of volcanic action sulphur probably is formed by the reduction of hydrogen sulphide H_2S by sulphur dioxide SO_2, thus: —

$$2\,H_2S + SO_2 = 2\,H_2O + 3\,S.$$

Sulphur also occurs in sedimentary deposits, where it is formed as a product of the decay of certain bacteria and algæ which are able to store up this substance in their organisms in form of minute particles. This sulphur originates from deposits of gypsum, from which it is liberated as hydrogen sulphide as the result of cellulose fermentation. This hydrogen sulphide is then taken up by the algæ and bacteria, which convert it into sulphates; but in this process they store up a reserve stock of free sulphur in their bodies. The sulphur which is found in sedimentary deposits then really occurs from the oxidation of hydrogen sulphide through the action of these organisms, thus: —

$$H_2S + O = H_2O + S.$$

Some of the sedimentary sulphur is, however, probably also formed by direct oxidation of hydrogen sulphide by the oxygen of the air. Especially rich sedimentary deposits of sulphur occur in Texas and Louisiana, where by means of superheated steam the sulphur in the lower strata is melted and forced up to the surface in the liquid state. On account of this rich deposit of sulphur, the amount produced in the United States in 1910 was 255,534 long tons, which is about half of the world's annual production of sulphur.

Sulphur further occurs as hydrogen sulphide in the waters of sulphur springs and in the air near active volcanoes, where sulphur dioxide is also frequently found. In combination with metals, sulphur occurs as sulphides, as in galenite PbS, pyrite FeS_2, zinc blende ZnS, cinnabar HgS, and copper pyrite $CuFeS_2$.

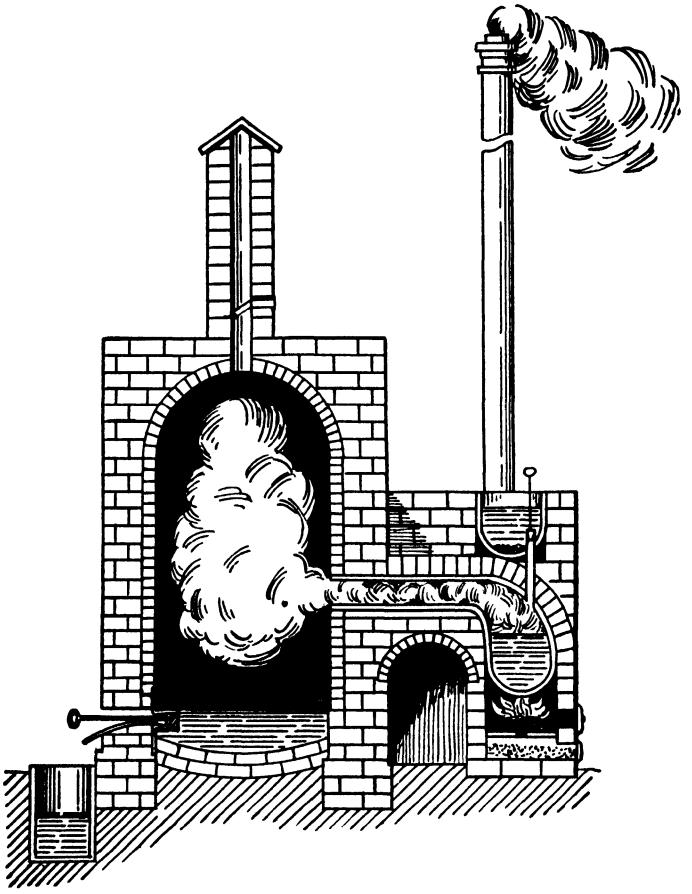


FIG. 42.

It is also found in form of sulphates of various metals. Thus ferrous sulphate $FeSO_4$, lead sulphate $PbSO_4$, heavy spar $BaSO_4$, are found in nature; but above all, gypsum $CaSO_4 \cdot 2\ H_2O$ and anhydrite $CaSO_4$ are found in very extensive deposits. The amount of gypsum produced in the United States alone in 1910 was 2,379,057 tons. Sulphur occurs in small quantities in com-

bination with other elements in nearly all plant and animal tissues, for it is a constituent of albumen. So it is found particularly in muscles, hair, nails, hoofs, and horns. In urine sulphur is found as sulphates. In some plants, like mustard, onions, garlic, and skunk cabbages, it enters into odoriferous compounds that have an irritating action on the mucous membranes and the skin.

The preparation of sulphur from the native deposits consists of melting it out of contact of the air and thus freeing it from the gypsum, calcium carbonate, sand, etc., with which it is commonly contaminated. Thus, a raw material about 90 per cent pure is obtained, which is placed in cast-iron retorts and distilled (Fig. 42). The vapors enter brick chambers, where they are condensed on the cold walls in form of fine powder which is placed on the market as **flowers of sulphur.** As the walls finally become hot the sulphur melts and collects on the bottom of the chamber, where it is drawn off from time to time and cast into sticks in moist, wooden, slightly conical molds. In this form it is called **roll sulphur** or brimstone. Sulphur is also prepared by heating pyrites FeS_2 and condensing the product. It is further prepared from the waste liquors of the Le Blanc soda process (which see), and from the sulphide of iron secured as a by-product in purifying illuminating gas.

Properties of Sulphur. — Native sulphur and roll sulphur form lemon-yellow crystals, of specific gravity 2.06, belonging to the *orthorhombic* system (Fig. 43). When heated, this **rhombic sulphur** melts at 114.5° to a mobile, light yellow liquid, which on further heating to 160° becomes dark brown and viscous. In the neighborhood of 200° the viscosity is so great that the vessel in which the sulphur is contained may be turned bottom upward without causing the sulphur to run out. On still further heating, the viscosity of the liquid diminishes, but its color remains dark brown. At 400° the liquid is quite mobile, and at 450° it boils, emitting a heavy, dark brown vapor.

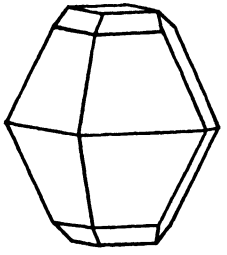


FIG. 43.

When sulphur is melted in a crucible and the mass is allowed to cool till a crust forms over the top of the liquid, and the latter is then poured out through a hole punctured in the crust,

it is found that the walls of the crucible are lined with needle-like, almost colorless crystals of sulphur that belong to the *monoclinic* system. These crystals of **monoclinic sulphur** melt at 119°. They have a specific gravity of 1.96. On standing they very slowly change to crystals of the orthorhombic system. *The rhombic crystals are thus the stable ones at ordinary temperatures, whereas the monoclinic crystals are stable at high temperatures.* The temperature at which the transition from the one form to the other takes place is 96.5°; at this point both rhombic and monoclinic sulphur remain side by side in equilibrium with each other without change. Below the transition point all passes over into rhombic sulphur, while slightly above that point all is converted into the monoclinic variety.

When sulphur heated almost to the boiling point is poured into cold water, an elastic mass is formed which is called **plastic sulphur.** After a few days it loses its plasticity and becomes hard, but for a while it remains non-crystalline, that is, *amorphous.* This **amorphous sulphur** is practically insoluble in all solvents; however, it very gradually passes over into rhombic sulphur. This is soluble in carbon disulphide to the extent of about 40 parts in 100 at room temperature. On evaporation, it may again be obtained from this solution in rhombic form. Rhombic sulphur is also soluble to a slight extent in liquids like alcohol, ether, turpentine, fats, and linseed oil. Flowers of sulphur dissolve only partially in carbon disulphide. They are a mixture of amorphous and rhombic sulphur.

Substances which are able to crystallize in two different systems are called **dimorphous.** This property is not uncommon. In passing from the monoclinic to the rhombic form, sulphur slowly evolves heat.

Precipitated sulphur, or **milk of sulphur,** is prepared by adding an acid to a polysulphide like K_2S_5: —

$$K_2S_5 + 2\,HCl = 2\,KCl + H_2S + 4\,S.$$

Thus formed, it is a grayish white powder, which is used in medicine. Precipitated sulphur is soluble in carbon disulphide.

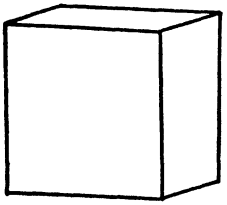
Sulphur is thus a *polymorphous* substance. The ability of an element to occur in different forms has been called allotropism, and so the different forms of sulphur are sometimes called the **allotropic forms of sulphur.** Their existence has been

explained by assuming that the molecules of the different modifications contain a different number of atoms, similar to the case of oxygen and ozone. It is doubtful, however, whether the cases are similar.

Sulphur is insoluble in water and is devoid of taste and smell. In contact with moist air it very slowly oxidizes superficially and passes into solution as sulphuric acid. Sulphur combines with many metals and non-metals, forming sulphides. Heated together with iron or copper, for instance, the union takes place with evolution of light and heat. In the air and in oxygen, sulphur burns to sulphur dioxide SO_2, which in presence of platinum black will take on more oxygen and form SO_3. The atomic weight of sulphur is 32.07. Investigations of the vapor density of sulphur show that at diminished pressure and low temperatures the molecular formula of sulphur is S_8, whereas at 800° to 1000° the density corresponds to the formula S_2. There is a gradual decomposition of the molecules from S_8 to S_2 as the temperature rises. In the neighborhood of 2000° the S_2 molecules are further largely dissociated into monatomic molecules S.

Uses of Sulphur. — Sulphur is used in the manufacture of sulphuric acid and sulphur dioxide, the latter being used as a bleaching and disinfecting agent. Sulphur is also used in making black gunpowder, fireworks, vulcanized caoutchouc, and hard rubber. In medicine it is employed as a specific.

Crystals and Crystal Systems. — Many substances are able to assume the crystalline state. Crystals are generally formed by allowing liquids to congeal or solutions to evaporate to a point at which the dissolved substances separate out. Crystals may, however, also be formed when vapors condense, as in the sublimation of iodine or sulphur; or they may form gradually from amorphous, solid substances, as in the case of the conversion of amorphous sulphur to rhombic sulphur. There are many substances which, like sulphur, are known in both the crystalline and amorphous states; others have never been found in crystalline condition, like cellulose and dextrine; whereas still others, like water, are always crystalline when solid. Crystalline substances are said to have crystallizing power, whereas those substances that are only known in amorphous form are said to be devoid of crystallizing power. We



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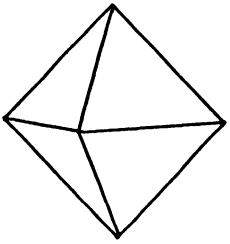

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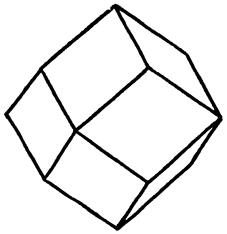

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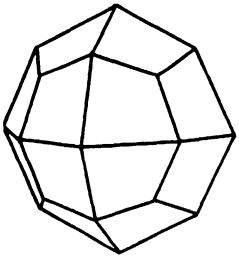

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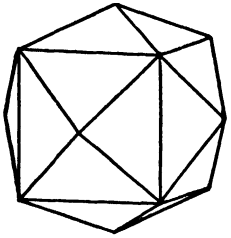

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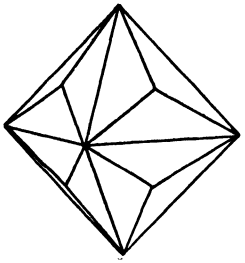

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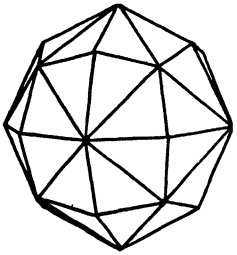

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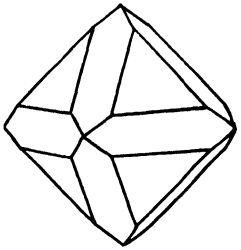

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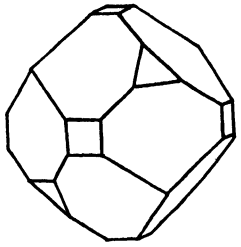

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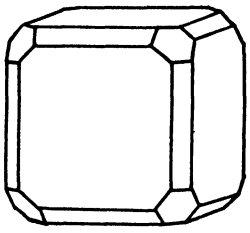

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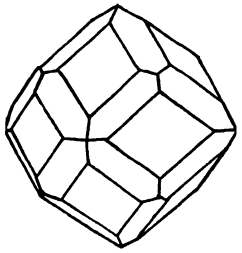


FIG. 54.

do not know of what this tendency to form crystals really consists, much less are we able to measure or compare quantitatively the crystallizing power of various substances.

The most striking external characteristic of a crystal is its regularity of form. A study of crystals has led to the conclusion that *a crystal is a solid bounded by plane faces which are the outcome of a regular internal arrangement of the molecules.* So

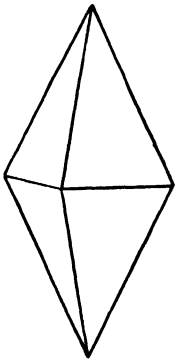


FIG. 55.

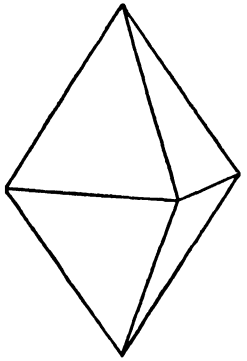
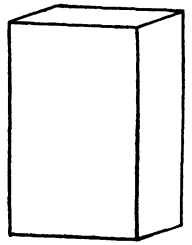


FIG. 56



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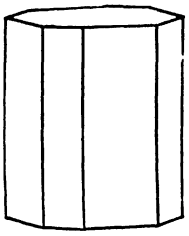
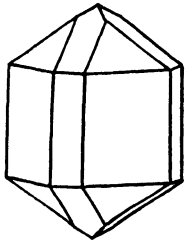


FIG. 58.



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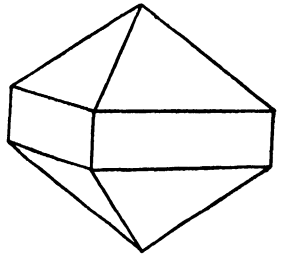


FIG. 60.

the hardness, color, index of refraction, crushing strength, resistance to corrosion by chemical agents, etc., may vary as different directions in one and the same crystal are considered.

It has been found that *all known crystals may be classified into six crystal systems, according to their symmetry.*

All crystals whose faces may be referred to a system of three axes of equal length and at right angles to one another are said to belong to the **isometric** or **regular system.** Some common forms are shown in Figs. 44 to 54. These crystals may have nine so-called planes of symmetry, a plane of symmetry being a plane which cuts a crystal in two halves that are to each other as an object is to its reflection in a mirror. Many

substances crystallize in the regular system. Among these are common salt, alum, fluorspar, galena, pyrite, garnet, diamond, gold, silver, mercury, and copper.

Crystals whose planes may be referred to a system of three axes, of which but two are of equal length but all at right angles to one another, are said to belong to the **tetragonal** or **quadratic system**, in which there are five planes of symmetry possible. Figures 55 to 60 show some common forms of crys-

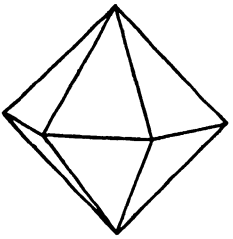
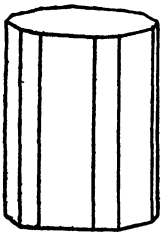


FIG. 61.



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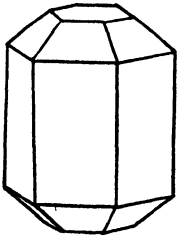


FIG. 63.

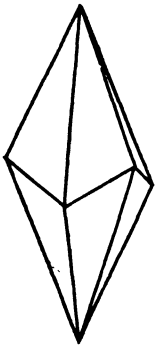
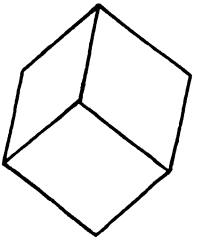


FIG. 64.



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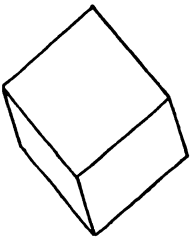

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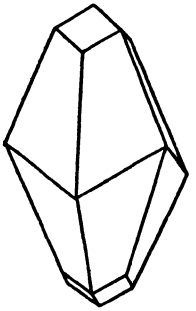


FIG. 67.

tals of this system as they occur in rutile, titanium dioxide TiO_2; in cassiterite, stannic oxide SnO_2, the most important ore of tin; and in calomel HgCl.

In the **hexagonal system**, the forms may be referred to four axes, three of which are of equal length, lie in the same horizontal plane, and bisect one another in a point so as to form six angles of sixty degrees each. The fourth axis is either longer or shorter than the others, and runs through their point of intersection at right angles to the horizontal plane, which bisects the vertical axis. In this system there are seven possible planes of symmetry. Figures 61 to 67 show some typical

crystals of the hexagonal system. To it belong the crystal forms assumed by many important substances, like water H_2O, quartz SiO_2, calcium carbonate $CaCO_3$, Chili saltpeter $NaNO_3$, and calcium phosphate $Ca_3(PO_4)_2$. The so-called **rhombohedral**

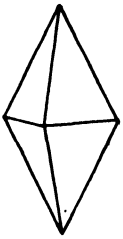


FIG. 68.

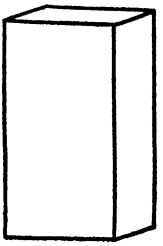


FIG. 69.

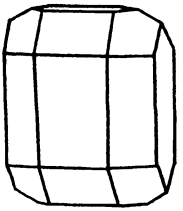


FIG. 70.

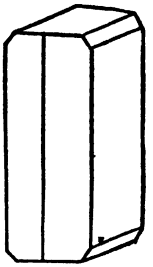


FIG. 71.

division of the hexagonal system in particular has many representatives. It has sometimes been termed a separate system, the *trigonal system.*

Crystal forms that can be referred to a system of three axes, all of which are at right angles to one another but of unequal lengths, are said to belong to the **orthorhombic** or **rhombic system**, in which there are but three possible planes of symmetry.

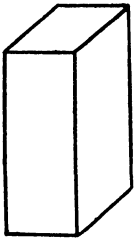


FIG. 72.

FIG. 73.

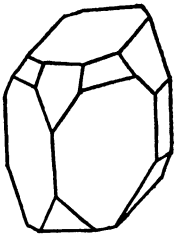


FIG. 74.

Figures 68 to 71 exhibit some typical rhombic forms. In this system crystallize many substances, like sulphur, iodine, olivine Mg_2SiO_4, saltpeter KNO_3, heavy spar $BaSO_4$, and magnesium sulphate $MgSO_4 \cdot 7\ H_2O$.

In the **monoclinic** or **monosymmetric system** the forms are referred to a system of three axes all of which are of unequal length. The two axes that lie in the vertical plane bisect each other at right angles, and the third axis is bisected at the point

of intersection of the other two, but it does not make a right angle with the plane in which the other two axes lie. The angle which it makes with that plane varies in different crystals. In this system there is but one plane of symmetry. Figures 72 to 74 show some representative monoclinic forms. Many compounds crystallize in this system, among which are monoclinic sulphur, gypsum, feldspar, cane sugar, Glauber's salt $Na_2SO_4 \cdot 10\ H_2O$, copperas $FeSO_4 \cdot 7\ H_2O$, and borax $Na_2B_4O_7 \cdot 10\ H_2O$.

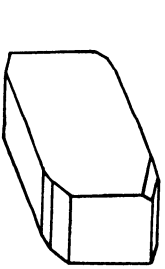


FIG. 75.

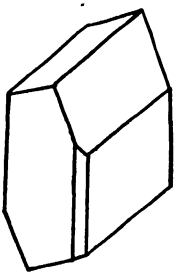


FIG. 76.

Finally, in the **triclinic** or **asymmetric system** the forms are referred to three unequal axes bisecting one another in a point at angles that are unlike and not right angles. In this system there is no symmetry whatever. Figures 75 and 76 show some triclinic forms. Copper sulphate $CuSO_4 \cdot 5\ H_2O$, plagioclase feldspar $NaAlSi_3O_8$ (albite), and $CaAl_2Si_2O_8$ (anorthite) crystallize in the triclinic system.

Under the same conditions a chemical substance always crystallizes in the same system.

Most substances crystallize in but one system. However, we have seen that under different conditions one and the same substance may crystallize in two different systems. This property is called **dimorphism**. Thus, sulphur may form rhombic or monoclinic crystals; calcium carbonate $CaCO_3$ may form hexagonal or rhombic crystals; iron pyrites may form isometric or rhombic crystals. These substances are consequently dimorphous. *Substances that have similar chemical composition generally crystallize in the same system and exhibit the same forms.* This is the **law of isomorphism**, discovered by Eilhard Mitscherlich. So, for instance, the carbonates $CaCO_3$, $FeCO_3$, $MgCO_3$ are rhombohedral; the chlorides NaCl, KCl, NH_4Cl are isometric.

Hydrogen Sulphide. — This is by far the most important compound which sulphur forms with hydrogen. The elements unite directly with each other at higher temperatures, forming the compound whose composition and vapor density are repre-

sented by the formula H_2S. So when a current of hydrogen is passed over heated sulphur in a tube, H_2S is formed; also when certain sulphides are similarly heated in a current of hydrogen, thus: —

$$Ag_2S + H_2 = 2\,Ag + H_2S.$$

The common way of preparing the gas consists of treating ferrous sulphide FeS (made by heating sulphur and iron together) with either dilute sulphuric or hydrochloric acid; —

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$
$$FeS + 2\,HCl = FeCl_2 + H_2S.$$

Instead of ferrous sulphide, which is the cheapest, other sulphides might be employed. The gas may also be prepared by reduction of sulphuric or sulphurous acids with nascent hydrogen: —

$$H_2SO_3 + 6\,H = 3\,H_2O + H_2S.$$

In nature hydrogen sulphide occurs in sulphur springs, volcanic gases, and wherever organic matter is decomposing, as in sewer gas, in the intestinal gases, and in some pathological cases in urine.

Hydrogen sulphide is a colorless gas which is 1.19 times as heavy as air. It boils at $-62°$ and melts at $-86°$. The gas has a very disagreeable odor, being that of rotten eggs, in which it is contained. *Hydrogen sulphide is a very poisonous gas and overcomes persons and animals suddenly, in which respect it resembles hydrocyanic acid.* Inhaled in small amounts, hydrogen sulphide produces headache and at times vomiting. The gas is combustible, burning with a blue flame to water and sulphur dioxide: —

$$2\,H_2S + 3\,O_2 = 2\,H_2O + 2\,SO_2.$$

In an insufficient amount of oxygen, the products are, in part, water and sulphur: —

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S.$$

In water, hydrogen sulphide is but slightly soluble, about 3 volumes being absorbed by 1 volume of water at ordinary temperature and pressure. On boiling this solution, all the gas escapes. On standing exposed to the air, the gas in the

solution is gradually oxidized to water and sulphur which separates out in the form of a precipitate.

When chlorine, bromine, or iodine act on hydrogen sulphide, the latter is decomposed, sulphur being liberated and hydrohalogen being formed, so for instance: —

$$H_2S + I_2 = 2\,HI + S.$$

The aqueous solution of hydrogen sulphide is feebly acid toward litmus, and in many ways it deports itself like a weak acid. So it will react with metals even at room temperature, forming sulphides and hydrogen, thus: —

$$2\,Ag + H_2S = Ag_2S + H_2.$$
$$Pb + H_2S = PbS + H_2.$$

Furthermore it reacts with many basic oxides and hydroxides, thus: —

$$PbO + H_2S = PbS + H_2O.$$
$$2\,NH_4OH + H_2S = (NH_4)_2S + 2\,H_2O.$$
$$KOH + H_2S = KSH + H_2O.$$
$$2\,KOH + H_2S = K_2S + 2\,H_2O.$$

The sulphides of sodium and potassium show a strong alkaline reaction toward indicators. They are salts of a very weak acid with a strong base, and hence are decomposed by water by hydrolysis. The reaction, which is reversible, may be written thus: —

$$K_2S + H_2O \rightleftarrows KSH + KOH.$$

When passed through a red-hot tube, hydrogen sulphide is decomposed to hydrogen and sulphur. It thus parts readily with its hydrogen, and is consequently a good reducing agent, as is evident, for instance, from the fact that it will reduce sulphuric or nitric acid, thus: —

$$H_2SO_4 + H_2S = 2\,H_2O + SO_2 + S.$$
$$2\,HNO_3 + 3\,H_2S = 4\,H_2O + 2\,NO + 3\,S.$$

Hydrogen sulphide is a very important reagent in chemical analysis, for while the sulphides which it forms with metals like sodium, potassium, calcium, and magnesium are soluble in water, other sulphides like those of iron, zinc, and nickel are not soluble in water, but soluble in dilute acids, and still other sulphides like those of arsenic, copper, and lead are insoluble

both in water and dilute acids. A very careful study of these and similar properties of the sulphides of the metals has led to a system by means of which the metals can be detected and separated when they occur together.

Polysulphides and Hydrogen Persulphide.—When sulphur is added to a solution of sulphide of potassium, sodium, calcium, ammonium, etc., it dissolves, forming polysulphides. Thus, with K_2S sulphur may form compounds varying in composition from K_2S to K_2S_5 according to the amount of sulphur dissolved. When such a persulphide is gradually added to a very dilute solution of hydrochloric acid, a thick, yellow oil of disagreeable odor separates out which has the composition H_2S_5, no matter what the sulphur content of the polysulphide was, thus:—

$$2\,K_2S_3 + 4\,HCl = 4\,KCl + H_2S + H_2S_5.$$
$$4\,Na_2S_2 + 8\,HCl = 8\,NaCl + 3\,H_2S + H_2S_5.$$

Hydrogen persulphide bleaches organic dyestuffs. It reacts with iodine, forming hydriodic acid and sulphur. It gradually decomposes into hydrogen sulphide and sulphur on standing.

Comparison of Hydrogen Sulphide with Water. — It is evident that hydrogen sulphide and water possess many points of analogy. Thus the one is H–S–H and the other H–O–H. With the univalent metals they form hydrosulphides MSH and hydroxides MOH, respectively; furthermore, the corresponding sulphides M_2S, and oxides M_2O, are also known. With elements of higher valence, analogous sulphides and oxides are formed. Thus we have FeS and FeO, P_2O_5 and P_2S_5, Sb_2O_3 and Sb_2S_3, etc. Again, just as oxygen and hydrogen form a peroxide H_2O_2, so sulphur and hydrogen form a persulphide, which, to be sure, has the composition H_2S_5. We shall later see further points of resemblance between oxygen and sulphur in their chemical behavior. The two elements indeed belong to the same family group.

Compounds of Sulphur with the Halogens. — Fluorine unites directly with sulphur to form **sulphur hexafluoride** SF_6, which consists of white crystals that melt at $-55°$. The substance boils but slightly above its melting point. The gas is colorless, odorless, tasteless, and practically as indifferent toward other reagents as nitrogen.

When dry chlorine is passed over molten sulphur in a tubulated retort, **sulphur monochloride** S_2Cl_2, boiling at 138°, is formed. It is a fuming yellowish red liquid of suffocating odor. Its specific gravity is 1.7. It dissolves sulphur readily, solutions containing over 60 per cent sulphur being obtainable. For this reason sulphur monochloride is used in preparing vulcanized rubber. Water decomposes sulphur monochloride, thus: —

$$2\ S_2Cl_2 + 2\ H_2O = 4\ HCl + SO_2 + 3\ S.$$

Sulphur dichloride SCl_2 is formed when sulphur monochloride is saturated with chlorine in the cold. It is an oil of reddish brown color and specific gravity 1.6. It readily decomposes at 64°, yielding sulphur and sulphur monochloride. It is also decomposed by water, thus: —

$$2\ SCl_2 + 2\ H_2O = 4\ HCl + SO_2 + S.$$

Sulphur tetrachloride SCl_4 is formed by saturating sulphur dichloride with chlorine at temperatures below − 25°. The substance forms crystals which melt at − 30°. It readily dissociates above − 22°, the decomposition being practically complete at + 6°. With water it reacts violently, thus: —

$$SCl_4 + 2\ H_2O = SO_2 + 4\ HCl.$$

With bromine, sulphur forms **sulphur monobromide** S_2Br_2, a brownish red liquid which congeals at − 46° and boils at about 200°, accompanied by partial decomposition.

With iodine, sulphur forms **sulphur monoiodide** S_2I_2, consisting of dark grayish crystals melting at 60°, and also **sulphur hexaiodide** SI_6, which forms dark crystals that readily decompose on standing, yielding free iodine.

Sulphur Dioxide and Sulphurous Acid. — When sulphur is burned in the air or in oxygen, the following reaction takes place: —

$$S + O_2 = SO_2.$$

The resulting sulphur dioxide occupies the same volume as the oxygen, which may be demonstrated by means of the apparatus of Victor Meyer shown in Fig. 77. The sulphur is burned in oxygen, with which the flask has been filled. On cooling, the manometer indicates that the volume of the gas in the apparatus has not changed.

Sulphur dioxide is a colorless gas of suffocating odor. It is 2.21 times heavier than air. It may readily be condensed to a liquid at ordinary pressure by cooling to $-10°$. Under a pressure of about two atmospheres it may be liquefied at room temperatures. The liquid boils at $-8°$, and the solid melts at $-76°$. Sulphur dioxide will not support combustion; nevertheless, at higher temperatures many metallic oxides unite vigorously with it with evolution of light, thus: —

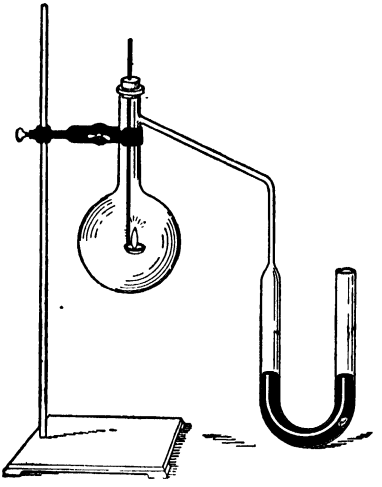


FIG. 77.

$$PbO_2 + SO_2 = PbSO_4.$$

Besides being produced by the burning of sulphur, sulphur dioxide is formed by heating sulphides of certain metals in the air; thus, pyrite acts as follows: —

$$2\ FeS_2 + 11\ O = Fe_2O_3 + 4\ SO_2.$$

In the laboratory, sulphur dioxide is commonly made by heating copper turnings with concentrated sulphuric acid: —

$$2\ H_2SO_4 + Cu = 2\ H_2O + CuSO_4 + SO_2.$$

It may also be formed by heating concentrated sulphuric acid with carbon or sulphur: —

$$2\ H_2SO_4 + C = 2\ H_2O + CO_2 + 2\ SO_2.$$
$$2\ H_2SO_4 + S = 2\ H_2O + 3\ SO_2.$$

When dilute sulphuric acid acts on sulphites, sulphur dioxide is formed; also when metallic oxides are heated with sulphur: —

$$NaHSO_3 + H_2SO_4 = NaHSO_4 + SO_2 + H_2O.$$
$$2\ MnO_2 + 4\ S = 2\ MnS + 2\ SO_2.$$
$$2\ CuO + 2\ S = Cu_2S + SO_2.$$

In the presence of water, sulphur dioxide bleaches many organic coloring matters. Figure 78 shows the bleaching of flowers by sulphur dioxide evolved by burning sulphur. This bleaching

does not depend upon the oxidation of the dyes, but rather upon their union with the sulphur dioxide, for on warming some of the articles thus bleached their color may be restored. In other cases, the bleaching action depends upon the subtraction of oxygen from the substances. Sulphur dioxide is used to bleach silk, wool, straw, and other fibers that would be destroyed by means of chlorine. It is also used as an antiseptic and disinfectant, for it is a powerful germicide. For these purposes it may now be obtained in liquid form in tin cans.

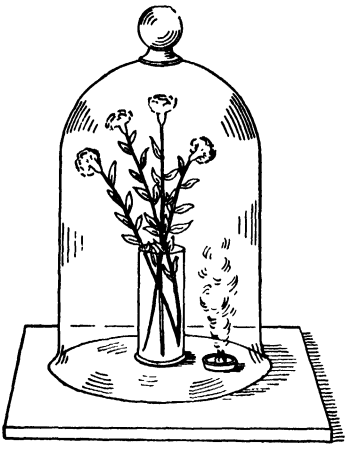


FIG. 78.

About 50 volumes of sulphur dioxide are dissolved by 1 volume of water at 15°, while at 40° but 18.8 volumes are thus absorbed. From the solution all of the sulphur dioxide may be expelled by boiling. The solution reacts acid and behaves as though it contained **sulphurous acid** H_2SO_3, but this substance has never been isolated, thus: —

$$SO_2 + H_2O = H_2SO_3.$$

With bases, sulphurous acid forms salts called **sulphites**, thus: —

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O.$$
$$H_2SO_3 + 2\,NaOH = Na_2SO_3 + 2\,H_2O.$$
$$H_2SO_3 + Ca(OH)_2 = CaSO_3 + 2\,H_2O.$$

Sulphurous acid is dibasic in character. Both the acid and the normal sulphites of the alkali metals are soluble in water, but other normal sulphites are sparingly soluble. From sulphites, sulphur dioxide may readily be regenerated by addition of sulphuric or hydrochloric acid. This fact is used in the detection of sulphites in chemical analysis.

Sulphur dioxide is a reducing agent, which property is possessed in a still greater degree by its aqueous solutions. This is because sulphurous acid is able to take up additional oxygen readily, thus passing over into sulphuric acid. Even the

oxygen from the air slowly converts sulphurous acid into sulphuric acid in solution, thus: —

$$2\,H_2SO_3 + O_2 = 2\,H_2SO_4.$$

Chlorine, bromine, or iodine rapidly change sulphurous acid into sulphuric acid, thus: —

$$H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2\,HCl.$$
$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2\,HI.$$

Sulphur Sesquioxide. — This compound has the composition S_2O_3. It may be prepared by treating molten sulphur trioxide SO_3 with pulverized sulphur. The product consists of bluish green crystals. With fuming sulphuric acid it forms a blue solution. Water decomposes the sesquioxide into sulphuric acid and sulphur.

Sulphur Trioxide and the Contact Process of making Sulphuric Acid. — Sulphur trioxide SO_3 is formed by heating sulphates of many of the heavy metals, thus: —

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3\,SO_3.$$

Oxygen unites but very slowly with SO_2 to form SO_3, in spite of the fact that the union is accompanied with considerable evolution of heat. However, when a mixture of sulphur dioxide and oxygen is passed over finely divided platinum, the union readily takes place, the action being practically complete at 450°. In this process, the platinum remains unchanged. It acts as a contact or **catalytic agent.** In place of finely divided platinum, ferric oxide or chromic oxide will also serve. The residues of the oxides obtained by roasting pyrites are sometimes used for this purpose. The sulphur dioxide obtained by burning sulphur or roasting native sulphides, generally pyrites, is mixed with air in such proportion that there is present a large excess of oxygen beyond what is needed to produce sulphur trioxide according to the equation: —

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3;$$

for this reaction is a reversible one and the presence of the excess of oxygen, according to the law of mass action, displaces the equilibrium toward the right. The temperature should be held at about 400° to 450°, for at higher temperatures the sulphur trioxide dissociates, that is, the action reverses. The

gases should be purified. It is especially necessary that they be freed from dust and from arsenic. The latter is generally present in the gases and is removed by means of steam. Both the residues from roasting pyrites, and platinized asbestus are used at present in thus preparing sulphur trioxide by what is known as the "**contact process.**" The bulk of this sulphur trioxide formed is used in making sulphuric acid, and to this end it is absorbed in sulphuric acid of 97 to 98 per cent strength. The strength of the acid is regulated by addition of water. Enormous quantities of sulphuric acid are now prepared annually by the contact process, both in Europe and

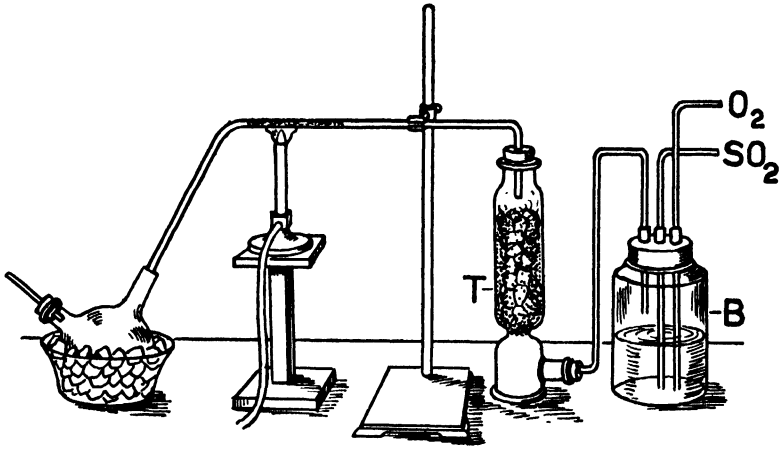


FIG. 79.

America; and this method, the success of which on a commercial scale is due to the labors of Knietsch (1901), has to a large extent displaced the lead chamber process for making sulphuric acid, at least so far as making concentrated sulphuric acid is concerned. On a small scale, in the laboratory, sulphur trioxide can readily be made by means of the apparatus shown in Fig. 79. Sulphur dioxide from a generator and oxygen from a tank are passed into the wash-bottle *B*; the mixed gases then pass through the drying tube *T*, filled with pumice soaked in sulphuric acid, and finally enter the tube containing the asbestus, which contains finely divided platinum heated to 400°. The SO_3 formed is condensed in the receiver.

Sulphur trioxide is also formed by heating fuming sulphuric

acid or warming concentrated sulphuric acid with phosphorus pentoxide, or by heating sodium or potassium pyrosulphate, thus: —

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$
$$H_2SO_4 + P_2O_5 = SO_3 + 2\,HPO_3.$$
$$K_2S_2O_7 = K_2SO_4 + SO_3.$$

Sulphur trioxide forms long, colorless, prismatic crystals that melt at 14.8°, forming a colorless, mobile liquid that boils at 46°. At 20° the specific gravity is 1.97. Below 27° sulphur trioxide forms sulphur hexoxide S_2O_6, the crystals of which look like long-fiber asbestus and melt at 50°. On further heating, it passes over into vapors that are identical with those of SO_3, *i.e.* it dissociates into SO_3, which on cooling yields a liquid boiling at 46°. Sulphur trioxide has great affinity for water. It fumes strongly in the air, and unites with water with great avidity and liberation of much heat which forms steam, causing a hissing noise as the substance is brought into contact with water. It is dangerous to bring large quantities of sulphur trioxide into contact with water at once, for the heat liberated causes explosions. At temperatures above 600° sulphur trioxide dissociates into sulphur dioxide and oxygen, the reaction being practically complete at 1000°.

Sulphuric Acid and the Lead Chamber Process. — Sulphuric acid H_2SO_4 has been known for a long time. The alchemists prepared it by heating ferrous sulphate, green vitriol $FeSO_4 \cdot 7\,H_2O$, hence the name **oil of vitriol.** This process was described by Basil Valentine in 1450, who also prepared the acid by burning sulphur in presence of saltpeter. In 1746 Roebuck, in England, made use of the principle of the latter method by burning sulphur mixed with saltpeter in closed leaden chambers in presence of moisture which absorbed the gases, forming sulphuric acid. By admitting more air to the chambers, and burning more sulphur in them, additional sulphuric acid was formed, and so on. This process was the beginning of what is to the present day known as the **lead chamber process** of the manufacture of sulphuric acid. In its essence the method consists of oxidizing sulphurous acid H_2SO_3 to sulphuric acid H_2SO_4, by means of nitric acid and its decomposition products.

In practice, the manufacture of sulphuric acid by the lead chamber process involves: (1) The burning of sulphur to sulphur dioxide, either by using sulphur or commonly by roasting native sulphides like pyrite FeS_2, copper pyrite, $CuFeS_2$, galenite PbS, zinc blende ZnS; (2) the oxidation of the sulphur dioxide in presence of water by means of nitric acid and nitrogen dioxide, one of its decomposition products; (3) the oxidation of the nitric oxide NO formed by the reduction of the nitric acid and NO_2; and (4) the concentration of the sulphuric acid obtained. In the roasting of the native sulphides mentioned, the latter are heated in a current of air, whereby sulphur dioxide and the oxides of the metals result. The nitric oxide is oxidized to NO_2 by means of oxygen of the air. We may write the chemical changes involved as follows:—

(1) $S + O_2 = SO_2$.

(2) $3\,SO_2 + 2\,H_2O + 2\,HNO_3 = 3\,H_2SO_4 + 2\,NO$.

(3) $2\,NO + H_2O + 3\,O = 2\,HNO_3$, and

(4) $NO + O = NO_2$.

(5) $SO_2 + H_2O + NO_2 = H_2SO_4 + NO$.

Thus it will be seen that when nitric acid acts on sulphur dioxide in presence of moisture (equation 2), sulphuric acid and nitric oxide result. The latter is then oxidized by oxygen from the air, in part to nitric acid (equation 3), and in part to nitrogen dioxide (equation 4). The nitric acid so formed then reacts with more sulphur dioxide, according to equation (2), and the nitrogen dioxide oxidizes sulphurous acid according to equation (5), the nitric oxide NO formed in both cases being again oxidized by oxygen, and in turn reduced by sulphurous acid with concomitant formation of sulphuric acid, and so on.

While the above equations may be used to represent what occurs in the manufacture of sulphuric acid, the actual process is no doubt of more complicated character. It has been studied by various investigators, among whom George Lunge holds that a compound $HO \cdot SO_2 \cdot O(NO)$, **nitrosyl sulphuric acid**, is formed in the chambers during the process, and that this compound is then decomposed by water with resulting formation of sulphuric

acid $HO \cdot SO_2 \cdot OH$. The reactions involved in this explanation are: —

(1) $$SO_2 + HNO_3 = HO \cdot SO_2 \cdot O(NO).$$

(2) $$2\,HO \cdot SO_2 \cdot O(NO) + H_2O = 2\,HO \cdot SO_2 \cdot OH + NO + NO_2.$$

(3) $$2SO_2 + NO + NO_2 + O_2 + H_2O = 2\,HO \cdot SO_2 \cdot O(NO).$$

The **nitrosyl sulphuric** acid is then again decomposed by water, according to equation (2), and so on. In nitrosyl sulphuric acid we have the univalent $-N=O$ group, which takes the place of one of the hydrogen atoms in sulphuric acid. Now, in the ordinary manufacture of sulphuric acid, when things are running properly, the formation of nitrosyl sulphuric acid, which consists of colorless crystals known as "**chamber crystals**," is not observed. It is only when the supply of water is deficient that these crystals are actually formed, for they are decomposed by water, as stated above. Although there is difference of opinion as to what actually occurs in the details of the sulphuric acid manufacture, the changes in which process are undoubtedly rather complicated, it nevertheless is certain that by this process sulphurous acid is completely and economically converted into the end product, sulphuric acid. The oxides of nitrogen can be used over and over again, though of course there is always some loss of the latter that must be replenished.

The accompanying Fig. 80 shows in diagrammatic form the essentials of a lead chamber sulphuric acid factory. In the furnaces *F*, the pyrites and other native sulphides are roasted in a current of air. The sulphur dioxide thus produced contains dust carried along mechanically, which deposits in a special long dust flue in which the gas is also mixed with air in proper proportion. The gases, which are at a temperature of about 300°, then pass into the Glover tower *G*. This is a structure about 10 meters high and 3 meters in diameter, lined inside with sheet lead and filled with acid proof stones, over which dilute sulphuric acid containing oxides of nitrogen in solution continually trickles from the reservoir on top of the tower. This acid is derived from the Gay-Lussac tower and from the chambers, and contains also some nitric acid, which has been added to replace the oxides of nitrogen that are inevitably lost during the process of manufacture. As the hot gases from the furnaces come into contact with this sulphuric acid of the Glover tower,

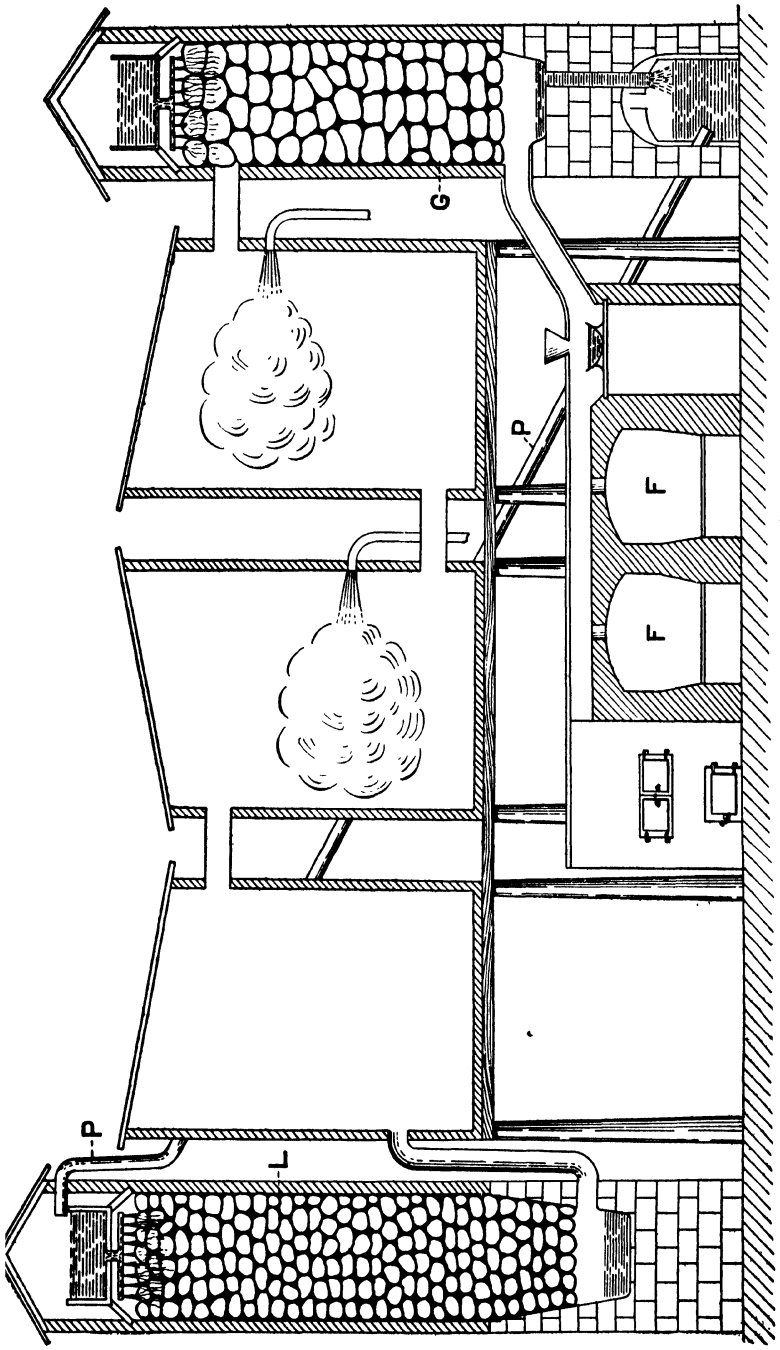


FIG. 80. Diagram of a sulphuric acid factory.

they are gradually cooled till they attain a temperature of about 70° when they reach the top. At the same time, the acid is heated up and thus concentrated, water being lost which is carried off with the gases in form of steam. Again, practically all of the oxides of nitrogen are carried off by the gases, which when they leave the tower pass into the first lead chamber laden with oxides of nitrogen and water vapor. The acid which flows from the bottom of the Glover tower contains only traces of oxides of nitrogen and is about 80 per cent strong. There are commonly three lead chambers, so connected that the gases enter at the top of each and pass out at the bottom. In these chambers, which often have a volume of 1000 cubic meters each, the reactions above mentioned take place. In the first and second chambers, water vapor is added to the gases. This is done either by blowing in steam from the boiler, or by forcing water into the chambers in form of a spray. In the third chamber the gases are cooled, and they then pass (charged with oxides of nitrogen regenerated during the formation of sulphuric acid in the chambers) into the bottom of the Gay-Lussac tower. This is lined with lead and filled with coke over which 80 per cent sulphuric acid continually trickles from the tank at the top of the tower *L*. This 80 per cent acid is obtained from the reservoir at the bottom of the Glover tower, from which place it is forced through a lead pipe *P* to the top of the Gay-Lussac tower. In the latter the 80 per cent acid dissolves practically all the oxides of nitrogen, and the residual gases, consisting mainly of nitrogen, leave the top of the tower and pass into a large chimney which keeps up a sufficient draught. The acid drawn from the bottom of the Gay-Lussac tower is thus strongly charged with oxides of nitrogen. It is the purpose of this tower to preserve these oxides. This acid, together with some of the chamber acid, is used again in the Glover tower as already explained.

The acid produced in the chambers is known as "chamber acid." It is about 60 to 70 per cent strong, *i.e.* of specific gravity of about 1.5 to 1.6. The acid may be further concentrated by evaporation in leaden pans to 78 per cent. Stronger acid than this attacks lead too much, and so the 78 per cent acid must be further concentrated by evaporation either in cast-iron, glass, or platinum vessels. The chamber acid is commonly used directly in the manufacture of so-called "superphosphate" fertilizers,

and the acid from the bottom of the Glover tower is employed in the Le Blanc soda process.

The concentrated sulphuric acid on the market has a specific gravity of from 1.83 to 1.84, and hence contains from 93 to 98 per cent of H_2SO_4. In making concentrated sulphuric acid, the contact process already described obviously has distinct advantages, and it is fast taking the place of the lead chamber method. The latter will, however, very likely continue to serve to prepare the more dilute acid, for which purpose it is well adapted.

The amount of sulphuric acid produced in the world annually is over four million tons. The material is used in making soda, aniline dyes, fertilizers, and explosives like gun cotton, nitro-powder, and dynamite. Again, it is used in storage batteries, in converting starch to sugar in the glucose industries, in refining petroleum, in making alum, copper sulphate, and many other sulphates that are used in medicine and in the arts.

Properties of Sulphuric Acid. — Sulphuric acid is a colorless, odorless, heavy, oily liquid of specific gravity 1.8384 at 15°. It has a very great affinity for water, with which it unites with great evolution of heat. For this reason *the acid, when it is to be diluted with water, must always be poured gradually into an excess of water.* It is dangerous to proceed in the reverse manner, that is to pour the water into the acid, for the great amount of heat suddenly liberated is very apt to lead to explosions throwing the acid out of the container. On account of its powerful affinity for water, sulphuric acid exercises a destructive action upon all plant and animal tissues, for it abstracts hydrogen and oxygen from them in proportions to form water, thus leaving a dark brown or black, charred mass behind. So wood, sugar, cork, muscular tissues, etc., are charred by sulphuric acid. When sulphuric acid is mixed with water a very appreciable contraction occurs; thus 500 cc. sulphuric acid mixed with 500 cc. water yield a mixture that has a volume of 971 cc. On account of its affinity for water, concentrated sulphuric acid is very often used as a drying agent in various chemical operations, particularly in drying certain gases that are not affected by the acid.

The commercial sulphuric acid commonly contains lead sulphate, arsenic, and oxides of nitrogen. By distilling it from retorts of platinum it may be purified. When pure anhydrous

sulphuric acid (that is, H_2SO_4, also called the **monohydrate** because it is $H_2O \cdot SO_3$) is heated, it begins to fume at about 150° because of the escape of SO_3. At 338° the acid boils and the distillate contains 1.5 per cent water.

This 98.5 per cent acid thus has a constant boiling point and cannot be further concentrated by fractional distillation. At 85 mm. pressure, pure H_2SO_4 boils without decomposition at 145°–146°. The monohydrate H_2SO_4 melts at +10°. The crystals are colorless and may be freed from adhering sulphuric acid by means of a properly constructed centrifugal machine.

Sulphuric acid is a very strong dibasic acid. It is capable of forming acid sulphates, like $NaHSO_4$, and normal sulphates, like Na_2SO_4. As it is also non-volatile except at comparatively high temperatures, it is very often used in liberating other acids from their salts. Besides acting as an acid, sulphuric acid may also play the rôle of an oxidizing agent toward many substances. So by means of hydrogen it may be reduced to sulphurous acid. When the metals act on sulphuric acid, the hydrogen liberated reduces the acid when the latter is used in concentrated form, sulphates and sulphurous acid being formed simultaneously. The sulphurous acid formed may, of course, be reduced still further. Gold and platinum do not act on sulphuric acid. The other metals react with it under certain conditions, forming sulphates. Dilute sulphuric acid acts readily on some metals, like zinc and magnesium, at room temperatures liberating the hydrogen, as was pointed out when the latter element was studied. Upon other metals, like copper and lead, for instance, sulphuric acid acts but slightly. Even hot, fairly concentrated sulphuric acid, as we have seen, does not attack lead much. This is due in part to the fact that the lead sulphate formed is difficultly soluble in sulphuric acid and so forms a protective coating on the lead. On the other hand, copper acts on hot concentrated sulphuric acid, forming copper sulphate and sulphur dioxide. By means of hydrobromic or hydriodic acid, sulphuric acid is readily reduced to sulphurous acid and to hydrogen sulphide. The sulphates are all soluble in water except the sulphate of barium. The sulphates of lead, strontium, and calcium are sparingly soluble in water. As a rule, sulphates are not as soluble as chlorides and nitrates. Sulphates of the alkalies are quite stable at high temperatures.

Sulphates of the heavy metals decompose at high temperatures, yielding oxides of the metals and sulphur trioxide.

Hydrates of Sulphuric Acid. — Pure H_2SO_4 is commonly called the monohydrate, as stated above. When one molecule of water is added to it, it forms crystals of the composition $H_2SO_4 \cdot H_2O$ or H_4SO_5, which melt at 8°. These are called the **dihydrate.** By a further addition of a molecule of water a **trihydrate** $H_2SO_4 \cdot 2\,H_2O$ or H_6SO_6, also called orthosulphuric or normal sulphuric acid, is formed. It is evident that it may be regarded as $S(OH)_6$, in which sulphur is combined with six hydroxyl groups. The trihydrate does not form crystals, except at very low temperatures. Its existence is largely based upon the fact that it represents the composition of the compound formed when sulphuric acid and water react with maximum contraction of volume. There are no salts of either H_4SO_5 or H_6SO_6 known. In all its salts sulphuric acid is distinctly dibasic.

Pyrosulphuric Acid. — When sulphur trioxide is dissolved in pure sulphuric acid, **pyrosulphuric acid** or **disulphuric acid** $H_2S_2O_7$ is formed. It consists of crystals that melt at 36°, and is sometimes called solid sulphuric acid. This acid fumes strongly in the air. The fuming sulphuric acid of commerce consists of sulphuric acid containing varying amounts of sulphur trioxide in solution. An acid containing 10 to 20 per cent of additional SO_3 in solution used to be called **Nordhausen sulphuric acid.** It was prepared by Basil Valentine at Erfurt in 1450 by heating partially dehydrated sulphate of iron. From pyrosulphuric acid, sulphur trioxide may readily be prepared by heating. The so-called "oleum" of commerce consists of about 80 per cent SO_3 and 20 per cent H_2SO_4. It is used industrially. The salts of pyrosulphuric acid are called the **pyrosulphates.** They are readily prepared by heating acid sulphates, thus: —

$$KHSO_4 \rightleftarrows K_2S_2O_7 + H_2O.$$

The water escapes as vapor. On moistening the pyrosulphate with water, the acid sulphate is again obtained, so that the above reaction is reversible.

Thiosulphates. — When a solution of a sulphite is boiled with sulphur, a thiosulphate results: —

$$Na_2SO_3 + S = Na_2S_2O_3.$$

We may look upon this salt as sodium sulphate in which one oxygen atom is replaced by a sulphur atom, whence the name thiosulphate. **Sodium thiosulphate** is used in photography, and in commerce it is frequently called hyposulphite of soda or "**hypo.**" These names are not in accord with chemical usage, since the salt is not a salt of an acid containing less oxygen than sulphurous acid H_2SO_3. By treating a thiosulphate with hydrochloric acid, the chloride of the metal, sulphur, sulphur dioxide, and water are formed, thus: —

$$Na_2S_2O_3 + 2\ HCl = 2\ NaCl + S + SO_2 + H_2O.$$

Thiosulphuric acid $H_2S_2O_3$ is not known in the free state. Its salts are very common, but attempts to isolate the acid fail because it decomposes into the products indicated by the above equation.

Persulphates. — By electrolyzing a concentrated solution of acid potassium sulphate, **potassium persulphate** KSO_4 is readily obtained. **Sodium persulphate** may be similarly prepared. It is used in photography. **Persulphuric acid** HSO_4 is unstable. It may be prepared by dissolving its anhydride, S_2O_7, **sulphur peroxide**, in water, thus: —

$$S_2O_7 + H_2O = 2\ HSO_4.$$

Sulphur peroxide or heptoxide was formed by Berthelot by the action of the silent electric discharge on a mixture of sulphur dioxide and oxygen. It is unstable, and but little is known about it. Persulphuric acid is formed to a slight extent in the lead storage cells, in which sulphuric acid of specific gravity 1.2 is commonly used.

Polythionic Acids. — Polythionic acids contain more than one sulphur atom. Of these thiosulphuric acid $H_2S_2O_3$ is the simplest example. The following acids are known: —

Thiosulphuric Acid	$H_2S_2O_3$, forms thiosulphates, like	$Na_2S_2O_3$.
Dithionic Acid	$H_2S_2O_6$, forms dithionates, like	$Na_2S_2O_6$.
Trithionic Acid	$H_2S_3O_6$, forms trithionates, like	$Na_2S_3O_6$.
Tetrathionic Acid	$H_2S_4O_6$, forms tetrathionates, like	$Na_2S_4O_6$.
Pentathionic Acid	$H_2S_5O_6$, forms pentathionates, like	$Na_2S_5O_6$.

With the exception of thiosulphuric acid (which is known only in form of salts), the free acids are known only in aqueous

solutions; and even in these they readily decompose. The salts, however, are as a rule quite stable.

Thionyl Chloride. — Thionyl chloride $SOCl_2$ is formed when phosphorus pentachloride acts on sulphur dioxide, or on a sulphite, thus: —

$$PCl_5 + SO_2 = POCl_3 + SOCl_2.$$
$$2\ PCl_5 + K_2SO_3 = 2\ POCl_3 + 2\ KCl + SOCl_2.$$

It is a colorless liquid of very pungent odor. It fumes in the air and is readily decomposed by water, thus: —

$$SOCl_2 + H_2O = SO_2 + 2\ HCl.$$

Thionyl chloride boils at 78°. Its specific gravity at 0° is 1.676. It may be regarded as SO_2 with one oxygen atom replaced by two chlorine atoms.

Sulphuryl Chloride. — This compound is made by the action of equal volumes of chlorine and sulphur dioxide on each other in sunlight, or in presence of a little camphor, thus: —

$$SO_2 + Cl_2 = SO_2Cl_2.$$

It may be regarded as SO_3 with one oxygen atom replaced by two chlorine atoms. It is a colorless liquid of very pungent odor. It boils at 70°, and has a specific gravity of 1.66 at 20°. In contact with the air it fumes strongly. By addition of one gram-molecule of water to one gram-molecule of sulphuryl chloride, **chlorsulphonic acid** is formed, thus: —

$$SO_2Cl_2 + H_2O = SO_2 \cdot Cl \cdot OH + HCl.$$

Chlorsulphonic acid $SO_2 \cdot Cl \cdot OH$ may be regarded as sulphuric acid $SO_2(OH)_2$ with one OH group replaced by chlorine. With more water, chlorsulphonic acid decomposes, thus: —

$$SO_2 \cdot Cl \cdot OH + H_2O = SO_2(OH)_2 + HCl.$$

Selenium. — This element belongs to the rarer elements, for though it is fairly widely distributed in nature, it generally occurs in extremely small quantities. It has been found in the free state in Mexico; but it occurs mainly in combination with metals like lead, copper, iron, silver, and thallium. Not infrequently it is present in small amount in pyrites, and so in roasting the latter the selenium is oxidized to selenium dioxide which is carried into the dust flues of sulphuric acid factories.

In these flues there is also deposited some free selenium, for the latter forms when hot sulphur acts on selenium dioxide. This gets into the lead chambers, where it is reduced to selenium by the action of sulphur dioxide, and so accumulates in the slime at the bottom of the chambers. In 1817 Berzelius discovered selenium in the slime of the lead chambers at Gripsholm. He named the element selenium, from the Greek word meaning moon, because of its similarity to tellurium, which is named from *tellus*, the earth.

There are three varieties of selenium: (1) a red amorphous precipitate which dissolves in carbon disulphide and separates from the latter solution in form of (2) red monoclinic crystals fusing at 170–180°, which are also soluble in carbon disulphide; and (3) a bluish gray, metallic form which crystallizes in the hexagonal system and is insoluble in carbon disulphide. This metallic form conducts electricity slightly, which property may be increased tenfold by exposure to light. The conductivity depends on the intensity of the light.

The metallic form has a specific gravity of 4.8, melts at 217°, and boils at 680°. The atomic weight of selenium is 79.2, and at high temperatures the molecular weight corresponds to the formula Se_2.

Compounds of Selenium. — These are similar to the compounds of sulphur. So **hydrogen selenide** may be formed by treating ferrous selenide with hydrochloric acid: —

$$FeSe + HCl = FeCl_2 + H_2Se.$$

The compound H_2Se is a gas that has the smell of horseradish and is more poisonous than hydrogen sulphide. The aqueous solution deposits selenium on exposure to the air or to oxygen. With the exception of the selenides of the alkalies, the compounds of the metals with selenium are difficultly soluble in water.

With chlorine, selenium forms **selenium monochloride** Se_2Cl_2 and **selenium tetrachloride** $SeCl_4$. The former is a dark, brownish yellow oil and the latter a light yellow crystalline solid.

Selenium dioxide SeO_2 is a solid formed by burning selenium in the air. *It is the only oxide of selenium known.* It forms long white prismatic crystals that sublime at about 300°.

When sulphur and selenium dioxide are heated together, sulphur dioxide and selenium are formed: —

$$S + SeO_2 = SO_2 + Se.$$

By oxidizing selenium with nitric acid, **selenious acid** H_2SeO_3 is produced. By means of sulphur dioxide, selenious acid is reduced to selenium: —

$$H_2SeO_3 + 2\ SO_2 + H_2O = 2\ H_2SO_4 + Se.$$

In this way the element is formed in the lead chambers of the sulphuric acid factories.

When SeO_2 and $SeCl_4$ react with each other, they form $SeOCl_2$, **selenyl chloride**: —

$$SeO_2 + SeCl_4 = 2\ SeOCl_2.$$

The compound melts at 10° and boils at 179°.

Selenic acid H_2SeO_4 is formed by oxidation of selenious acid by means of chlorine: —

$$H_2SeO_3 + H_2O + Cl_2 \rightleftarrows 2\ HCl + H_2SeO_4.$$

The action is reversible, for selenic acid is able to liberate chlorine from hydrochloric acid. Selenic acid is thus a more powerful oxidizing agent than sulphuric acid. The latter oxidizes hydrobromic acid, but not hydrochloric acid. Pure selenic acid is a solid melting at 62°. The 95 per cent solution is a thick, oily liquid not unlike sulphuric acid in appearance.

When hydrogen sulphide is passed into a solution of selenious acid, **selenium sulphide** SeS is precipitated. It is yellow in color and does not dissolve in ammonium sulphide.

Tellurium. — Tellurium is one of the rare elements. It has been found in the free state, and also in the form of tellurides in combination with gold, silver, lead, and bismuth. It occurs in Colorado, California, Hungary, Brazil, and the Liparian Islands. It is a brittle, crystalline, silvery white substance having metallic luster. In precipitated amorphous form it is a black powder. In metallic form it conducts heat and electricity like other metals. It has a specific gravity of 6.26 and melts at 455°. Its atomic weight is 127.5; and at 1400°, its boiling point, the vapor density corresponds to the formula Te_2. Tellurium was discovered in 1782 by Müller von Reichenstein, whose work was confirmed by Klaproth in 1798. The latter called the element tellurium, from *tellus*, earth.

Compounds of Tellurium. — By the action of hydrochloric acid upon zinc telluride ZnTe, hydrogen telluride H_2Te is formed: —

$$ZnTe + 2\ HCl = ZnCl_2 + H_2Te.$$

The product is generally contaminated with some hydrogen, which is liberated simultaneously. Hydrogen telluride is a colorless, poisonous gas of disagreeable odor. It is combustible and fairly soluble in water. Its aqueous solutions when in contact with oxygen or air gradually deposit tellurium. When conducted into solutions of metallic salts, tellurides of the metals are in general precipitated. Such tellurides may also be prepared by heating metals with tellurium.

With chlorine, tellurium forms **tellurium dichloride** $TeCl_2$ and **tellurium tetrachloride** $TeCl_4$. These are formed when chlorine is passed over hot tellurium. If the chlorine is in large excess, the tetrachloride is formed; if less chlorine is used, the dichloride forms together with some tetrachloride. The dichloride is a black crystalline substance melting at 175° and boiling at 324°. The tetrachloride forms white, shining crystals that melt at 224° and boil at 380°. Both chlorides are decomposed by water. It is to be noted that the dichloride $TeCl_2$ is not analogous to the lower chloride of sulphur, which is S_2Cl_2. **Tellurium dibromide** $TeBr_2$ and **tetrabromide** $TeBr_4$ have also been prepared. **Tellurium diiodide** TeI_2 and **tellurium tetraiodide** TeI_4 are also known.

When sulphur trioxide acts on tellurium, **tellurium sulphur trioxide** $TeSO_3$, a red amorphous solid, forms, which on heating is decomposed into sulphur dioxide and **tellurium monoxide** TeO. The latter is a black, amorphous substance, which on heating yields tellurium dioxide TeO_2 and tellurium.

When heated in the air, tellurium is oxidized to **tellurium dioxide** TeO_2. This is a white crystalline powder which is volatile at red heat (*i.e.* at higher temperatures than tellurium itself) and difficultly soluble in water. By means of nitric acid, tellurium may be oxidized to **tellurous acid** H_2TeO_3. This is a feeble acid that forms a white powder which is slightly soluble in water. On heating, it decomposes into water and tellurium dioxide. With strong bases it forms both acid and normal **tellurites**, like $KHTeO_3$ and K_2TeO_3. However, towards strong acids it behaves like a base. The salts thus formed

may be considered as derivatives of $Te(OH)_4$, that is, $H_2TeO_3 \cdot H_2O$. So, for instance, **tellurium sulphate** $Te(SO_4)_2$ has been prepared. Moreover, the salt $TeCl_4$ may be retained in aqueous solutions in presence of an excess of hydrochloric acid. Being both a weak base and also a weak acid, the salts that tellurous acid forms with either bases or acids are not very stable. This is generally the case with substances that do not have pronounced chemical characteristics.

On fusing together barium nitrate and tellurium dioxide, **barium tellurate** may be formed: —

$$Ba(NO_3)_2 + TeO_2 = BaTeO_4 + 2\,NO_2.$$

By decomposing barium tellurate with the calculated quantity of sulphuric acid, barium sulphate, which is insoluble in water, and **telluric acid** H_2TeO_4, which remains in solution, result: —

$$BaTeO_4 + H_2SO_4 = BaSO_4 + H_2TeO_4.$$

The latter may also be prepared by first making **potassium tellurate** K_2TeO_4, by fusing either tellurium or tellurium dioxide with potassium carbonate and potassium nitrate, or by passing chlorine into an alkaline solution of **potassium tellurite.** The potassium tellurate is then converted into the barium salt by means of barium chloride, thus: —

$$K_2TeO_4 + BaCl_2 = 2\,KCl + BaTeO_4;$$

and the barium tellurate is then decomposed by dilute sulphuric acid as before. From the aqueous solution, telluric acid separates in form of monoclinic crystals of the composition $H_2TeO_4 \cdot 2\,H_2O$ or $Te(OH)_6$. On heating these, H_2TeO_4 forms, which loses water at 160°, yielding **tellurium trioxide** TeO_3, an orange-yellow, crystalline substance that unites with water extremely slowly and decomposes into tellurium dioxide and oxygen on ignition. While telluric acid forms tellurates with the alkalies and other metals, its resemblance to sulphuric acid and selenic acid is extremely slight. Like tellurous acid, telluric acid may act as a base toward strong acids.

General Considerations. — Oxygen is commonly considered as forming with sulphur, selenium, and tellurium a natural family group of elements. We have already seen that fluorine, chlorine, bromine, and iodine form such a group in which

fluorine is rather less closely related to chlorine, bromine, and iodine, than these three are to one another. Now, the relation of oxygen is similarly less close to sulphur, selenium, and tellurium. From oxygen to tellurium we have a gradation of physical properties, as the following table shows:—

Name	Color	Atomic Weight	Specific Gravity	Melting Point	Boiling Point
Oxygen	blue	16.0	1.124 (at −181°)	. . . . .	−181.4
Sulphur	yellow	32.07	1.96 to 2.0	114.5	450
Selenium	red or metallic	79.2	4.8	217	680
Tellurium	black or metallic	127.5	6.3	455	1400

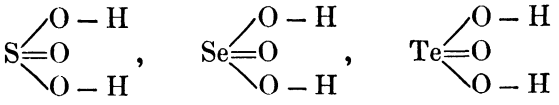
All of these elements exhibit allotropism.

Toward hydrogen these elements are bivalent, forming compounds of the type H_2X, thus:—

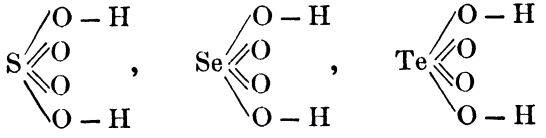
$$H_2O,\ H_2S,\ H_2Se,\ H_2Te.$$

The stability of these compounds decreases as the atomic weight of the elements in question increases.

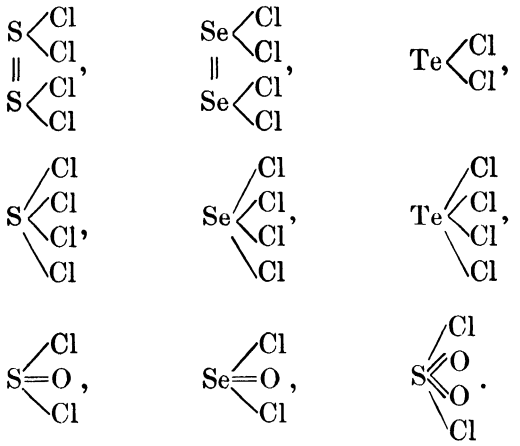
Sulphur, selenium, and tellurium form compounds with oxygen, whose composition is represented by the types XO_2 and XO_3. In the former, that is SO_2, SeO_2, and TeO_2, the elements are tetravalent; whereas in the latter, namely, SO_3, SeO_3, and TeO_3, the elements in question are hexavalent, which is the highest valence they are capable of exhibiting. Again, in the acids of the type H_2XO_3, namely H_2SO_3, H_2SeO_3 and H_2TeO_3, and in those of the type H_2XO_4, namely H_2SO_4, H_2SeO_4, and H_2TeO_4, we plainly have striking analogies. In the compounds H_2XO_3, the elements are quadrivalent, thus:—



In the compounds H_2XO_4, the elements are hexavalent, thus:—



Toward the halogens, sulphur, selenium, and tellurium are bivalent and quadrivalent, while in some oxy-halogen derivatives they are hexavalent, thus: —



The halogen compounds of selenium are more stable than those of sulphur, and those of tellurium are more stable than the selenium halides. One may regard the very unstable compound Cl_2O as analogous to Cl_2S, Cl_2Se, and Cl_2Te. Thus, it is apparent that as the atomic weight of the elements of the oxygen group increases, their affinity for halogen increases. This is also evident from the fact that in the halogen compounds, sulphur is readily replaced by selenium, and the latter is in turn replaced by tellurium.

Sulphur, selenium, and tellurium, like chlorine, bromine, and iodine, form a group of three, in which the atomic weight of the middle element is very nearly equal to one-half the sum of the atomic weights of the other two, thus: —

$$\overset{S}{\frac{1}{2}}(32.07 + \overset{Te}{127.5}) = 79.78; \text{ whereas, } Se = 79.2.$$

In spite of the relationships noted, it should be borne in mind, however, that tellurium after all shows some decided points of departure in its chemical behavior from sulphur and selenium, so that the closeness of relationship between the latter elements and tellurium has repeatedly been called into question.

REVIEW QUESTIONS

1. Where is sulphur found and in what forms? What are the allotropic forms of sulphur?

2. How is sulphur refined, and for what purposes is it used?

3. Make a list of the six crystal systems and mention at least two substances that crystallize in each system. What is dimorphism? State the law of isomorphism.

4. How much hydrogen sulphide may be prepared from 85 kilograms of ferrous sulphide? What volume would this gas occupy under standard conditions?

5. What are the chief properties of hydrogen sulphide? Illustrate each of its important chemical properties by means of an appropriate equation.

6. Complete the following equations and state what property of hydrogen sulphide is illustrated in each case: —

$$NH_4OH + H_2S = \qquad Ag + H_2S =$$
$$H_2SO_4 + H_2S = \qquad CuSO_4 + H_2S =$$
$$H_2S + I = \qquad H_2S + SO_2 =$$

7. Explain the apparent contradiction of the following reactions: —

$$HgCl_2 + H_2S = HgS + 2\,HCl.$$
$$ZnS + 2\,HCl = ZnCl_2 + H_2S.$$

8. What is the formula of sulphur monochloride? Why? How may this substance be prepared? For what purpose is it used?

9. When 12 liters of hydrogen sulphide, measured under standard conditions, are burned to water and sulphur dioxide, what volume of oxygen will be required, and what is the volume of the sulphur dioxide formed?

10. What is a sulphite? Give five examples. How do sulphites act when treated with hydrochloric or sulphuric acid? Illustrate by means of an equation.

11. How does bleaching with sulphur dioxide differ from bleaching with chlorine or hydrogen peroxide?

12. What is sulphurous acid? How may it be changed to sulphuric acid by action of the halogens? Write appropriate equations.

13. How would you make sulphuric acid from the elements? Write the equations.

14. By what two processes is sulphuric acid prepared commercially? Write the equations.

15. What three important properties does sulphuric acid possess? Which of these is illustrated in the charring of wood and sugar?

16. What is sulphuric acid used for? How does this substance act when poured into water? Why?

17. What is sodium thiosulphate? How may it be prepared? Of what use is it?

18. What two other elements are analogous to sulphur? Why?

19. How much sulphuric acid could be prepared from 350 tons of sulphur?

20. Why is oxygen classified with sulphur, selenium, and tellurium?

21. What is the valence of sulphur in hydrogen sulphide? In sulphur dioxide? In sulphuric acid? In sulphur trioxide? In sulphur monochloride?

22. Assuming the air to consist of 20 per cent oxygen and 80 per cent nitrogen by volume, what will be the resulting volume if 1 gram of sulphur is burned in 10 liters of air? How much of the final volume is due to each of the gases present?

CHAPTER XIV

CARBON AND SOME OF ITS TYPICAL COMPOUNDS

Occurrence and Allotropic Forms of Carbon. — Carbon occurs in the free state in nature as diamond and graphite, which are crystalline in character. It is also known in amorphous form as charcoal, coke, soot, lampblack, bone black, etc., resulting from the charring of animal and vegetable matter, and various compounds of carbon. Diamond, graphite, and amorphous carbon are the **allotropic forms** of the element.

Carbon is a most important constituent of all plants and animals. Large quantities of carbon are found in form of coal, which represents the remains of vegetation of past geological ages. Coal is consequently not pure carbon. Indeed, the amount of free carbon in different kinds of coal varies considerably. In natural gas and petroleum, carbon occurs in combination with hydrogen. In form of carbon dioxide, carbon is found in the air and in many natural waters. As carbonates, especially calcium carbonate and magnesium carbonate, carbon is found in huge masses widely distributed in various parts of the earth. Calcium carbonate is commonly found in form of chalk, limestone, and marble; whereas calcium magnesium carbonate, or dolomite, also called magnesian limestone, occurs very frequently and covers extensive areas of the earth's crust, often forming mountains.

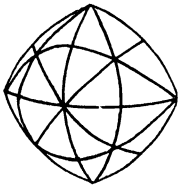


FIG. 81.

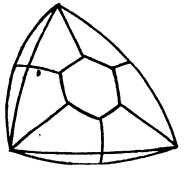


FIG. 82.

Diamond. — The diamond is a crystalline form of carbon, and belongs to the regular or isometric system, Figs. 81 and 82. It is colorless when pure, but frequently it is dark-colored or black, in which form it is known as **carbonado**, or **bort**. Sometimes diamonds are colored blue, green, yellow, or red by small amounts of foreign substances. The diamond is very hard. It will scratch all other minerals. For this reason diamond

dust, usually in form of bort, is used by lapidaries in cutting and polishing. Drills of carbonado, which sometimes occurs in pieces as large as one's fist, are used in boring rocks, and glaziers make use of the diamond in cutting glass. Diamonds are found in Brazil, South Africa, India, and Australia, and sometimes also in the United States. They are usually corroded, and so their brilliant luster does not appear till the outer layer is removed by the lapidary, who, by grinding suitable artificial faces on the diamonds, brings out their highly prized brilliancy. The diamond has a specific gravity of 3.5 to 3.6 and a refractive index of 2.416 to 2.43. That it consists of carbon only, appears from the fact that on combustion in oxygen the sole product formed is carbon dioxide. Diamonds of microscopic dimensions have been prepared artificially by Moissan, by dissolving carbon in molten iron and then chilling the same suddenly. Under the great pressure thus produced in the interior of the iron, graphite and some very small diamonds crystallize out. The diamond is not attacked by acids. It is a non-conductor of electricity, and becomes electrically charged when rubbed with a cloth. On heating it highly out of contact with the air, it may be changed to graphite; whereas when heated highly in oxygen, it burns with great brilliancy to carbon dioxide.

The diamonds found are usually small; only rarely do they weigh as much as 20 grams. The largest diamond known was found near Pretoria, South Africa. It is called the Cullinan, and weighed about 600 grams when found.

Graphite. — Graphite crystallizes in the monoclinic system in plates that simulate hexagonal forms. It is widely distributed in nature in form of small flakes or granules in various granite rocks. It is black or grayish black, having metallic luster. It is very soft, and may readily be crushed to a fine powder, which is frequently employed as a lubricant. Graphite is also used in making "lead pencils." At one time it was thought that graphite contained lead, hence the name **plumbago**, by which graphite is also known. Graphite conducts electricity, and in its artificial forms it is used as electrodes for electric arcs and in electro-chemical work, especially in making chlorine and caustic soda from common salt. Graphite powder is employed in electrotyping, in making stove polish, etc. The specific gravity

of graphite varies from 1.8 to 2.5. It burns with great difficulty even in oxygen, and the natural varieties leave from 3 to 20 per cent ash, which usually consists of silicates of various bases. Graphite is very refractory and not readily attacked by chemical reagents, for this reason it is frequently employed together with fire clay in making crucibles. A mixture of concentrated nitric acid and potassium chlorate converts graphite into **graphitic acid**, which consists of small yellow crystals that explode on heating, leaving a mass of finely divided carbon. Graphitic acid consists of 56 per cent carbon, 2 per cent hydrogen, and 42 per cent oxygen. On treating graphite with concentrated nitric acid, and then igniting the material strongly, various samples show a different behavior. Thus, graphite found in the State of New York greatly increases in volume when so treated, whereas Siberian graphite is not so affected at all. Ceylon and Siberia furnish most of the natural graphite. Artificial graphite is formed when carbon dissolved in molten iron crystallizes out, and when coke is heated to very high temperatures in the electric furnace out of contact of the air and then allowed to cool slowly. By the latter process, known as the **Acheson process**, much graphite of excellent quality is made at Niagara Falls. By first grinding up the coke, mixing it with a binder, like coal tar or black strap molasses, and molding it into desired forms and baking these in ovens, carbons for batteries, electric arc lights, and other purposes are obtained. These carbons may readily be converted into graphite by heating them in the electric furnace as above stated. Artificial graphite is now much employed in the arts in place of natural graphite.

Electric furnaces are either *resistance furnaces* or *arc furnaces*. In the former the heat is generated by passing a strong current of electricity through conducting material which is thus heated to high temperatures. In the arc furnaces, the high temperatures are obtained by means of the electric arc; in principle, the arrangement is similar to that of the arc lamp. The **Acheson graphite furnace** is a form of resistance furnace, Fig. 83. The molded sticks of carbon are piled between two carbon terminals which are about two feet square and thirty feet apart. The whole is then covered with a thick layer of granular carbon and carborundum (which see), and a current

of 3000 amperes at a pressure of 220 volts is turned on which is gradually changed to 9000 amperes at 80 volts at the end of

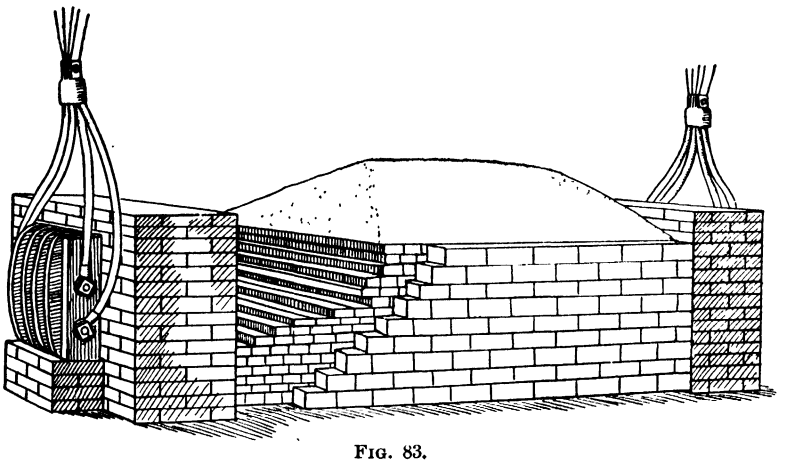


FIG. 83.

the twenty-four hours during which the furnace is run. The whole is then allowed to cool, and the carbon is found to be converted to graphite. The heat is largely generated by the current as it passes through the granular carbon lodged in the interstices between the carbon sticks. Smaller resistance furnaces of different types are used in the arts and also for experimental purposes.

Figure 84 shows a typical arc furnace for experimental work. The poles are of carbon, and the walls of the furnace are usually built of quicklime or magnesia. In the case of larger furnaces, this material is then reënforced on the outside by bricks made of crude magnesia. We shall have occasion to refer to electric furnaces again as we proceed, for they are now used for various purposes that require high temperatures.

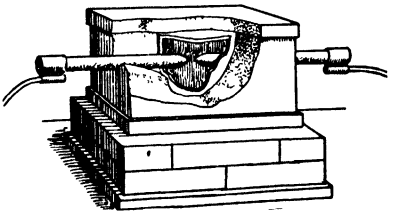


FIG. 84.

Amorphous Carbon. — Amorphous carbon is formed when animal or vegetable matter, coal, or various compounds of carbon are heated while access of air is excluded entirely or in part. Thus, by heating wood in this way **charcoal** is produced.

Similarly, **bone black** is made by heating bones in closed iron cylinders; **coke** is formed by heating coal; and **blood charcoal** is produced by heating blood till it chars. On burning hydrocarbons, like kerosene or turpentine, **lampblack**, or **soot**, is deposited on a cold object held in the smoky flame. Lampblack is nearly pure carbon. All of these forms of amorphous carbon differ according to the source from which they are obtained.

Charcoal contains about 85 per cent carbon. It is very porous and when freshly heated it has the power of absorbing many gases. So freshly ignited charcoal absorbs from 50 to 100 times its own volume of ammonia, hydrogen sulphide, bromine vapor, etc., which are again given off on heating the charcoal. This process of absorption consists of condensation of the gases on the surface of the charcoal and is called *adsorption*. Figure 85 illustrates the adsorption of ammonia (which has been collected over mercury) by means of charcoal. Charcoal is frequently used as a deodorant of vaults, cisterns, etc., because it absorbs the noxious gases. Bone black acts similarly. The latter is much used to decolorize various solutions. So in the refining of sugar, bone black serves to remove the brown coloring matter. Bone black contains from 70 to 80 per cent calcium phosphate, and only from 8 to 12 per cent carbon, together with some calcium carbonate and calcium sulphate. By repeated treatment with acids and water, nearly pure carbon may be prepared from bone black. A very pure amorphous carbon may be prepared by charring sugar. All animal charcoal contains some nitrogen, which is very tenaciously held. Very finely divided. dry charcoal has a strong affinity for oxygen; indeed, it may catch fire on being thrown from its container into the open air, — **pyrophoric carbon.** The various forms of amorphous carbon differ in their physical nature, and in the chemical character and the amounts of the impurities they contain.

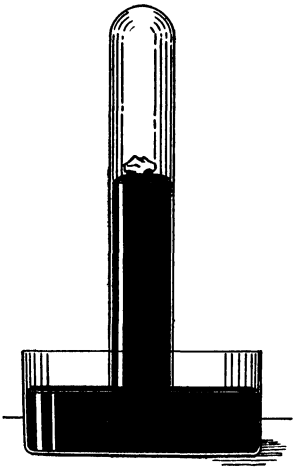


FIG. 85.

Lampblack is much used as a pigment in paints, India ink, etc., whereas coke is used for fuel and in the reduction of ores, particularly iron ore. In the production of coke, the gaseous products, tar, etc., should be saved and not allowed to burn and go to waste as is still frequently done. Similarly many valuable volatile products are lost when charcoal is made by heating wood in a pile covered with sod and earth in the old-fashioned way. By heating wood and coal in retorts, these gaseous and other volatile products may be saved and used. The process of thus heating and decomposing substances in retorts is called **destructive** or **dry distillation**.

Coal. — Coal is found in large deposits in various parts of the earth. It represents the plant remains of various geological periods from the carboniferous to the tertiary. Coal has been formed by the gradual abstraction of carbon, hydrogen, and oxygen, mainly in form of water, marsh gas, etc., from the vegetable remains. Much marsh gas (which see) is found associated with coal. There are many varieties of coal, which are commonly roughly divided into two great classes, namely, soft coal and hard coal. **Hard coal**, or **anthracite**, contains much less volatile matter than **soft coal**, which is also called **bituminous coal**. The latter burns with a sooty flame, and evolves more hydrocarbon gases than anthracite when heated. It is consequently used in manufacturing illuminating gas (which see). The amount of carbon in charcoal, coke, or anthracite is generally in the neighborhood of 95 per cent, whereas soft coal contains about 80 per cent carbon.

Chemical Behavior of Carbon. — The various forms of carbon above mentioned are practically not at all attacked by chemical reagents at room temperatures. When heated in the air, carbon burns; that is, it unites with oxygen. When a sufficient supply of oxygen is at hand, the product formed is carbon dioxide, a gas whose composition corresponds to the formula CO_2. When an insufficient amount of oxygen is furnished, some carbon monoxide is also formed. The latter substance is also a gas; its composition is expressed by the formula CO.

The very careful work of Dumas and Stas has shown that 3 parts of carbon by weight unite with 8 parts of oxygen by weight to form carbon dioxide gas. Under standard conditions

the weight of 22.4 liters of carbon dioxide is nearly 44 grams. The molecular weight of carbon dioxide is consequently 44. However, 44 parts of carbon dioxide by weight contain 12 parts of carbon and 32 parts of oxygen. Now, since we have previously chosen 16 as the atomic weight of oxygen, it is clear that the molecule of carbon dioxide contains $32 \div 16$ or 2 atoms of oxygen. The question now arises, how many carbon atoms there are in a molecule of carbon dioxide? To answer this question really involves choosing the atomic weight of carbon from the combining weight. A study of all of the gaseous compounds of carbon that are known has revealed the fact that in no case do these contain less than 12 grams of carbon in 22.4 liters under standard conditions; that is to say, there is no compound into which carbon enters whose molecule contains less than 12 parts of carbon by weight. For this reason, the atomic weight of carbon is taken as 12, rather than some fraction or multiple thereof. Having thus determined upon 12 as the atomic weight of carbon, it is obvious from what has been said that the molecule of carbon dioxide contains one atom of carbon and two atoms of oxygen, and its formula is therefore CO_2. The specific heat of carbon increases with the temperature, becoming nearly constant in the neighborhood of 1000°. Between 900° and 1000° it is about 0.46, which fact also yields approximately 12 as the atomic weight of carbon according to the law of Dulong and Petit.

When carbon is burned in oxygen, the volume of the carbon dioxide formed is the same as that of the original oxygen, measured, of course, under the same conditions of temperature and pressure. Figure 77 represents an apparatus for demonstrating this fact. Carbon on a platinum spoon is burned in the flask which is filled with oxygen. After the whole has again cooled to room temperature, the mercury manometer, attached as shown, indicates that there has been no change of volume. Therefore we have: —

$$\underset{\text{(1 volume)}}{C} + \underset{\text{(1 volume)}}{O_2} = CO_2$$

which is quite in harmony with what we should expect on the basis of Avogadro's hypothesis. It will be recalled that when sulphur is similarly burned in oxygen the volume of the SO_2 formed is also the same as that of the oxygen.

Carbon does not unite directly with hydrogen except at very high temperatures such as are produced by the electric arc, and even then the union takes place with difficulty. Very many compounds of hydrogen and carbon are known, however, for they may be prepared by indirect methods. Similarly carbon does not combine directly with the halogens, except in the case of fluorine. However, by indirect methods compounds of carbon with the halogens may be formed fairly readily. With sulphur carbon unites directly at high temperatures. At the temperature of the electric furnace, carbides of calcium, aluminum, silicon, and boron may be formed, and iron generally contains some carbon which is present in form of carbide of iron.

With nitrogen carbon does not unite directly, though by indirect means it is quite possible to effect the union of these two elements.

In general, carbon is rather inert chemically, though its compounds, when once formed, frequently have a very considerable degree of stability. We shall see that *the carbon atom has a great tendency to unite with other carbon atoms, which often results in building up of large and complex molecules.* At high temperatures carbon is generally bivalent, whereas at lower temperatures it is quadrivalent. Sometimes carbon is regarded as quadrivalent in all of its compounds. This view would necessitate that a goodly number of carbon compounds be regarded as unsaturated. The number of carbon compounds known is very great, so that it is customary to treat these in a separate division of chemistry, namely, **organic chemistry.** *The term organic chemistry, as used at present, signifies that branch of the science which deals with the compounds of carbon, or with the hydrocarbons and their derivatives;* for *all the carbon compounds may be considered as derived from compounds of carbon and hydrogen by substituting other elements in place of the hydrogen.* Since carbon is an essential constituent of all living beings, the study of the carbon compounds is closely associated with the study of the chemistry of the products that are formed in organic beings. Hence the name organic chemistry. Indeed, till 1828 it was quite generally held that compounds that are produced by the life process could not be prepared artificially in the laboratory, but Wöhler's synthesis of urea (which see)

showed that such syntheses are quite possible; and now many of the products that are formed by the metabolic processes in plants and animals have been prepared in the laboratory.

Carbon Dioxide. — As already mentioned, there are two oxides of carbon known, namely, carbon monoxide CO, and carbon dioxide CO_2. Carbon dioxide is the final oxidation product of carbon. It always results when carbon is burned in a sufficient amount of air or oxygen. It is moreover exhaled as a product of respiration of both plants and animals. It will be recalled that every 1000 volumes of air contain 3 volumes of carbon dioxide. This gas is also contained dissolved in all natural waters. Many spring waters, like those at Saratoga, Colorado Springs, Selters, Vichy, and Narzan, are so highly charged with carbon dioxide, under pressure, that the gas escapes with effervescence when the pressure is released. In volcanic regions, like those of Italy, South America, and Java, large quantities of carbon dioxide issue from fissures in the earth's crust. In fermentation and in the decay of animal and vegetable matter carbon dioxide is always formed. It is thus evident that the air is continually receiving carbon dioxide from quite a variety of sources.

Carbon dioxide may be produced by the oxidation of carbon: —

$$C + O_2 = CO_2.$$

In the process of fermentation of sugar by means of yeast, alcohol and carbon dioxide result. Thus the fermentation of glucose may be expressed by the following equation: —

$$\underset{\text{glucose}}{C_6H_{12}O_6} = 2\ \underset{\text{alcohol}}{C_2H_5OH} + 2\ \underset{\text{carbon dioxide}}{CO_2}.$$

However, the simplest way of obtaining carbon dioxide is by the action of an acid upon a carbonate, like calcium carbonate $CaCO_3$, or sodium carbonate: —

$$CaCO_3 + 2\ HCl = CaCl_2 + H_2O + CO_2.$$
$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

It will be recalled that when an acid acts on a sulphite, H_2SO_3 is not formed, for it at once decomposes, yielding H_2O and SO_2. Similarly, when an acid acts on a carbonate, we do not get H_2CO_3, **carbonic acid,** but H_2O and CO_2. The latter is clearly carbonic acid anhydride. It is probable that the compound

H_2SO_3, sulphurous acid, exists in aqueous solutions of SO_2; and it is also likely that aqueous solutions of CO_2 contain H_2CO_3, carbonic acid. While an aqueous solution of any of the ordinary acids will decompose carbonates, owing to the weakness of carbonic acid and the volatility of carbon dioxide, calcium carbonate, in form of marble, and hydrochloric acid are commonly employed, because these materials are cheap, and the calcium chloride is readily soluble in water. A Kipp apparatus (Fig. 86) is very convenient for evolving carbon dioxide from marble and hydrochloric acid.

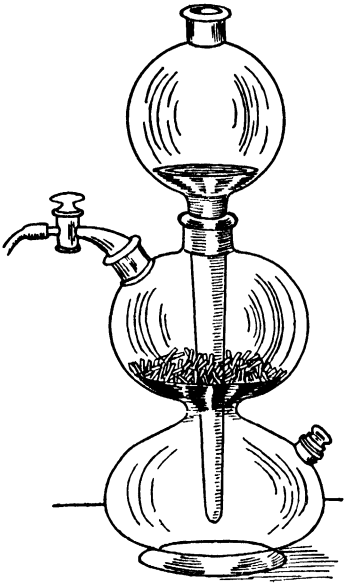


FIG. 86.

Just as sulphites are salts of sulphurous acid H_2SO_3, so **carbonates** may be regarded as salts of the dibasic acid H_2CO_3. We have then normal carbonates, like Na_2CO_3, and acid carbonates, or **bicarbonates**, like $NaHCO_3$. **Basic carbonates** of many metals, like zinc, copper, lead, etc., are also known.

When carbon dioxide is conducted into clear limewater, a white precipitate of **calcium carbonate** is formed, thus: —

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

On continuing to conduct in more carbon dioxide the calcium carbonate again dissolves, the solution becoming clear. In this process **calcium bicarbonate** is formed: —

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

On boiling the solution, however, carbon dioxide is expelled and calcium carbonate is reprecipitated: —

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

The fact that limewater, or baryta water $Ba(OH)_2$, is rendered turbid by carbon dioxide is commonly used as a means for detecting the latter, though in some cases such a test requires further confirmation. Breathing into limewater renders the

latter turbid, due to the formation of a precipitate of calcium carbonate, and this demonstrates the presence of carbon dioxide in the breath.

Many natural waters contain lime and magnesia in solution in form of the bicarbonates, $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. When such waters are boiled, carbon dioxide escapes and the normal carbonates, $CaCO_3$ and $MgCO_3$, are precipitated. Water containing carbonate or bicarbonate of calcium in solution is called **hard water.** Since boiling decomposes the bicarbonate and thus removes some of the calcium salts in form of a precipitate of $CaCO_3$, it is clear that after boiling the water has lost some of its "hardness." Thus it is common to speak of **temporary hardness** of water, which can be removed by boiling, and **permanent hardness**, which remains even after boiling. The carbonates of the alkalies, like sodium carbonate Na_2CO_3, and potassium carbonate K_2CO_3, may be fused without decomposition. But the carbonates of other metals are commonly decomposed on ignition, yielding carbon dioxide and the oxide of the metal, thus: —

$$CaCO_3 = CaO + CO_2.$$
$$SrCO_3 = SrO + CO_2.$$

Properties of Carbon Dioxide. — Carbon dioxide is a colorless gas, of slightly acid taste and a feeble, agreeably pungent smell. It is 1.529 times as heavy as air. Being so heavy, it may be readily poured or even siphoned from one jar to another (Fig. 87). It neither supports combustion nor respiration. At and below 31°, its critical temperature, carbon dioxide may be liquefied by pressure. The liquid boils at − 79° under atmospheric pressure. Solid carbon dioxide readily forms when the liquid is allowed to evaporate rapidly in the air, for thus much heat is absorbed and the remaining liquid is chilled below the melting point. The solid looks like snow, and melts at − 57°. In the air it evaporates without first passing into the liquid state, which is quite natural, since its boiling point under atmospheric pressure is much lower than its melting point. The large amounts of carbon dioxide evolved by fermentation in the brewing industries are now collected, washed, and pumped into cylinders made of mild steel (Fig. 13.) In this process the carbon dioxide is chilled and put into the cylinders under pressure.

It is used for making **soda water**, which consists of water charged with carbon dioxide under pressure. When the pressure is released, a portion of the gas escapes, for under atmospheric pressure and room temperature, water dissolves only about its own volume of the gas. The solution has a faintly acid reaction toward litmus. The name "soda water" comes from the fact that sodium bicarbonate $NaHCO_3$, also popularly called bicarbonate of soda or simply soda, is at times used in preparing carbonated water.

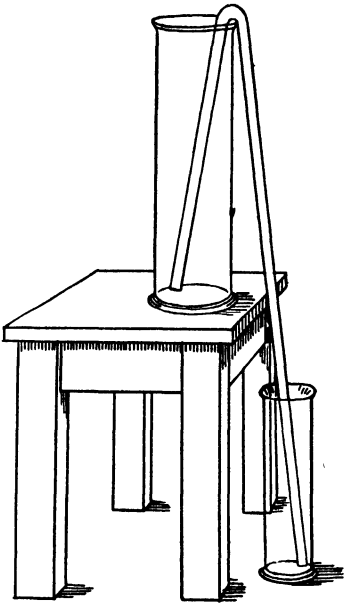


FIG. 87.

Solid carbon dioxide is frequently used for securing low temperatures. For this purpose it is often employed mixed with ether in order to secure more rapid evaporation. Thus temperatures as low as $-80°$ may be secured, and in a partial vacuum even $-100°$ may be reached. Natural carbon dioxide, as it issues from the earth, is also frequently bottled in steel cylinders as described, and placed on the market. Thousands of tons of carbon dioxide are thus sold annually.

Carbon dioxide is also used as a fire extinguisher. The reason why it does not burn or support combustion is that it contains all the oxygen it can hold, and retains this very tenaciously. At high temperatures potassium will burn brilliantly in carbon dioxide, for potassium is under these conditions able to rob carbon dioxide of its oxygen, thus: —

$$3\,CO_2 + 4\,K = C + 2\,K_2CO_3.$$

Here again we see the relative character of the process of combustion.

Physiological Effects of Carbon Dioxide. — In pure carbon dioxide, living beings will die for lack of oxygen, just as they would succumb in nitrogen, for example. Air containing over 20 per cent of carbon dioxide may also finally produce death

when breathed; for in respiration carbon dioxide is given off and oxygen is taken up from the air, which processes are greatly impeded by a high content of carbon dioxide in the air. Upon the mucous membranes, carbon dioxide has a stimulating action which is agreeable and refreshing, for this reason carbonated drinks are highly esteemed. Water from which all carbon dioxide has been expelled by recent boiling tastes flat, as already stated. Carbon dioxide colors the blood dark brown, and so when air containing even but 6 per cent of carbon dioxide is breathed continuously drowsiness results. The anæsthetic effects of carbon dioxide are similar to those of nitrous oxide. These effects may be counteracted by taking the person affected into fresh air that contains only the usual amount of carbon dioxide, for thus the blood again is able to get its needed oxygen, and so the intoxication gradually disappears. The necessity of good ventilation of buildings, especially sleeping rooms and audience halls, is consequently apparent. The evil effects of re-breathing carbon dioxide are great in themselves, but the exhalations aside from their carbon dioxide content are much more injurious to health.

Relations of Carbon Dioxide to Plant and Animal Life. — All animals exhale carbon dioxide, which is produced during the life process as a result of slow oxidation of their tissues. The heat of the animal body is a result of the oxidation that is continually going on while the animal lives. Now the carbon dioxide thus exhaled enters the atmosphere, and is again taken up by the green leaves of plants in which in the sunlight in presence of the chlorophyll, water and carbon dioxide react with each other, forming compounds containing carbon, hydrogen, and oxygen, notably starch $(C_6H_{10}O_5)_x$, and free oxygen, the latter being exhaled. Thus, carbon dioxide is decomposed and starch is formed, which may again serve as food for animals, in whose bodies it is oxidized to carbon dioxide and water. And so the cycle, often spoken of as the **carbon cycle**, repeats itself over and over. The energy is furnished by the sun's rays, which produce the decomposition of carbon dioxide and water into starch and oxygen in the green leaf of the plant. The starch and free oxygen formed contain more energy than the carbon dioxide and water; and this excess of energy in the starch and oxygen is again given off in the animal body, when carbon dioxide and

water are formed as a result of the oxidation of the starch. In connection with the study of the element nitrogen, we have seen that here too a somewhat similar cycle occurs.

Early Work on Carbon Dioxide. — J. B. van Helmont (1577–1644) showed that the same gas is formed during alcoholic fermentation, during the action of acids on chalk, and during the combustion of carbon. He demonstrated that this gas is also found issuing from fissures in volcanic regions, and that it is contained in the waters of mineral springs. Indeed, it was he who first used the term *gas*. He called carbon dioxide "gas sylvestre" or "gas carbonum." He was aware of the fact that carbon dioxide does not support combustion or respiration. Stephen Hales was the first to collect gases over water by displacement, as is still in vogue, while Priestley taught how to use mercury for this purpose instead of water. The fact that carbon dioxide is absorbed by caustic alkalies was discovered by Joseph Black in 1757. He called the gas "fixed air" because it is thus absorbed or fixed by caustic alkalies. Black demonstrated that soluble salts are formed when carbon dioxide acts on caustic potash or soda, and that an insoluble precipitate results when the gas is conducted into limewater. He also found that carbon dioxide is liberated when limestone is strongly heated, as in the process of making lime. McBride showed that the gas is liberated during putrefaction. Priestley demonstrated its presence in the air, and Lavoisier proved that carbon dioxide is formed during respiration and the reduction of metallic oxides by charcoal. The latter also showed that the gas contains only carbon and oxygen, while to the work of Berzelius, Dumas, Stas, and Roscoe we owe the careful determination of the percentage composition of carbon dioxide.

Carbon Monoxide. —Carbon monoxide occurs in gases that issue from volcanoes. It is a constituent of illuminating gas and particularly of so-called water gas. Furthermore, it often occurs in the gases issuing from blast furnaces in which iron ores or other metallic oxides are being reduced.

The gas may readily be formed by passing carbon dioxide over red-hot carbon, thus : —

$$CO_2 + C \rightleftarrows 2\,CO.$$

The reaction is reversible. At 1000° it is nearly complete in

the sense of the upper arrow, while at 450° it is practically completely reversed. Carbon monoxide is commonly formed in ordinary coal fires, where the carbon dioxide passes upward through red-hot layers of coal. The blue flame so frequently observed in a coal fire is due to the combustion of carbon monoxide. This gas is always formed to some extent when carbon is burned in an insufficient supply of oxygen. In this case, however, it is never pure, being always associated with carbon dioxide. The latter may be readily removed by passing the gases through caustic potash solution, which absorbs the carbon dioxide, but not the carbon monoxide.

When air is passed through beds of incandescent coke or coal, in furnaces of special type, the issuing gas consists of 28 to 30 per cent carbon monoxide, 63 per cent nitrogen, and smaller amounts of carbon dioxide. This gas is known as **producer gas** and is extensively used for fuel, being readily obtained. The nitrogen and carbon dioxide greatly dilute the gas and diminish its heating power.

When steam is passed over carbon heated to 1000° to 1400° C. (see apparatus, Fig. 4), carbon monoxide and hydrogen, a mixture which is known as **water gas**, is produced, thus : —

$$C + H_2O = CO + H_2.$$

This water gas is frequently made on a large scale and used as a fuel. In America it is also often used for illuminating purposes, in which case, since it burns with a non-luminous flame, it must be *enriched* or "carbureted" by the addition of the vapors of hydrocarbons that are rich in carbon (see illuminating gas).

Carbon monoxide is produced when many metallic oxides are heated with excess of carbon, thus : —

$$ZnO + C = Zn + CO.$$

Indeed, it was by means of this reaction that carbon monoxide was first observed (1776).

Carbon monoxide is further formed by heating carbonates with carbon or zinc dust, thus : —

$$CaCO_3 + C = CaO + 2\,CO.$$
$$MgCO_3 + Zn = ZnO + MgO + CO.$$

The gas is also formed by heating many organic acids with concentrated sulphuric acid, which abstracts water from the organic acids and so decomposes them. The resulting carbon monoxide generally contains carbon dioxide, which may, however, be removed by means of caustic potash, as already described. In the laboratory carbon monoxide is often prepared by heating oxalic acid with sulphuric acid, thus : —

$$(COOH)_2 + H_2SO_4 = H_2SO_4 \cdot H_2O + CO_2 + CO.$$

When formic acid is used, carbon monoxide only is obtained: —

$$HCOOH + H_2SO_4 = H_2SO_4 \cdot H_2O + CO.$$

Frequently, when larger quantities of carbon monoxide are required for experimental work, the gas is prepared by heating together potassium ferrocyanide with ten times its weight of concentrated sulphuric acid in a flask of relatively large capacity. The reaction which occurs is as follows : —

$$6\,H_2SO_4 + K_4Fe(CN)_6 + 6\,H_2O = 2\,K_2SO_4 + 3\,(NH_4)_2SO_4 + FeSO_4 + 6\,CO.$$

Properties of Carbon Monoxide. — Carbon monoxide is a colorless, odorless, tasteless gas which is 0.9672 time as heavy as air. At and below $-139.5°$ it may be condensed to a liquid by pressure. The critical pressure is 35.5 atmospheres. The liquid boils at $-190°$, and the white, snowlike solid melts at $-207°$. In the air and in oxygen, the gas burns with a rather small blue flame, forming carbon dioxide, thus : —

$$\underset{(2\text{ vols.})}{2\,CO} + \underset{(1\text{ vol.})}{O_2} = \underset{(2\text{ vols.})}{2\,CO_2}.$$

It is found by exploding a mixture of carbon monoxide and oxygen that 2 volumes of the former and 1 volume of the latter form 2 volumes of carbon dioxide, as indicated in the above equation. From this fact and the one that 22.4 liters of carbon monoxide under standard conditions weigh 28 grams, it follows that the formula for the gas is CO. The composition of carbon dioxide must, of course, be known as a result of independent experiment. In the volumetric relation of the combination of carbon monoxide and oxygen, we have another excellent illustration of the law of Gay-Lussac of combination of gases by volume, which law serves as the main support of Avogadro's hypothesis.

Carbon monoxide is a strong reducing agent. It is able to abstract oxygen from many metallic oxides at higher temperatures, thus: —

$$CuO + CO = Cu + CO_2.$$
$$Fe_2O_3 + 3\ CO = 2\ Fe + 3\ CO_2.$$

In sunlight carbon monoxide unites with chlorine, forming an addition product, **phosgene** $COCl_2$; while on heating sulphur vapor with carbon monoxide, **carbon oxysulphide** COS is formed. Phosgene, or carbonyl chloride, boils at + 8° and is readily decomposed by water: —

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

Carbon oxysulphide is a colorless, inflammable gas with an odor like that of hydrogen sulphide. When burned, the products formed are carbon dioxide and sulphur dioxide: —

$$COS + 3\ O = CO_2 + SO_2.$$

With nickel and iron, carbon monoxide forms the carbonyl compounds $Ni(CO)_4$ and $Fe(CO)_5$.

The chemical behavior of carbon monoxide is readily explained by regarding it as an unsaturated compound, the two free bonds of the carbon atom enabling the formation of the various addition products to take place. On the other hand, it must be remembered that while carbon monoxide is a strong reducing agent, it may itself in turn be reduced by still stronger reducing agents like magnesium and aluminum, whose oxides at the high temperatures at which the reaction takes place are very stable and non-volatile, thus: —

$$3\ CO + 2\ Al = Al_2O_3 + 3\ C.$$
$$CO + Mg = MgO + C.$$

In these reactions, then, carbon monoxide is compelled to play the rôle of an *oxidizing agent*, which again shows us that oxidation and reduction are processes that are relative in character.

Carbon monoxide is readily absorbed by an ammoniacal or hydrochloric acid solution of cuprous chloride at room temperatures. The latter solution is much used in estimating carbon monoxide in gas analysis. From these solutions carbon monoxide may be expelled by heating.

Physiological Effects of Carbon Monoxide. — *Carbon monoxide is a very poisonous gas*, and is all the more dangerous because it is odorless, and so does not betray its presence till it has already produced toxic effects. The gas unites with the hemoglobin of the blood, forming an addition product which is bright red in color and very stable. This fact was discovered in 1826 by Piorry. The carbon monoxide hemoglobin is much more stable than the oxyhemoglobin. Air containing as low as one-twentieth of one per cent carbon monoxide exerts toxic effects. These manifest themselves as headache, unconsciousness, convulsions, and finally death, which is caused by about 100 cc. of pure carbon monoxide for every 10 kilograms of weight of the person or animal inhaling the substance. The resuscitation of persons poisoned by inhaling carbon monoxide is effected by means of fresh air, in very mild cases. In serious cases, oxygen must be supplied, preferably under pressure of from one and one half to two atmospheres. As carbon monoxide is commonly produced in coal stoves, it is necessary to provide suitable draught to burn the gas completely, or at any rate to carry off the products of combustion so that they cannot escape into the room. Water gas, which, as we have seen, contains about 50 per cent carbon monoxide, is doubtless more poisonous than ordinary illuminating gas made by heating coal.

Carbon Bisulphide. — When sulphur vapor is passed over charcoal or coke heated to redness, carbon bisulphide CS_2 is formed. It is also called carbon disulphide. The carbon is heated in a tall iron cylinder, and the sulphur vapors are passed upward through the hot coal, the product being conducted off in tubes and condensed to a liquid. The heating is now generally accomplished by means of electricity. The continuous process thus devised by E. R. Taylor represents a very great improvement over older methods. Figure 88 represents the Taylor furnace. Pieces of coke are placed between the electrodes *E*, which are supplied with a strong alternating current. The heat produced melts and volatilizes the sulphur *S*, which is continuously supplied through *B*. The coke is renewed through *C*. The tower is filled with charcoal which is introduced from above through *D*. The carbon disulphide vapors pass off through *A* to the condensers. This furnace is 40 ft. high and 16 ft. in diameter.

Carbon bisulphide forms a colorless, volatile liquid of not unpleasant ethereal odor when pure. As it usually comes in the market, it is slightly yellowish in color and has a disagreeable odor, which is due to impurities. These readily form on standing, especially in presence of moisture, because of slight decomposition of the carbon disulphide. The latter has a specific gravity of 1.262 at 20°; its vapor is 2.68 times as heavy as air. *Carbon disulphide is an extremely inflammable liquid and is consequently* **dangerous** *to handle.* The vapors catch fire in the air when heated to but 232°. *Mixed with air, its vapors are explosive.* Carbon disulphide burns with a blue flame, forming carbon dioxide and sulphur dioxide: —

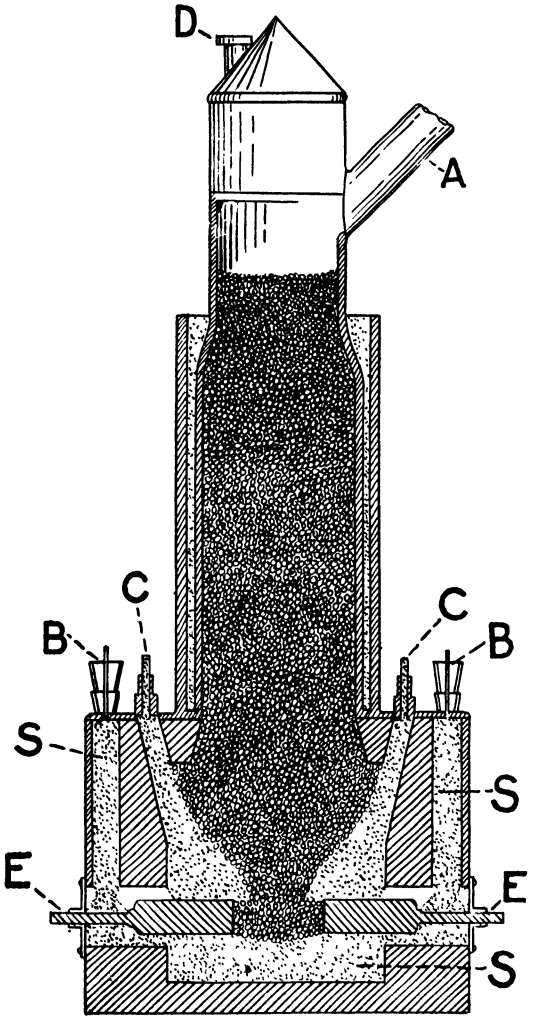


FIG. 88.

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

Carbon disulphide is a good solvent for fats, oils, iodine, rubber, and sulphur. It is used as a solvent for fats and oils on a large scale, also for vulcanizing rubber. It is further employed in exterminating ants, lice, and other insect pests. When in-

haled, its vapors act as an anæsthetic, large quantities producing intoxications and serious disturbances of the nervous system.

Carbon disulphide CS_2 is analogous to carbon dioxide CO_2. Just as CO_2 forms carbonates with oxides of alkalies, so CS_2 forms analogous compounds, namely **trithiocarbonates**, with sulphides of alkalies: —

$$CaO + CO_2 = CaCO_3.$$
$$CaS + CS_2 = CaCS_3.$$
$$K_2S + CS_2 = K_2CS_3.$$

By treating a trithiocarbonate with a dilute acid, **trithiocarbonic acid** H_2CS_3 is liberated as an unstable oil which decomposes readily into CS_2 and H_2S, thus showing great analogy to H_2CO_3: —

$$H_2CO_3 = H_2O + CO_2.$$
$$H_2CS_3 = H_2S + CS_2.$$

Cyanogen. — Under ordinary conditions, carbon and nitrogen do not combine with each other; but at high temperatures in presence of carbonates of the alkalies or oxides of the alkaline earth metals, **cyanides** are formed. These are compounds containing carbon, nitrogen, and the alkali metal employed. Thus, nitrogen passed over a mixture of carbon and fused potassium carbonate yields potassium cyanide: —

$$K_2CO_3 + 3\,C + N_2 = 2\,KCN + CO + CO_2.$$

In this reaction, metallic potassium is formed, which then unites with the carbon and nitrogen to form potassium cyanide. *Whenever any carbon compound containing nitrogen is heated with metallic potassium, potassium cyanide results*, which fact is used as a test for nitrogen in organic compounds. When calcium oxide is employed, the cyanide of calcium is formed: —

$$CaO + 3\,C + N_2 = Ca(CN)_2 + CO.$$

On passing ammonia over carbon heated to redness, ammonium cyanide is produced: —

$$2\,NH_3 + C = NH_4CN + H_2.$$

The cyanides are salts derived from hydrocyanic acid HCN (which see). On heating mercuric cyanide $Hg(CN)_2$, it decomposes, yielding mercury and cyanogen, thus: —

$$Hg(CN)_2 = Hg + (CN)_2.$$

This reaction is quite similar to that of the decomposition of mercuric oxide by heat. Cyanogen is an extremely poisonous, colorless gas of sharp characteristic odor. It may be condensed to a colorless liquid that boils at $-21°$. The solid melts at $-35°$. The gas burns with a beautiful purple flame. In water, the gas is readily soluble, also in alcohol. Cyanogen gets its name from the fact that it enters into a number of compounds that are blue in color.

Hydrocyanic Acid. — Hydrocyanic acid, or **Prussic acid,** has the composition HCN. It is formed when **potassium cyanide** is treated with hydrochloric acid: —

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

It may also be prepared by treating **potassium ferrocyanide** $K_4Fe(CN)_6 + 3\,H_2O$ with dilute sulphuric acid, thus: —

$$2\,K_4Fe(CN)_6 + 3\,H_2SO_4 = 6\,HCN + 3\,K_2SO_4 + K_2Fe\cdot Fe(CN)_6.$$

The potassium ferrocyanide is prepared by heating animal refuse, like blood, hoofs, horns, etc., with iron and potassium carbonate. The product, when purified, forms beautiful lemon-yellow crystals of the composition $K_4Fe(CN)_6 + 3\,H_2O$. It is known also as the **yellow prussiate of potash.**

Hydrocyanic acid is an **extremely poisonous,** colorless, mobile liquid, which smells like bitter almonds. It boils at 26°. The colorless crystalline solid melts at $-11°$. Hydrocyanic acid is a very weak acid which is readily soluble in water and alcohol. Its salts are also **very poisonous.** One twentieth of a gram of hydrocyanic acid is sufficient to cause death in case of a human being. The best antidote consists of a 3 per cent solution of hydrogen peroxide, which acts thus: —

$$H_2O_2 + 2\,HCN = H_2NOC - CONH_2.$$

The latter compound is called **oxamide.**

Hydrocyanic acid is used to kill insects that infest shrubs and fruit trees. It is also at times used in medicine. It affects chiefly the respiratory organs.

Cyanates and Sulphocyanates. — On heating potassium cyanide with lead oxide, potassium cyanate KCNO is formed: —

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

The free **cyanic acid** HCNO is a liquid which readily decomposes into ammonia and carbon dioxide when treated with water : —

$$H_2O + HCNO = NH_3 + CO_2.$$

Fused with sulphur, potassium cyanide forms **potassium sulphocyanate** KCNS : —

$$KCN + S = KCNS.$$

The free acid HCNS is extremely unstable. With ferric salts potassium sulphocyanate forms ferric sulphocyanate $Fe(CNS)_3$, which is blood-red in solution, and serves as a delicate test for ferric salts.

The fact that cyanides pass over into cyanates and sulphocyanates shows that cyanides are really unsaturated in character.

REVIEW QUESTIONS

1. What are the different allotropic forms of carbon? How do we know that the different substances you have mentioned consist of carbon only?

2. How is artificial graphite produced? Mention some of its uses. What use is made of the other forms of carbon you have named in answer to question 1.

3. Discuss the occurrence, kinds, and supposed origin of coal.

4. Describe three methods of preparing each of the two oxides of carbon, giving the equations expressing the changes that take place.

5. How much carbon dioxide could be prepared from 37 grams of carbon? What volume would this gas occupy under standard conditions? What was the volume of the oxygen consumed in preparing the carbon dioxide?

6. What are the chief chemical characteristics of carbon?

7. What use is made of carbon dioxide? Upon what property of this substance does each use mentioned depend?

8. What is a carbonate? Give five illustrations, and write the equation showing how each reacts when treated with hydrochloric and sulphuric acid respectively. Compare this with the action of these acids upon the corresponding sulphites.

9. What is a bicarbonate? Give two examples. Are bicarbonates of practical importance? Why? How do carbonates and bicarbonates behave when heated?

10. Why does the percentage of carbon dioxide in the atmosphere not increase continually due to the breathing of animals and the combustion of fuel?

11. What is meant by the carbon cycle?

12. What is the valence of carbon in sodium carbonate? In carbon monoxide? What use is made of the latter gas?

13. What is water gas? Write the equation expressing its mode of formation. What is producer gas, and how is it made?

14. How much carbon disulphide could be made from two tons of sulphur? How could this be done? What use could be made of the carbon bisulphide? Why is the latter a dangerous substance?

15. Describe a way of making Prussic acid. What other name has the substance? What are its characteristics and uses?

16. Give the formulas of the following and write one characteristic reaction in which each occurs: potassium ferrocyanide, potassium sulphocyanate, mercuric cyanide.

17. State the volume relations in each of the following equations:

$$CO_2 + C = 2\,CO;\quad S + O_2 = SO_2;\quad 2\,NO + O_2 = 2\,NO_2;$$
$$2\,H_2S + 3\,O_2 = 2\,SO_2 + 2\,H_2O;\quad 2\,NH_3 + 3\,Cl_2 = 6\,HCl + N_2.$$

18. How much barium carbonate can be made from 18 grams of barium hydroxide?

19. How much calcium sulphate may be formed by treating 25 pounds of calcium carbonate with sulphuric acid, and how much acid would this require?

20. Write the equation showing how nitric acid acts when used as an oxidizing agent, and then use this equation to show the oxidation of carbon to carbon dioxide by means of nitric acid.

CHAPTER XV

HYDROCARBONS AND ADDITIONAL COMPOUNDS OF CARBON

Hydrocarbons. — Hydrocarbons are compounds of hydrogen and carbon. They are very numerous, nearly three hundred being known. The simplest hydrocarbon is **marsh gas**, or **methane** CH_4. It issues from the decaying vegetable matter in ditches and marshes on warm summer days, hence its popular name, marsh gas. Methane, together with hydrogen, is a prime constituent of **natural gas**, which is found in the coal and oil regions of Indiana, Ohio, Pennsylvania, and other states. Methane may be prepared artificially by a process to be described later. **Petroleum** is essentially a mixture of hydrocarbons. The chief petroleum fields are located in Pennsylvania, New York, Ohio, Indiana, Kentucky, Kansas, Texas, Colorado, California, and Canada. Less extensive deposits are found in Russia near the Caspian Sea and Black Sea, in China, India, and Japan. The hydrocarbons in American petroleum practically all belong to the so-called **paraffin series**, of which methane is the first and simplest member. The following table gives a number of hydrocarbons of this series : —

Name	Formula	Boiling Point
Methane	CH_4	− 160°
Ethane	C_2H_6	− 93°
Propane	C_3H_8	− 45°
Butane	C_4H_{10}	+1°
Pentane	C_5H_{12}	37°
Hexane	C_6H_{14}	69°
Heptane	C_7H_{16}	98°
Octane	C_8H_{18}	125°
Nonane	C_9H_{20}	149.5°

It will be noted that the boiling points increase with the carbon content, and that the first three substances are gases at

ordinary temperatures. *The difference in composition between any two adjacent members is* CH_2, *and any series of compounds in which this is the case is called an* **homologous series.** The series above given is the so-called **normal paraffin series.** The general formula for any of its members is C_nH_{2n+2}. Of this series, compounds containing up to sixty carbon atoms are known. The higher members are solids. Thus pentadecane $C_{15}H_{32}$ melts at $+10°$; eicosane $C_{20}H_{42}$ melts at 36.7°; heptacosane $C_{27}H_{56}$ melts at 59.5°; and hexacontane $C_{60}H_{122}$ melts at 102°. In the members of this series, carbon is quadrivalent, and the compounds are called saturated hydrocarbons.

When crude petroleum is placed in a retort and subjected to fractional distillation the following fractions are obtained:—

Cymogene (mainly butane),	B. P. about 0° C.
Rhigolene (butane and pentane),	B. P. about 16°.
Petroleum ether (pentane and hexane),	B. P. about 50° to 60°.
Gasoline (hexane and heptane),	B. P. about 70° to 90°.
Naphtha (heptane and octane)	B. P. about 90° to 120°.
Benzine (octane and nonane),	B. P. about 110° to 140°.
Kerosene (nonane to heptadecane),	B. P. about 150° to 300°.

Naphtha is also sometimes called **ligroin.** Above 300° heavy oils pass over which are used as **lubricating oils.** At still higher temperatures, **vaseline** is obtained, which consists mainly of $C_{19}H_{40}$ to $C_{21}H_{44}$. Finally, from the residue in the retort **paraffin** is separated out at low temperatures. Paraffin is a white waxlike substance consisting of $C_{21}H_{44}$ to $C_{32}H_{66}$ and melting from 45° to 70° C. according to composition. **Petroleum ether** is used as a solvent, also in making illuminating gas, and as an anæsthetic. For the latter purpose it must be specially purified. Sometimes a mixture of the first four products named in the last table is called petroleum ether. **Gasoline, naphtha,** and **benzine** are also used as solvents and frequently as fuels in stoves and engines. They are also employed in gas manufacture. Benzine is frequently used in paints and varnishes as a substitute for turpentine. **Kerosene** is used as a fuel and for purposes of illumination. There are different grades of kerosene. These vary as to color and fire test or flash point; *i.e.* the temperature at which evaporation is sufficient so that the vapors may be lighted in the air. Kerosene having a flash point of 110° F. is safe for use in lamps;

this is the standard flash test fixed by law in most of the states, but sometimes a test of 150° F. is required. In purifying kerosene it is washed with sulphuric acid, then with an alkali, and finally with water.

Paraffin lubricating oils are now very much used particularly in gas and gasoline engines. Vaseline is used in ointments of various kinds. In crude form, it serves as **cup grease** and **axle grease**. Paraffin is used in making candles and chewing gum, also in making paper and fabrics waterproof, in insulating wires and electrical apparatus of various kinds, in manufacturing matches, and in the laundry. Crude oils from the Texas and California fields are used for the preservation of railroad ties, which are saturated with the oils before using.

Hydrocarbons may be prepared in several ways. *The common method of making methane is by heating sodium acetate with lime or caustic soda:* —

$$CH_3COONa + NaOH = Na_2CO_3 + CH_4.$$

The higher hydrocarbons may be prepared in a similar way by using salts of acids of higher carbon content. Thus to prepare propane, sodium butyrate is heated with a caustic alkali: —

$$C_3H_7COONa + NaOH = Na_2CO_3 + C_3H_8.$$

Hydrocarbons may also be formed by treating carbides of metals with water. Thus aluminum carbide and water yield methane: —

$$Al_4C_3 + 12\ H_2O = 4\ Al(OH)_3 + 3\ CH_4.$$

The carbide of aluminum may be prepared by heating oxide of aluminum with carbon in the electric furnace, when the following reaction occurs: —

$$2\ Al_2O_3 + 9\ C = 6\ CO + Al_4C_3.$$

Other simple methods of preparing hydrocarbons consist of treating halogen substitution products with nascent hydrogen or with sodium: —

$$\underset{\text{methyl iodide}}{CH_3I} + 2\ H = HI + \underset{\text{methane}}{CH_4}.$$

$$2\ CH_3I + 2\ Na = 2\ NaI + \underset{\text{ethane}}{C_2H_6}.$$

Hydrocarbons act neither as acids nor as bases, and thus they differ materially from the hydrides of such elements as nitrogen, sulphur, and the halogens.

Ethylene C_2H_4, also called **olefiant gas**, is the first of an homologous series of unsaturated hydrocarbons whose general formula is C_nH_{2n}. Ethylene may be prepared by heating alcohol with concentrated sulphuric acid, which abstracts water from the alcohol: —

$$C_2H_5OH + H_2SO_4 = H_2SO_4 \cdot H_2O + C_2H_4.$$

The relation of ethylene to **ethane** C_2H_6 is readily seen from the following graphic formulæ: —

$$\underset{\text{ethane}}{\begin{matrix} H & H \\ | & | \\ H-C-C-H, \\ | & | \\ H & H \end{matrix}} \qquad \underset{\text{ethylene}}{\begin{matrix} H & H \\ | & | \\ C=C, \\ | & | \\ H & H \end{matrix}} \qquad \text{or} \qquad \begin{matrix} H & H \\ | & | \\ -C-C- \\ | & | \\ H & H \end{matrix}$$

When ethane is treated with bromine, substitution takes place: —

$$C_2H_6 + Br_2 = C_2H_5Br + HBr;$$

ethylene, however, reacts as follows: —

$$C_2H_4 + Br_2 = C_2H_4Br_2.$$

That is, **ethylene bromide** $C_2H_4Br_2$, a colorless liquid, is formed, showing that ethylene is unsaturated, the two free bonds manifesting themselves in the fact that the hydrocarbon is able to unite with two atoms of bromine by simple addition. This is characteristic of all of the members of the ethylene series, and is often expressed by the so-called **double bond**, $\begin{matrix} | & | \\ -C=C- \end{matrix}$, which, however, is not a source of additional strength. It simply indicates that the compound is unsaturated, *i.e.* is capable of forming addition products, as above illustrated. *Ethylene gas burns with a luminous flame.*

Acetylene C_2H_2 is the lowest member of an homologous series of hydrocarbons of the general formula C_nH_{2n-2}. Acetylene gas may be produced by passing ethylene through red-hot tubes: —

$$C_2H_4 = C_2H_2 + H_2.$$

It is also formed to some extent when a Bunsen burner burns below, that is, has "struck back." However, the gas is best prepared by the action of calcium carbide on water: —

$$CaC_2 + 2\ H_2O = Ca(OH)_2 + C_2H_2.$$

Acetylene burns with a very bright, luminous flame. It is consequently often used for illuminating purposes. Acetylene is still less saturated than ethylene, which fact is expressed by the formula $HC \equiv CH$, or more frequently by $H - C \equiv C - H$. The **triple bond**, or **acetylene bond**, indicates the unsaturated condition of the compound, *i.e.* its ability to unite with four additional atoms of halogen, for instance.

Benzene C_6H_6 (not to be confounded with the petroleum product, benzine, which is entirely different) is a colorless, mobile liquid of specific gravity 0.8799 at 20°, boiling at 80°. The compound forms crystals that melt at 6°. Benzene is obtained as the light oil from coal tar. It is the first member of an homologous series of hydrocarbons of the general formula C_nH_{2n-6}. It burns with a luminous flame, and is an excellent solvent for fats, resins, iodine, sulphur, and phosphorus. *From benzene many very important substances like carbolic acid, aniline, the coal-tar dyes, and many medicinal and aromatic substances are derived.* Because of the aromatic odor of the hydrocarbons of the benzene series and their derivatives, they are commonly called the **aromatic series.** The hydrocarbons of the paraffin series and their derivatives are also known as the **fatty series,** for the fats commonly belong to this series.

Naphthalene $C_{10}H_8$ forms shining leaflets that melt at 79°. It occurs in coal tar and gives the latter its peculiar odor. In form of **moth balls** naphthalene is used to protect woolen goods from moths. Naphthalene is closely related to benzene.

General Behavior of Hydrocarbons. — *All hydrocarbons burn, and when the combustion is complete, the products formed are carbon dioxide and water. Gaseous hydrocarbons, or the vapors of all light hydrocarbon oils, are inflammable.* With oxygen or air, they form mixtures that explode when brought in the neighborhood of a flame. The larger the carbon content of the molecule of a hydrocarbon, the more luminous is the flame with which it burns (see luminosity of flames).

On the whole, hydrocarbons are rather inert substances chemically. They are practically insoluble in water, but they are miscible with one another in all proportions. They dissolve fats, oils, ether, alcohol, carbon disulphide, and many other substances of kindred character.

Halogen Substitution Products. — When methane is treated with chlorine in the sunlight, the hydrogen atoms may be replaced one after another by chlorine as indicated by the following equations: —

$$CH_4 + Cl_2 = \underset{\text{methyl chloride}}{CH_3Cl} + HCl.$$

$$CH_3Cl + Cl_2 = \underset{\text{dichlormethane}}{CH_2Cl_2} + HCl.$$

$$CH_2Cl_2 + Cl_2 = \underset{\text{chloroform}}{CHCl_3} + HCl.$$

$$CHCl_3 + Cl_2 = \underset{\text{carbon tetrachloride}}{CCl_4} + HCl.$$

Chloroform, a heavy colorless liquid boiling at 61°, is very important as an anæsthetic. The corresponding bromine compound, **bromoform** $CHBr_3$, is also known. It is a liquid boiling at 151°; while **iodoform** CHI_3, a yellow crystalline solid melting at 119°, is used in dressing wounds.

Carbon tetrachloride boils at 76°. It is not inflammable like gasoline, though like the latter it dissolves fats readily. Hence carbon tetrachloride is often used as a solvent, particularly for cleaning clothes, being less dangerous to handle than volatile hydrocarbons.

We have already seen that unsaturated hydrocarbons may form simple addition products with halogens.

Alcohols. — On treating **methyl chloride** with caustic potash, the following reaction occurs: —

$$CH_3Cl + KOH = KCl + \underset{\text{methyl alcohol}}{CH_3OH}.$$

The radical CH_3 is called **methyl.** There are many similar hydrocarbon radicals, which are also called **alkyl radicals.** So, for instance, we have: **ethyl** C_2H_5, in **ethyl chloride** C_2H_5Cl; **propyl** C_3H_7, in **propyl iodide** C_3H_7I; **phenyl** C_6H_5, in **phenol** C_6H_5OH. *These radicals may pass from one compound to another precisely as the radical ammonium* NH_4 *does in ammonium compounds.*

Now CH_3OH or methyl hydroxide is **methyl alcohol.** It is also called **wood alcohol,** or spirit of wood, for it may be obtained as one of the products of the dry distillation of wood. We note that methyl alcohol is an hydroxide. Indeed, we may regard it as water with one hydrogen atom replaced by methyl, or as

sodium hydroxide with the sodium atom replaced by methyl. *All alcohols are hydroxides of alkyl radicals, and the general formula of an alcohol is* R—OH *where* R *stands for an alkyl radical.* Thus, C_2H_5OH, or ethyl alcohol, is ordinary alcohol; C_3H_7OH is propyl alcohol; C_4H_9OH, butyl alcohol; and so on up the homologous series, the higher members of which, like $C_{16}H_{33}OH$, cetyl alcohol, and $C_{30}H_{61}OH$, melissyl alcohol, are waxlike solids.

Ethyl alcohol, or ordinary alcohol, is also called **spirit of wine**, for it may be obtained by distilling wine. When thus prepared it contains other aromatic substances from the wine.

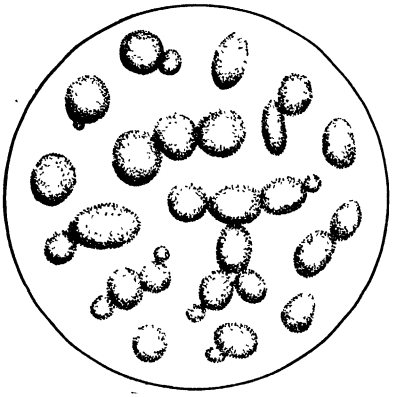


FIG. 89.

Alcohol is contained in all fermented liquors. It may readily be prepared by fermentation of glucose with yeast, thus: —

$$\underset{\text{glucose}}{C_6H_{12}O_6} = 2\,\underset{\text{alcohol}}{C_2H_5OH} + 2\,CO_2.$$

Figure 89 shows a common form of yeast cells as they appear under the microscope.

Pure alcohol boils at 78° and solidifies at about — 130°. **Beers** contain from 3 to 5 per cent alcohol, **wines** from 8 to 20 per cent, and **brandy**, **whisky**, and **rum** from 45 to 65 per cent.

By adding wood alcohol or other poisonous substances to ethyl alcohol, the latter is made unfit for use as a beverage, and is said to be "denatured." Usually about 10 volumes of wood alcohol and half a volume of benzene are added to 100 volumes of 90 per cent alcohol to make so-called **denatured alcohol**. The latter may be used as fuel or for purposes of manufacturing, without the payment of duty.

When ethyl alcohol is treated with phosphorus trichloride, the following change takes place: —

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

Thus chlorine is substituted for the OH group. *All alcohols undergo a similar change when treated with either phosphorus chloride, bromide, or iodide.* The halogen takes the place of the

hydroxyl, and phosphorous acid is formed. Indeed, this fact is used to ascertain whether the OH group is present in a compound. The number of such groups may also be determined thus by the number of halogen atoms that enter the molecule. Water itself reacts perfectly analogously with phosphorus trichloride, as is evident from the following equations: —

$$3\ H_2O + PCl_3 = P(OH)_3 + 3\ HCl.$$
$$3\ C_4H_9OH + PCl_3 = P(OH)_3 + 3\ C_4H_9Cl.$$

When treated with sodium, the hydrogen of the OH group of an alcohol is replaced, thus:

$$2\ C_2H_5OH + 2\ Na = 2\ \underset{\substack{\text{sodium}\\\text{alcoholate}}}{C_2H_5ONa} + H_2.$$

This is perfectly analogous to what happens when water is treated with sodium: —

$$2\ H_2O + 2\ Na = 2\ HONa + H_2.$$

Just as we have hydroxides of the metals which contain more than one hydroxyl group, like $Ca(OH)_2$, $Bi(OH)_3$, $Sn(OH)_4$, so we also have alcohols that contain two or more hydroxyl groups. Thus, we have: —

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$ glycol,
$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$ glycerine, and
$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$ mannite.

Glycol and **glycerine** are rather viscous liquids that mix with water in all proportions. They are slightly sweet. Moreover, the sweet taste increases as we go up the series from glycol to mannite. **Erythrite**, which contains four carbon atoms and four hydroxyl groups, and **arabite**, which contains five carbon atoms and five hydroxyl groups, are also well known, though they are of no practical importance. These alcohols are called **polyhydric alcohols.** They may act towards acids like bases, forming salts which are called esters (which see). **Mannite** is

a beautifully crystalline substance which readily dissolves in water, but not in hydrocarbons. It is closely allied to the sugars (which see). Taken internally, mannite acts as a mild purgative. All the polyhydric alcohols are soluble in water, and from erythrite up they are solids under ordinary conditions.

Phenols. — The hydroxyl derivatives of benzene C_6H_6 are called **phenols.** The simplest of these is C_6H_5OH. It is called phenol, or more commonly *carbolic acid.* It is really not an acid, though it does exhibit acidic properties to some extent. Thus with caustic alkalies it forms **phenolates**:

$$C_6H_5OH + KOH = \underset{\substack{\text{potassium}\\\text{phenolate}}}{C_6H_5OK} + H_2O.$$

Alcohols do not form alcoholates when treated with caustic alkalies. It will be recalled that it is necessary to treat alcohols with metallic sodium or potassium to form the corresponding alcoholates.

Carbolic acid crystallizes in long needles that melt at 42° and turn pink when exposed to the air. In water it is but sparingly soluble, about 1 part dissolves in 15 parts of cold water; but in alcohol and many other organic liquids it dissolves much more copiously. Carbolic acid has a characteristic odor and is very poisonous, whence its use as a disinfectant and antiseptic. When brought in contact with the skin it exerts a corrosive action.

Among the phenols containing more than one hydroxyl group **hydroquinone** $C_6H_4(OH)_2$ and **pyrogallol** $C_6H_3(OH)_3$, also called **pyrogallic acid**, are of importance as developers in photography (which see). Further, in the incomplete combustion and dry distillation of wood there are formed, along with other products, phenols, notably **guajacol** $C_6H_4(OCH_3)OH$ and **kreosol** $C_6H_3(CH_3)(OCH_3)OH$, a mixture of which is called **creosote.** These give the smoke a penetrating odor and antiseptic value that is used in preserving meats, sausages, and fish.

Aldehydes. — On careful oxidation of alcohols, aldehydes are formed, which are compounds containing two hydrogen atoms less than the alcohol from which they may be obtained, whence the name alcohol dehydrogenatum, abbreviated aldehyde. So when methyl alcohol is partially oxidized by means of potassium

permanganate, or incomplete combustion, the following change takes place: —

$$CH_3OH + O = H_2O + \begin{matrix} H \\ | \\ C \\ | \\ H \end{matrix} = O.$$

The product, **formaldehyde**, is a gas which may be condensed to a liquid that boils at − 21°. It has a penetrating, suffocating odor, acts strongly on the mucous membranes, and is a powerful antiseptic. In water it dissolves up to about 40 per cent, and it is this aqueous solution that is sold under the name of **formaline.** It is used as a disinfectant, antiseptic, or preservative in various strengths as required. All the aldehydes are very active chemically, being specially strong as reducing agents. We may regard formaldehyde as carbon dioxide with one oxygen atom replaced by two hydrogen atoms (see formula above). By some it is thought that formaldehyde is the first product formed when water and carbon dioxide act upon each other in the green leaf of the plant in the sunlight, forming starch and liberating oxygen.

Just as the hydrocarbons, their halogen substitution products, and the alcohols form homologous series, so the aldehydes form similar series. Thus, we have formaldehyde HCHO, **acetic aldehyde** CH_3CHO, **propionic aldehyde** C_2H_5CHO, etc.; further, **benzoic aldehyde** C_6H_5CHO, also called **oil of bitter almonds**, and its homologues.

When the hydrogen atoms of the methyl group in acetic aldehyde are replaced by chlorine, $CCl_3 \cdot CHO$ is formed. This is trichloraldehyde, or **chloral.** It readily unites with water, forming the white crystalline addition product $CCl_3CH(OH)_2$, **chloral hydrate,** which is so much used in medicine as a soporific.

The general formula of an aldehyde is $R - \begin{matrix} C = O, \\ | \\ H \end{matrix}$ *in which* R *represents either hydrogen or an alkyl radical.*

Organic Acids. — On further oxidation of aldehydes, acids are produced. In this process one molecule of aldehyde takes up an additional atom of oxygen. The reactions in the formation of formic and acetic acids from formic and acetic aldehydes may be represented as follows: —

$$\begin{array}{lll} H-C=O & +O= & H-C=O; \\ \quad | & & \quad | \\ \quad H & & \quad OH \\ \text{formic aldehyde} & & \text{formic acid} \end{array}$$

$$\begin{array}{lll} CH_3-C=O & +O= & CH_3-C=O. \\ \quad | & & \quad | \\ \quad H & & \quad O-H \\ \text{acetic aldehyde} & & \text{acetic acid} \end{array}$$

In general, the reaction may be represented thus: —

$$\begin{array}{lll} R-C=O & +O= & R-C=O, \\ \quad | & & \quad | \\ \quad H & & \quad OH \\ \text{aldehyde} & & \text{organic acid} \end{array}$$

R representing either hydrogen or any organic radical. *The last formula above given is the general formula of an organic acid.* The characteristic group which it contains, namely, $-C=O$ (with OH below the C), or COOH, is called the **carboxyl group**. The hydrogen in this group is replaceable by metals or radicals, just as, for instance, the hydrogen in nitric acid may be thus replaced.

Only a few typical organic acids can be mentioned here. **Formic acid** H·COOH occurs in red ants and stinging nettles. It is a colorless liquid boiling at 101°. It is soluble in water in all proportions, has a pungent odor, and blisters the skin. With bases it forms the formates, thus: —

$$HCOOH + NaOH = \underset{\text{sodium formate}}{HCOONa} + H_2O.$$

The acid is consequently monobasic, only one hydrogen atom being replaceable by a metal. When heated in closed vessels to 160°, formic acid yields carbon dioxide and hydrogen: —

$$HCOOH = CO_2 + H_2.$$

Sodium formate may be obtained by passing carbon monoxide over heated caustic soda, and from the formate the free acid may be obtained by means of sulphuric acid, thus: —

$$NaOH + CO = HCOONa;$$
$$HCOONa + H_2SO_4 = NaHSO_4 + HCOOH.$$

Acetic acid CH_3COOH occurs in combination with organic radicals in many odoriferous plant oils. It is formed as one of

the products of the dry distillation of wood. It is made on a large scale in vinegar factories, the process depending on (1) the formation of alcohol by fermentation of sugar produced from the starch in grain, and (2) the oxidation of this alcohol to acetic acid, which is brought about by *Mycoderma aceti*, "mother of vinegar," a bacterium shown in Fig. 90. In practice, the dilute alcohol, 8 to 15 per cent, is allowed to trickle over beechwood shavings contained in a barrel. Thus the alcohol is thoroughly exposed to the oxygen of the air, and the acetic-acid-forming bacteria cause the oxidation to take place. The oxidation process may be represented thus : —

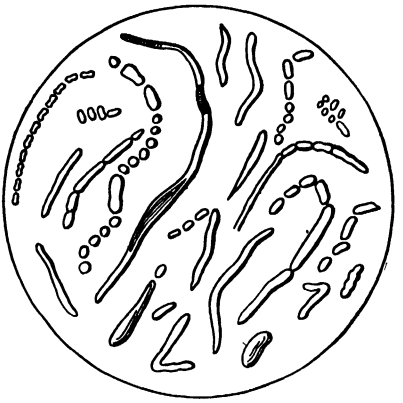


FIG. 90.

$$C_2H_5OH + O_2 = H_2O + CH_3COOH.$$

When alcohol is treated with oxygen alone, this process does not occur ; however, the spores of the acetic-acid-forming bacteria are commonly present in the air, and so various alcoholic solutions like beer and wines get sour because of the oxidation of the alcohol to acetic acid. Cider slowly ferments, forming alcohol, which is then similarly converted into acetic acid. Vinegar obtained as above described is a solution containing essentially 4 to 10 per cent acetic acid. **Anhydrous acetic acid** may be obtained from this solution by forming sodium acetate and then treating the latter salt with sulphuric acid and distilling. The reactions are : —

$$\underset{\text{(in solution)}}{2\ CH_3COOH} + Na_2CO_3 = H_2O + CO_2 + 2\ CH_3COONa.$$

$$\underset{\text{(dry salt)}}{CH_3COONa} + H_2SO_4 = NaHSO_4 + \underset{\text{(glacial acetic acid)}}{CH_3COOH}.$$

The process is then quite similar to the preparation of hydrochloric acid.

Pure acetic acid boils at 118°. It forms crystals that melt at 16.5°, so that it is easy to cause it to solidify on a cold day,

whence the popular name **glacial acetic acid.** The acid has a pungent odor and corrodes the skin. It is a monobasic acid, only one hydrogen atom being replaceable by a basic element or radical. The salts formed are called **acetates.**

Among the homologues of acetic acid are **propionic acid** C_2H_5COOH, **butyric acid** C_3H_7COOH, which smells like rancid butter (in which it occurs), **palmitic acid** $C_{15}H_{31}COOH$, and **stearic acid** $C_{17}H_{35}COOH$. The last two are solids at ordinary temperatures. They occur in fats and oils of plant and animal origin, commonly together with **oleic acid** $C_{17}H_{33}COOH$, an unsaturated acid belonging to another homologous series. These acids occur in fats and oils as esters (which see), not as free acids.

Benzoic acid C_6H_5COOH is the first of an homologous series of acids derived from benzene. It occurs in gum benzoin and Peru balsam; and a derivative of benzoic acid, **hippuric acid** $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot COOH$, occurs in the urine of herbivorous animals. Benzoic acid crystallizes in shining flakes that melt at 121.5°. The boiling point is 249°, but the acid sublimes readily even at 100°. In alcohol, ether, and hot water it readily dissolves, while in cold water it is but sparingly soluble, 1 part in 400. Its odor is very characteristic, and its vapor when inhaled irritates the throat and nasal passages, causing coughing and sneezing. It is much used as an antiseptic and preservative, commonly in the form of **sodium benzoate** C_6H_5COONa. The free acid forms readily by oxidation of benzaldehyde.

Oxalic acid is the simplest dibasic organic acid. Its formula is $H_2C_2O_4$, or

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix};$$

that is, it consists of two carboxyl groups. It is readily formed by oxidizing sugar, sawdust, glycol, fats, and many other organic substances with strong nitric acid. On a commercial scale, sawdust is employed. The normal sodium salt may be obtained by passing carbon dioxide over sodium at 350°, thus: —

$$2\ CO_2 + 2\ Na = (COONa)_2,\ \textit{i.e.}\ Na_2C_2O_4.$$

This salt is also formed when sodium formate is quickly heated to 250°, thus: —

$$2\ HCOONa = H_2 + Na_2C_2O_4.$$

The calcium salt is difficultly soluble in water, and this fact is often used in analytical chemistry, in detecting and estimating calcium. When **calcium oxalate** is heated, there is first formed calcium carbonate and carbon monoxide, after which the carbonate decomposes to calcium oxide and carbon dioxide on further heating, thus: —

$$CaC_2O_4 = CaCO_3 + CO,$$
$$CaCO_3 = CaO + CO_2;$$

or

$$CaC_2O_4 = CaO + CO + CO_2.$$

This behavior is typical of the oxalates of many other metals.

Oxalic acid is oxidized to carbon dioxide and water by oxidizing agents like potassium permanganate, for example, thus: —

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + O = 2\ CO_2 + H_2O.$$

It is evident, then, that *oxalic acid is a good reducing agent.* In the market the acid is commonly sold in form of its white crystalline hydrate $H_2C_2O_4 \cdot 2\,H_2O$. By heating this, the anhydrous acid may be obtained, which on further heating passes over into carbon dioxide and formic acid: —

$$(COOH)_2 = CO_2 + HCOOH.$$

Just as there are homologous series of monobasic organic acids, so there are homologous series of the dibasic acids. So we have **malonic acid** $CH_2(COOH)_2$, **succinic acid** $(CH_2COOH)_2$, etc.

Hydroxycarboxylic acids. — The simplest of these is **glycolic acid**, or hydroxyacetic acid, $CH_2OHCOOH$, which may be produced by careful oxidation of glycol: —

$$\underset{\text{glycol}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}} + 2\,O = \underset{\text{glycolic acid}}{\begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}} + H_2O.$$

Glycolic acid is monobasic, only the hydrogen atom in the carboxyl group being replaceable by a basic element or radical. The other OH group is alcoholic in character. This compound is therefore both an alcohol and an acid. Its homologue, $C_2H_4 \cdot OH \cdot COOH$, is **lactic acid**. It is of great practical

importance. In its pure form it is a thick, colorless, odorless, hygroscopic liquid of pronounced acidic properties. The acid is monobasic, and forms the **lactates** with bases, thus : —

$$C_2H_4 \cdot OH \cdot COOH + KOH = H_2O + C_2H_4OHCOOK.$$

Lactic acid is readily miscible with water, alcohol, and ether in all proportions. Like other hydroxyacids, it cannot be distilled, for it decomposes into various simpler products like CO, H_2O, CH_3CHO, etc., on heating. *Lactic acid is the acid that causes the acidity of sour milk*, whence the name lactic acid. Lactic acid is produced by a special form of fermentation caused by lactic-acid-forming bacteria. These are shown in Fig. 91, together with a few yeast cells to indicate approximately the relative size of the organisms. By the action of these bacteria, starch and sugars are converted into lactic acid, which is consequently formed in many liquids that contain starch, sugars, or kindred organic substances. So, for example, lactic acid occurs in sauerkraut, in sour pickles, in fermented beet juice, and at times in the contents of the alimentary tract. The lactates of strontium and of silver are used in medicine.

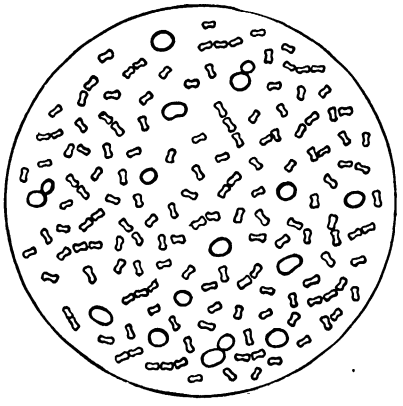
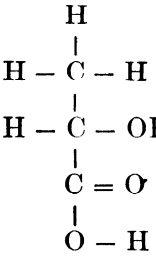


FIG. 91.

Lactic acid also occurs in muscular tissues, but this acid is not quite identical with that in sour milk. So the acid in the muscles, **sarcolactic acid**, has the power to rotate the plane of polarized light; that is, it possesses **optical activity**, a property not exhibited by lactic acid produced by fermentation, which is consequently termed **inactive lactic acid.** Sarcolactic acid turns the plane of polarized light to the right. When the fungus *Penicillium glaucum* is allowed to grow in solutions of fermentation lactic acid, the latter also acquires the power to turn the plane of polarized light to the right, *i.e.* it becomes *dextroactive*, and is in every way identical with sarcolactic acid. Now when the bacillus *Acidi lævolactici* feeds upon

solutions of fermentation lactic acid, the latter acquires the power to turn the plane of polarized light to the left, that is, it becomes *lævoactive*. Fermentation lactic acid is consequently a mixture of equal parts of dextro and lævo lactic acid, which accounts for its optical inactivity. The optical activity is produced as described, because one organism feeds on the dextro variety of the acid, whereas the other organism lives upon the lævo variety. The formula of lactic acid is



This, like all other chemical formulæ, has been established by a study of the methods of synthesizing the compound, and by its deportment toward various reagents. It will be observed that lactic acid has one carbon atom, the center one, whose four bonds are satisfied by four different elements or radicals. Such a carbon atom is called an **asymmetric carbon atom**. *All carbon compounds that are optically active possess at least one asymmetric carbon atom in the molecule;* though, as we have seen, the possession of such an asymmetric carbon atom does not necessarily make the compound optically active, for the substance under consideration may be a mixture of equal parts of the dextro and lævo varieties, as in the case of fermentation lactic acid. In general, for every dextroactive compound there is a lævoactive compound that rotates the plane of polarized light in the opposite direction to the same degree. In order to represent the difference between dextro and lævo compounds by means of formulæ, Le Bel and van't Hoff simultaneously and independently of each other (1874) proposed to represent the carbon atom by a regular tetrahedron the corners of which indicate the four valences. Figure 92 shows the two formulæ for dextro and lævo lactic acids.

It will be observed that the formulæ are alike, but not superposable; that is, they are to each other as the right hand

is to the left hand, or as an object is to its image in the mirror. The study of the composition of carbon compounds by the aid of formulæ thus represented in three dimensions has been carried on with marked success, and has in recent years also been extended to the investigation of compounds of other elements, notably those of nitrogen. The branch of chemistry which seeks to further inquiry by the use of formulæ in three dimensions is called **stereo-chemistry.**

Compounds that contain the same elements in the same proportions by weight are said to be **isomers.** So acetic acid CH_3COOH and methyl formate $HCOOCH_3$ are isomers, for

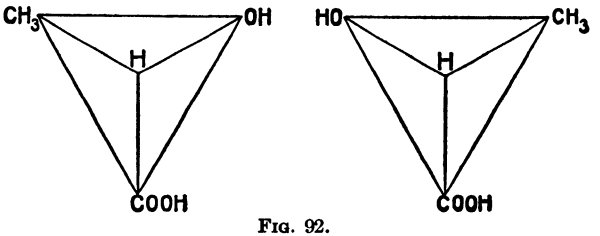


FIG. 92.

they contain the same elements in the same proportions by weight, and yet they are quite different compounds. Dextro and lævo lactic acids also contain the same elements in the same proportions by weight, and in addition they are in every way identical in their chemical behavior. The difference between them lies simply in their behavior toward polarized light and they are consequently called **optical isomers**, or **stereo-isomers**, and the property they thus exhibit is called **stereo-isomerism.**

When an aqueous solution of formaldehyde HCHO is evaporated, an amorphous white substance $(HCHO)_2$, **paraformaldehyde**, separates out. On careful heating, this may be transformed into **metaformaldehyde** $(HCHO)_3$, a crystalline compound melting at 171°, which on being heated to 140° with much water is again decomposed into formaldehyde. Other aldehydes exhibit similar properties. The process of forming larger molecules by simple aggregation of two or more molecules is called **polymerization**, and the new products formed are said to be **polymers.** Polymerization is quite a common process. It will be noted that polymers contain the same elements in the same propor-

tions by weight as the simple compounds from which they have sprung; they are consequently isomers as above defined. When, however, the molecular weight of two isomeric compounds is identical, they are said to be **metameric**, in contradistinction to polymeric, which latter term is applied when the isomerism depends upon difference in molecular weight, as already explained.

The optical activity of substances is examined by means of a **polariscope**, also called a polarimeter, a common form of which

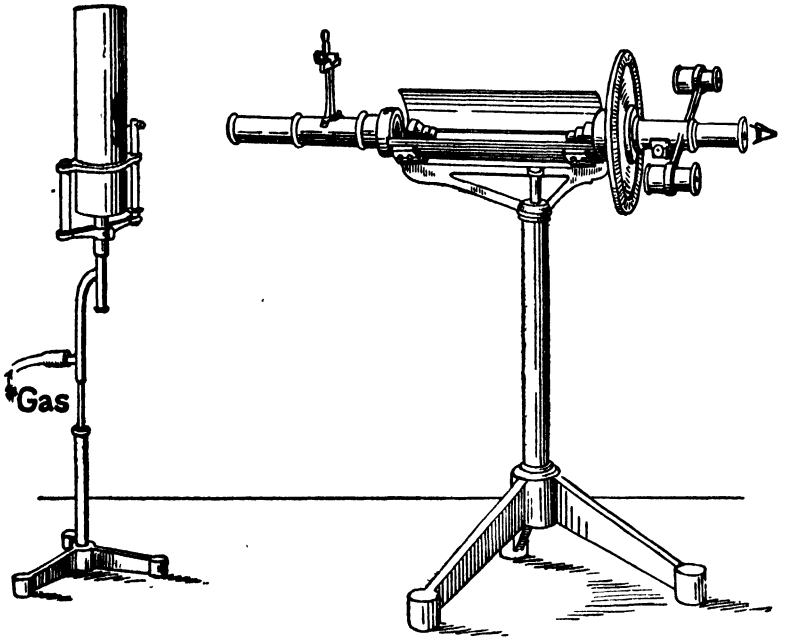
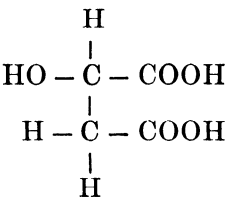


FIG. 93.

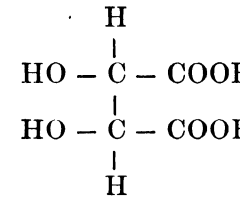
is shown in Fig. 93. The substance to be tested, commonly in the form of a liquid or solution, is placed in a tube between the polarizer and analyzer; that is, the nicol prisms which constitute the vital part of the instrument. The degree of rotation is read off on the scale attached to the analyzer, the yellow sodium flame being usually employed as a source of monochromatic light. The rotation is proportional to the length of the tube and the concentration of the solution or other liquid employed. By concentration is meant the number of grams of active substance contained in one cubic centimeter. *The*

specific rotatory power of any substance is the number of degrees of rotation it exhibits in a tube 1 *decimeter long when* 1 *gram of active substance is contained in* 1 *cc.* Many important substances of commerce, notably sugars, essential oils, and other compounds obtained from plants, possess optical activity. The polariscope serves in detecting the presence of such substances, and also in estimating their amounts when present. So, for example, in estimating the amount of sugar in the juice of sugar beets, the polariscope enables one to obtain very rapid and accurate results.

Malic, tartaric, and citric acids are important fruit acids. Malic acid occurs in sour apples, in mountain ash berries, and in many other fruits. It is monohydroxysuccinic acid:



From the formula it is evident that the acid is dibasic, and that its molecule contains an asymmetric carbon atom. The acid is optically active. This is also true of tartaric acid, which is dihydroxysuccinic acid: —



This acid occurs in grapes as the acid potassium salt $C_4H_5O_6K$, which is difficultly soluble in water and is commonly known as **cream of tartar.** In its pure form this salt is perfectly white; but in its crude state it commonly has a brownish red appearance from the coloring matter of the grapes. In this crude state it is called **argol.** Sodium potassium tartrate $C_4H_4O_6NaK$ is called **Rochelle salt.** It is used as a mild purgative. The acid sodium salt and the normal sodium and potassium salts of tartaric acid are readily soluble in water. They are all optically active. The common variety of tartaric acid is dextro-

active. It forms beautiful monoclinic prisms. The dextro and lævo varieties crystallize in forms that are to each other as an object is to its image in the mirror; that is, they are *enantiomorphous* forms. The fact that dextro and lævo tartaric acids also exhibit dextro and lævo character in their crystal forms was discovered by Louis Pasteur. It was his first notable scientific discovery. Figure 94 shows crystals of dextro and lævo tartaric acid.

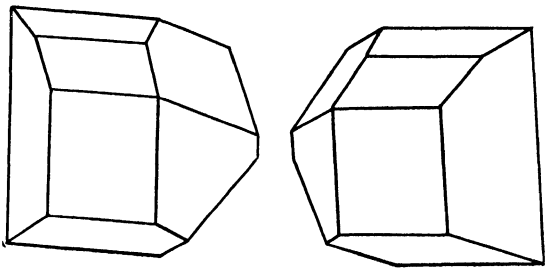
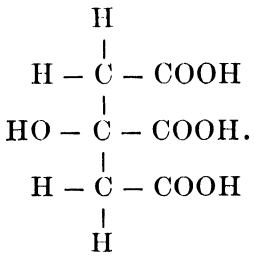


FIG. 94.

In lemons and other citrus fruits citric acid abounds. This is a strong tribasic hydroxyacid whose composition is represented by the following formula: —



It crystallizes with one molecule of water in beautiful rhombic prisms. These melt at 100° and lose their water at 130°. This acid forms three series of salts, for there are three replaceable hydrogen atoms in the molecule. Thus we have: $C_6H_5O_7K_3$, the normal or tertiary potassium citrate; $C_6H_6O_7K_2$, secondary potassium citrate; and $C_6H_7O_7K$, primary potassium citrate.

Malic, tartaric, and citric acids were discovered by the great Scheele. He prepared them by treating fruit juices with lime, thus obtaining the calcium salts, and then decomposing these with sulphuric acid, forming calcium sulphate, which is difficultly soluble, and the free acids. The latter remained in the solutions, from which they were obtained by evaporation.

Esters. — *Esters, or ethereal salts, are formed by replacing the hydrogen of an acid by an alkyl radical.* Just as metallic hydroxides react with acids forming salts and water, so alcohols, which are hydroxides of alkyl radicals, react with acids to form esters and water:—

$$NaOH + HCOOH = HCOONa + H_2O.$$
$$CH_3OH + HCOOH = HCOOCH_3 + H_2O.$$

The compound HCOONa is sodium formate, whereas $HCOOCH_3$ is **methyl formate.** The latter is a typical ester. In making esters, it is common practice to add a dehydrating agent to take up the water formed; usually hydrochloric acid gas is employed, for it has great affinity for water, and can readily be removed afterwards because of its volatility. Ethereal salts of either inorganic or organic acids may be formed. Thus, we have such compounds as **methyl iodide** CH_3I, **ethyl nitrate** $C_2H_5NO_3$, **ethyl nitrite** $C_2H_5NO_2$, **methyl hydrogen sulphate** CH_3HSO_4, **amyl acetate** $CH_3COOC_5H_{11}$, **propyl tartrate** $C_4H_4O_6(C_3H_7)_2$, etc. Many of the simpler esters are mobile liquids of pleasant aromatic odor, which can readily be distilled and purified. *The general formula of an ester of an organic acid is* RCOOR′, *where* R *and* R′ *represent alkyl radicals that may or may not be alike.* Esters occur in flowers, fruits, and other parts of plants, and impart to these their characteristic perfumes or flavors. So amyl acetate, or banana oil, smells like bananas; **methyl butyrate** $C_3H_7COOCH_3$ is known as **pineapple oil**; **methyl salicylate** $C_6H_4(OH)COOCH_3$ is the **oil of wintergreen** (*Gaultheria procumbens*). Again, *many of our well-known fats and oils are esters.* So **olive oil** and **cotton-seed oil** are essentially **trioleine**, an ethereal salt in which the oleic acid radical is united with the glycerine radical which acts as base, thus: $(C_{17}H_{33}COO)_3 \cdot C_3H_5$. Similarly in beef tallow, tripalmitine $(C_{15}H_{31}COO)_3 \cdot C_3H_5$ and tristearine $(C_{17}H_{35}COO)_3 \cdot C_3H_5$ are found together with some trioleine. In fact, *these three esters in which glycerine is the base make up the* **fats.** Trioleine is a liquid at ordinary temperatures, whereas tristearine and tripalmitine are solids. In mutton tallow, which is hard, tristearine predominates, whereas in beef tallow there is more tripalmitine and trioleine. In lard, trioleine is still more abundant, which is indicated by the soft, pasty consistency of the material.

On treating esters with caustic alkalies, decomposition occurs, thus: —

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH.$$

A similar action occurs when esters are boiled simply with water: —

$$CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOH + C_2H_5OH.$$

In this case we have a typical instance of hydrolysis. The action is incomplete, being reversible.

When fats are boiled with caustic soda, glycerine and the sodium salts of stearic, palmitic, and oleic acids result. The latter are soaps. The reactions may be expressed thus: —

$$(C_{15}H_{31}COO)_3C_3H_5 + 3\,NaOH = 3\,C_{15}H_{31}COONa + C_3H_5(OH)_3.$$
$$(C_{17}H_{35}COO)_3C_3H_5 + 3\,NaOH = 3\,C_{17}H_{35}COONa + C_3H_5(OH)_3.$$
$$(C_{17}H_{33}COO)_3C_3H_5 + 3\,NaOH = 3\,C_{17}H_{33}COONa + C_3H_3(OH)_3.$$

In each case the sodium salts are solids soluble in water. By addition of common salt brine these soaps are precipitated or "salted out," while the glycerine remains dissolved. *The potassium salts of mixtures of these higher fatty acids are* **soft soap,** *and the sodium salts are* **hard soap.** The real nature of fats became known through the investigations of the French chemist Chevreul.

The process of decomposing any ester by means of an alkali is called **saponification.** This process is essentially the same in nature, no matter which ester is decomposed.

When a soap solution is mixed with hard water, a curdy white precipitate is formed; this is the calcium soap or calcium salt of the fatty acid. Writing the reaction for **sodium oleate, Castile soap,** and calcium sulphate solution, we have: —

$$2\,C_{17}H_{33}COONa + CaSO_4 = Na_2SO_4 + (C_{17}H_{33}COO)_2Ca.$$

The latter compound is the insoluble calcium soap.

The **cleansing power of soap** depends upon the fact that soap is soluble in water due to its content of sodium or potassium, and that the soap also coalesces with fats because of the large fatty radical it contains. Thus soap loosens the greasy material from the skin or fabrics, forming an emulsion which may be washed away.

Butter fat consists of about 92 per cent of a mixture of triolein, tripalmitine, and tristearine, and about 7.7 per cent of tributyrine, together with smaller amounts of other glycerides that give butter its characteristic flavor. **Butter** usually contains from 12 to 15 per cent water, also minor amounts of salt, casein, and milk sugar. The butter fat in butter amounts to from 82 to 85 per cent.

Nitroglycerine $C_3H_5(NO)_3$ is an ester made by adding glycerine to a well-cooled mixture of nitric and sulphuric acid. The latter serves as a dehydrating agent. Nitroglycerine is a colorless, odorless, viscous liquid which explodes violently when heated rapidly to 200°, or when jarred mechanically. Mixed with infusorial earth, nitroglycerine forms a mass called **dynamite**, which may be transported with far less danger. On treating nitroglycerine with caustic soda, sodium nitrate and glycerine are formed.

Ethers. — *Just as the alcohols are the hydroxides, so the ethers are the oxides of alkyl radicals.* The relations between water, alcohol, and ether on the one hand and metallic hydroxides and oxides on the other hand are illustrated by the following formulæ: —

H_2O water, NaOH sodium hydroxide, Na_2O sodium oxide, $(C_2H_5)OH$ alcohol, $(C_2H_5)_2O$ ether.

Ethers are readily formed by treating alcohols with a dehydrating agent like sulphuric acid. *Ordinary ether is ethyl oxide.* It is made by carefully running alcohol into concentrated sulphuric acid at 140–145°. The reaction is $2\ C_2H_5OH = (C_2H_5)_2O + H_2O$, the water being taken up by the sulphuric acid. For the reason that sulphuric acid is used in the manufacture of ether, the latter is often termed **sulphuric ether.** It, however, does not contain sulphuric acid, for the latter remains behind as the ether distills off.

Ethyl ether is a mobile liquid of agreeable odor. It boils at 35° and its specific gravity at 0° is 0.736. It is **very inflammable.** It is used as an anæsthetic and also as a solvent for fats, oils, and kindred substances. By using other alcohols, ethers of various composition may be prepared.

Sulphur ethers are compounds in which the oxygen of ordinary ethers is replaced by sulphur. Sulphur ethers are volatile, inflammable liquids with an extremely nauseating odor.

They may be regarded as derived from H_2S by replacing the hydrogen atoms by alkyl groups; thus, we have **methyl sulphide** $(CH_3)_2S$, **ethyl sulphide** $(C_2H_5)_2S$, etc.

Ketones. — Acetone is the simplest representative of a class of organic compounds called ketones. It may be prepared by the dry distillation of sodium acetate:

$$2\ CH_3COONa = Na_2CO_3 + \underset{\text{acetone}}{(CH_3)_2CO}.$$

By heating the sodium salts of other acids, other ketones may similarly be formed. The general formula of a ketone is $\begin{matrix} R \\ R \end{matrix}\!\!\rangle C = O$.

Acetone is a colorless, mobile liquid of agreeable odor. Its specific gravity is 0.792 at 20°. It boils at 56.5° and is miscible in all proportions with water or alcohol. Both ketones and aldehydes contain the **carbonyl group** C=O. *In ketones two radicals are combined with the* CO *group, whereas in aldehydes one hydrogen atom and one radical are combined with this group.* Acetone is important as a solvent. It commonly occurs in wood alcohol, being one of the products of the destructive distillation of wood. Acetone is also used in making iodoform.

Carbohydrates. — The carbohydrates are compounds that consist of carbon, hydrogen, and oxygen, the last two elements being present in the same proportions as in water, whence the name carbohydrates. *This is one of the most important groups of compounds, for it contains the substances that are found in greatest abundance in the vegetable world, namely,* (1) *the sugars,* (2) *the starches,* (3) *the celluloses,* (4) *dextrine and gums.*

The most important **sugars** may be divided into two groups, the **monoses**, having the empirical formula $C_6H_{12}O_6$, and the **bioses**, having the formula $C_{12}H_{22}O_{11}$. The monoses are not altered by dilute acids, whereas the bioses are converted into monoses by the action of dilute acids. Among the important monoses are (1) *glucose* $C_6H_{12}O_6$ or $CH_2 \cdot OH \cdot (CH \cdot OH)_4 \cdot CHO$, also known as *grape sugar* or *dextrose;* and (2) *lævulose* $C_6H_{12}O_6$ or $CH_2(OH) \cdot (CHOH)_3CO \cdot CH_2 \cdot OH$, also called *fructose* or *fruit sugar.* From the formulæ, it is evident that these sugars are polyalcohols and that in addition glucose is an aldehyde and lævulose a ketone.

Glucose or **dextrose** occurs in the juice of grapes (whence its name, **grape sugar**) and in many other sweet fruits. It is also found in honey, in the blood, and in the urine of diabetic patients. Solutions of dextrose turn the plane of polarized light to the right, whence the name dextrose. A lævo variety has been made in the laboratory. Dextrose may be prepared from cane sugar by the action of dilute acids. The process, which is called **inversion of cane sugar**, may be represented thus: —

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{lævulose}}{C_6H_{12}O_6}.$$

On evaporation, lævulose remains in solution, while dextrose separates out. Dextrose crystals obtained from aqueous solutions have the composition $C_6H_{12}O_6 + H_2O$. They melt at 86°, whereas the anhydrous substance melts at 146°. The action of yeast readily converts dextrose to alcohol and carbon dioxide, thus: —

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

Solutions of glucose readily reduce hot, alkaline solutions of copper sulphate and Rochelle salt, known as **Fehling's solution**, causing a red precipitate of cuprous oxide Cu_2O to form. This test is much used in practice, particularly in testing the urine of diabetics.

Glucose is only about three fifths as sweet as cane sugar. Glucose is manufactured in large quantities from starch by boiling the latter with dilute sulphuric acid, the reaction being —

$$\underset{\text{starch}}{C_6H_{10}O_5} + H_2O = \underset{\text{glucose}}{C_6H_{12}O_6}.$$

The acid is finally removed by treating with calcium carbonate and filtering off the calcium sulphate formed. In the United States large quantities of glucose are thus made annually from starch obtained from corn.

Lævulose, or **fructose**, commonly occurs with glucose in fruits and in honey. As already stated, it is formed together with glucose, by inverting cane sugar. Crystals of lævulose may be obtained from alcoholic solutions. They melt at 95°. Solutions of lævulose turn the plane of polarized light to the left, whence the name lævulose. Pure lævulose may be obtained

from **inulin** (a starch that occurs in dahlia roots and many other plants) by boiling with dilute sulphuric acid, thus: —

$$\underset{\text{inuline}}{C_6H_{10}O_5} + H_2O = \underset{\text{lævulose}}{C_6H_{12}O_6}.$$

Fructose also reduces Fehling's solution, and by means of yeast it may be converted into alcohol and carbon dioxide.

Among the most important **bioses** are (1) sucrose, or cane sugar, (2) maltose, or malt sugar, (3) lactose, or milk sugar Each of these has the empirical formula $C_{12}H_{22}O_{11}$.

Cane sugar, also called **saccharose** or **sucrose**, $C_{12}H_{22}O_{11}$, is very widely distributed in the vegetable kingdom. Sugar cane contains from 15 to 20 per cent sucrose, and sugar beets in some cases contain up to 20 per cent. It is further found in the juice of the sugar maple, in sorghum, in the flowers of plants, and in many varieties of nuts. Cane sugar crystallizes in beautiful monoclinic prisms (**rock candy**). It is very soluble in water; 1 part dissolves in one third its weight of water at room temperatures. At 160° sucrose melts, and on cooling it solidifies to an amorphous glassy mass called **barley sugar**, which on long standing again becomes crystalline. On heating cane sugar somewhat over 200°, water is given off and a brown substance called **caramel** is formed. As already stated under dextrose, sucrose yields dextrose and lævulose on hydrolysis, the biose being thus split into two monoses. *A cane sugar solution does not reduce Fehling's solution. It does not readily ferment with yeast.* The latter, however, contains an enzyme called **invertase**, which inverts cane sugar, and the fructose and glucose thus formed are then converted into alcohol and carbon dioxide by fermentation.

Nearly ten million tons of sugar are produced annually from sugar cane and sugar beets. The process of preparing sugar commercially consists of expressing the juice from the cane or beets and boiling this with about a 1 per cent solution of milk of lime to neutralize acids, coagulate vegetable albuminous matter, and prevent fermentation. The solution so obtained is then treated with carbon dioxide to remove the excess of lime, and filtered through bone black to decolorize it. It is then concentrated by evaporation in a partial vacuum in so-called vacuum pans, which are heated with steam. The crystals which are deposited on cooling are freed from the adhering

brown mother liquor by centrifugal force in the "centrifugals." The latter consist of sieves rapidly rotated by machinery. The mother liquor is hurled through the meshes of these sieves, and the crystals remain behind almost dry. The drying is completed with the aid of heat. The mother liquor, from which crystals will no longer form because of the presence of various impurities, is called **molasses.** The residue of the cane or beets from which the juice has been extracted is called the **begasse.** It is made into paper or used as fuel.

With lime, cane sugar forms **calcium sucrate** $C_{12}H_{22}O_{11} \cdot CaO$, which is soluble in water. The analogous **strontium sucrate** $C_{12}H_{22}O_{11} \cdot SrO$ is used as a means of recovering further crystallizable sugar from molasses.

Cane sugar solutions rotate the plane of polarized light to the right. The specific rotatory power of cane sugar for sodium light is $+ 66.5°$, while that of dextrose is $+ 52.7°$, and of lævulose $- 93°$. Consequently, solutions of invert sugar, which contain equal parts of dextrose and lævulose, always exhibit lævorotatory power.

Maltose $C_{12}H_{22}O_{11} + H_2O$ crystallizes with one molecule of water, as its formula indicates. It may be formed by the action of **diastase,** a ferment contained in malt, upon starch. Maltose is of importance as an intermediate product in the manufacture of alcohol from starch. Maltose is strongly dextrorotatory, its specific rotatory power being $+ 137°$. On boiling it with dilute mineral acids, dextrose only is produced, showing that maltose is an anhydride of dextrose. Unlike cane sugar, *maltose reduces Fehling's solution, and readily ferments with yeast.*

Lactose $C_{12}H_{22}O_{11} + H_2O$, milk sugar, is found in milk. Like maltose, its crystals contain one molecule of water. It is not as sweet as cane sugar, and is much less soluble in water; 1 part dissolves in 6 parts of water. Lactose is dextrorotatory, its specific rotation being $+ 52.5°$. On boiling with dilute mineral acids, it yields glucose and another monose called **galactose** $C_6H_{12}O_6$, thus: —

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{galactose}}{C_6H_{12}O_6}.$$

Lactose reduces Fehling's solution. But the reduction is less rapid than when glucose is used. Pure yeast does not produce fermentation of milk sugar; but ordinary yeast acts upon milk sugar

as it does upon cane sugar. The products formed are alcohol and lactic acid. Cow's milk contains nearly 5 per cent milk sugar.

Fermentation and Enzymes. — Under fermentation are classed a large number of chemical processes that are produced directly or indirectly by organisms commonly termed **ferments.** These organisms are yeasts, molds, or fungi, and bacteria. They secrete complex compounds called **enzymes,** the chemical nature of which is not yet understood. They seem to be closely related to the albumins and peptones (which see). In the presence of these enzymes, which are also called **unorganized ferments,** fermentation takes place, each enzyme causing its own particular chemical change, which commonly progresses at room temperatures, being accomplished with evolution of heat and frequently with liberation of gas. As a rule the action is checked by either raising or lowering the temperature materially, also by the addition of various poisons. The action of the enzymes is often termed catalytic, for a small amount of enzyme may produce a large amount of change without being itself seemingly affected. Among the common enzymes are: **zymase,** contained in yeast cells, producing alcoholic fermentation; malt **diastase,** contained in malt, converting starch into malt sugar; **invertase,** contained in ordinary yeast, inverting cane sugar and lactose; **emulsin,** contained in bitter almonds; **pepsin,** contained in the stomach juices, aiding in the digestion of albumins; **trypsin,** contained in the intestinal juices, aiding in so-called tryptic digestion.

Starch and Dextrine. — Starch $(C_6H_{10}O_5)_x$ is a carbohydrate found in large quantities in all plants, particularly in tubers like potatoes, and in grains like corn, rye, oats, wheat, rice, etc. Starch is insoluble in water and occurs as a nodular deposit of varying sizes and forms in different plant cells. Figure 95 shows grains of potato starch as they appear under the microscope. Figure 96 shows grains of wheat starch, and Figure 97 shows grains of corn starch. Figure 98 shows potato starch grains as they look in polarized light. Starch is prepared mainly from potatoes and corn, the former being commonly used in Europe and the latter in America. The potatoes or grains are ground so as to break up the plant cells and lay the starch granules bare. These are then washed out with water, forming a thin milky paste which is passed through fine sieves that retain the

pulp. The starch is allowed to settle, the water is drained off, and the remaining material is dried at low temperatures. Though starch is insoluble in cold water, its granules swell up and burst when treated with boiling water, and the contents of

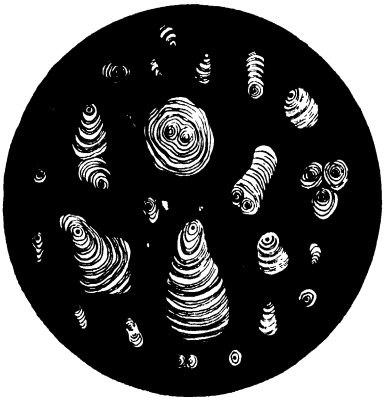


FIG. 95.

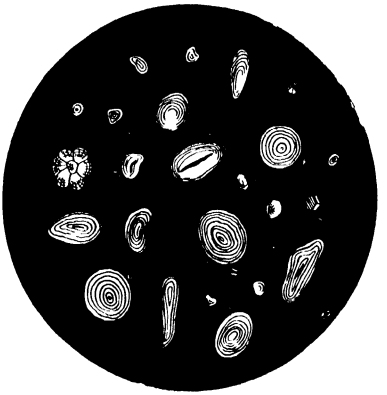


FIG. 96.

the cells, the **granulose**, dissolves, whereas the cell walls remain undissolved and can be filtered off. From the filtrate, the granulose or **soluble starch** may be precipitated by adding alcohol. **Starch paste** is prepared by grinding starch with a little cold

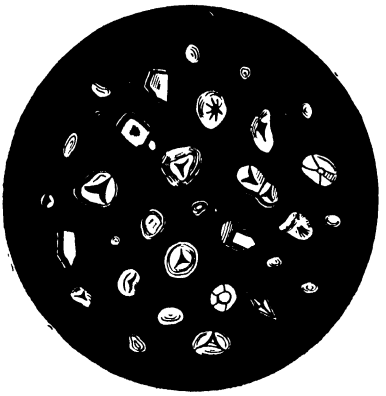


FIG. 97.

FIG. 98.

water and then adding boiling water with constant stirring. Thus a semi-transparent, gelatinous mass results, which is used as an adhesive. It is also employed in the laundry for stiffening clothes, the hot sad iron converting the starch into dextrine,

which covers the linen, imparting to it a characteristic luster. Starch has the empirical formula $C_6H_{10}O_5$. Its molecular weight is unknown, but it is probably some rather high multiple of the formula given. *Starch is an exceedingly important article of food.* Wheat flour, for instance, consists of about 70 per cent starch, 10 per cent **gluten**, a sticky nitrogenous substance closely allied to albumins like white of egg, and minor amounts of water, sugar, and inorganic material. Gluten, like starch, is valuable as food material.

On heating starch to about 210° it is converted into **dextrine** ($C_6H_{10}O_5$), which is also obtained as an intermediate product in the conversion of starch to glucose by means of dilute sulphuric acid. Dextrine is a colorless, amorphous substance that has a strong adhesive property. It is consequently frequently used as a cheap gum.

Cellulose. — This carbohydrate has the same empirical formula as starch $(C_6H_{10}O_5)_x$. Its molecular weight is unknown, but it is probably rather high. Cellulose is very widely distributed in nature, constituting the material out of which the cell walls of plants are made. Thus *wood, cotton, linen, hemp, flax, etc., when freed from the mineral matter they contain, are almost pure cellulose.* Filter paper after extraction with hydrochloric and hydrofluoric acids and washing with water is a nearly pure form of cellulose. Cellulose is insoluble in water but soluble in a solution of copper in strong ammonia water, which is known as **Schweitzer's reagent.** From this solution cellulose may be precipitated by means of acids in the form of a gelatinous mass that may be filtered off and dried to an amorphous powder. Cellulose gradually dissolves in concentrated sulphuric acid. On diluting the solution and boiling, dextrine is formed, which is finally converted into glucose. Thus wood may be changed to glucose, from which in turn alcohol may be obtained by fermentation. **Paper** consists essentially of thin sheets of fibers of cellulose matted together.

On heating cotton with a mixture of nitric and sulphuric acids, **nitrates of cellulose** are formed. This action is similar to the formation of glycerine nitrate, *i.e.* nitroglycerine. The composition of cellulose nitrates varies according to the length of time that the nitric acid has acted upon the cellulose, and the concentration of the acid. Cellulose hexanitrate

$C_{12}H_{14}(NO_3)_6O_4$ is called **nitrocellulose**, or **gun cotton**. It does not dissolve in a mixture of alcohol and ether. Gun cotton looks like ordinary cotton, but it is not as soft to the touch. It burns rapidly and quietly, producing no smoke. By means of fulminating mercury it can be made to explode violently. It is used as an explosive, frequently together with nitroglycerine. Gun cotton and nitroglycerine are made into threads with the aid of acetone and vaseline and are thus used as **smokeless gunpowder**. **Celluloid** consists of camphor and gun cotton. It is not explosive, but it burns readily. The tetra- and petranitrates of cellulose $C_{12}H_{16}(NO_3)_4O_6$ and $C_{12}H_{15}(NO_3)_5O_5$ readily dissolve in a mixture of alcohol and ether. This solution is known as **collodion**. It is used in photography for making films, and in surgery for protecting wounds from the air, for when collodion solution is poured out in thin layers, the alcohol and ether evaporate, leaving a tough, amorphous, transparent layer of nitrocellulose. On treating nitrocellulose with caustic soda, cellulose and sodium nitrate are formed, showing that *nitrocellulose is a nitrate of cellulose.*

Nitrobenzene $C_6H_5NO_2$ is a light yellow oil formed by the action of nitric acid on benzene. Its boiling point is 208°. It is used as a perfume for laundry soaps, under the name **oil of mirbane**. By reducing nitrobenzene with nascent hydrogen, **aniline** $C_6H_5NH_2$ is formed. Aniline is a base which forms salts like ammonia. Thus, $C_6H_5 \cdot NH_2 \cdot HCl$ is **aniline hydrochloride**. Aniline is a nearly colorless liquid which boils at 189°. On exposure to the air, it soon turns brown. Aniline may be regarded as ammonia in which one hydrogen atom has been replaced by the phenyl group, C_6H_5. Many similar substituted ammonias are known; they are called **amines**. So we have **methyl amine** $CH_3 \cdot NH_2$, **ethyl amine** $C_2H_5 \cdot NH_2$, **propyl amine** $C_3H_7 \cdot NH_2$, etc. In general, their chemical behavior is similar to that of ammonia. The **aniline dyes** are derivatives of **pararosaniline** $HO \cdot C(C_6H_4NH_2)_3$ and **rosaniline** $HO \cdot C(C_6H_4NH_2)_2 \cdot C_6H_3 \cdot CH_3 \cdot NH_2$. The hydrochloride of the latter is the dyestuff **magenta**. Many aniline dyes are known. They represent very many beautiful colors. The aniline dyestuff industry is an important one. It will be noted that the dyes are all derived from benzene, which is obtained from coal tar, whence the name coal-tar dye.

Alkaloids are complex basic substances that occur in plants. These compounds are so named because they form salts with acids, thus playing the rôle of alkalies. The base **pyridine** C_5H_5N is a colorless, odoriferous liquid boiling at 115°, which is found in coal tar and in the products of the dry distillation of green bones. **Quinoline** C_9H_7N occurs with pyridine. Many of the plant alkaloids are related to these two bases. **Nicotine** $C_{10}H_{14}N_2$ is found in tobacco. It is a poisonous liquid, boiling at 247°. **Atropine** $C_{17}H_{23}O_3N$ occurs in nightshade, *Atropa belladonna.* It forms very poisonous crystals which melt at 115.5°. It is used by oculists to cause expansion of the pupil of the eye. **Cocaine** $C_{17}H_{21}O_4N$ is found in coca leaves. It consists of crystals that melt at 98°. It is used as a local anæsthetic. **Quinine** $C_{20}H_{24}O_2N_2$ and **cinchonine** $C_{19}H_{22}O_2N_2$ are found in Peruvian bark, which also contains other alkaloids. Quinine is usually administered in form of the sulphate. It is a specific for malarial fever. **Morphine** $C_{17}H_{19}O_3N$, **narcotine** $C_{22}H_{23}O_7N$, and **codeine** $C_{18}H_{21}NO_3$ occur in **opium**, which is the dried sap of the unripe seed pods of the opium poppy. Morphine is a crystalline powder which was first isolated in 1806. It induces sleep. As a rule it is administered in form of the hydrochloride. **Strychnine** $C_{21}H_{22}O_2N_2$ and **brucine** $C_{23}H_{26}N_2O_4$ occur in **nux vomica**. *These alkaloids are very poisonous, causing death accompanied by muscular contraction and rigor.* Strychnine forms crystals that melt at 265°. They are nearly insoluble in water. Strychnine compounds have a very bitter taste. In minute quantities they are often prescribed in medicine as a tonic.

Proteins. — *These are very important compounds, consisting of carbon, hydrogen, nitrogen, oxygen, and sulphur, which make up a large share of the bodies of animals and also play an important rôle in plants.* Exclusive of water, fats, and mineral constituents, the animal matter consists of proteins, formerly called **proteids.** Without proteins as food, animals will finally die. The chemical structure of the proteins is very complicated. On the average, proteins have about the following composition: —

Carbon	50.5 to 54.5 per cent
Hydrogen	6.5 to 7.3 per cent
Nitrogen	15.0 to 17.7 per cent
Oxygen	21.0 to 24.0 per cent
Sulphur	0.3 to 2.3 per cent
Phosphorus	0.4 to 0.8 per cent

Nucleoproteins may contain from 5 to 6 per cent phosphorus.

Among some of the common protein substances may be mentioned the **albumins**, as they occur for instance in serum, in eggs, in milk, in muscular tissues, and in leguminous and other seeds. Albumins are coagulated by heat and by acids. **Albuminoids** are closely related to albuminous bodies. Among the albuminoids are **gelatine**, **elastine**, and **keratine**. Elastine enters into the composition of connective tissues, while keratine is the main substance found in hoofs, horns, feathers, hair, nails, and the epidermis. By the action of pepsin albumins are converted into **peptones**, which process involves an addition of the elements of water to the molecule.

The molecular weight of the protein molecule as determined by the freezing point method (which see) is approximately 15,000. Proteins are consequently regarded as colloidal substances. The fact that they diffuse very slowly in solutions also accords with this view. The idea that proteins are very complicated bodies comes from the fact that a large number of products may be obtained from them by treatment with various reagents like acids, alkalies, oxidizing agents, etc. The study of proteins has of recent years been prosecuted with special success by Professor Emil Fischer of the University of Berlin, to whom we also owe much of our knowledge of the constitution of sugars.

When protein substances, like meat, fish, etc., putrefy, **ptomaines** are often formed. These are basic substances which act like the alkaloids in many respects. They are poisonous. Among them are **putrescine** $C_4H_8(NH_2)_2$ and **cadaverine** $C_5H_{10}(NH_2)_2$. *Illness from eating spoiled meat is commonly due to ptomaine poisoning.*

REVIEW QUESTIONS

1. What is a hydrocarbon? Give five illustrations. What are the ultimate products of combustion of a hydrocarbon? Compare the chemical properties of hydrocarbons with: (*a*) the hydrohalogens, (*b*) ammonia, hydrazine, and hydrazoic acid, (*c*) hydrogen sulphide.

2. Give the methods for preparing two typical hydrocarbons, writing the equations.

3. Mention the more important products that are made from petroleum. Where is petroleum found and how is it refined?

4. What is meant by the term "halogen substitution product"? Illustrate by giving three examples of halogen substitution products and the equations showing their formation.

5. What are the formulas and uses of the following: chloroform, iodoform, carbon tetrachloride, ether, carbolic acid?

6. What is an alcohol? Give the names and formulas of five alcohols. How is ordinary alcohol made and how may it be converted into vinegar?

7. What is denatured alcohol? About what is the alcoholic content of beer, wine, whisky?

8. What is the chemical nature of glycerine? Mention five other substances that belong in the same general class of compounds as glycerine. Give the formulas of each of these and state the characteristic properties of this class of compounds.

9. What is hydroquinone? Pyrogallic acid? Creosote? What are these used for? How are they related to: (*a*) alcohol, (*b*) phenol, (*c*) glycerine?

10. What is an aldehyde? Give two illustrations and the equations showing their formation?

11. What is formaline? What use is made of it?

12. What is an organic acid? Write the formulas of the following organic acids: formic, acetic, propionic, butyric, lactic, oxalic, benzoic, stearic, oleic, tartaric, malic, citric. State where each of these occurs, or how it may be prepared. Mention also the chief properties of each of these acids.

13. What is meant by optical activity? Give six examples of optically active substances and state what they have in common that causes the optical activity.

14. To what class of substances do fats belong? How may a fat be converted into a soap? What other product is formed simultaneously? Write the equations showing the change of olive oil into castile soap.

15. Why is soft water superior to hard water for washing purposes? Give a chemical equation showing how hard water acts on soap. Discuss the cleansing power of soap.

16. What is oil of wintergreen, banana oil, pineapple oil? To what general class of substances do these belong?

17. What is nitroglycerine, and how does it differ from dynamite?

18. Write the general formula for: (*a*) an alcohol, (*b*) an aldehyde, (*c*) an organic acid, (*d*) a ketone, (*e*) an ester, (*f*) an ether, (*g*) a sulphur ether, and give a concrete example of each.

19. What is a carbohydrate? Classify the important carbohydrates.

20. What is a sugar? Classify the important sugars. State how the sugars you have mentioned react with Fehling's solution.

21. What is fermentation? What is an enzyme? Give an illustration of each.

22. What is each of the following: smokeless powder, celluloid, collodion, nitrobenzene, aniline, quinine, morphine?

23. What is meant by the term "protein"? Give an illustration. What is the cause of so-called ptomaine poisoning?

24. How much carbon dioxide and how much water may be obtained from the combustion of a pound of tartaric acid?

CHAPTER XVI

ILLUMINATING GAS AND FLAMES

Illuminating Gas. — Illuminating gas is often produced by the destructive distillation of soft coal. During this process there are formed coal gas, coal tar, and water containing ammonia and other products in solution. **Coal gas** consists mainly of hydrogen, carbon monoxide, and methane, together with a small amount of higher hydrocarbons known as illuminants. Impurities like nitrogen, carbon dioxide, and hydrogen sulphide are also present in small quantities. The tar from the gas works is distilled, and the benzene obtained therefrom is used in manufacturing dyestuffs and many medicinal preparations. The remaining tar is then employed for roofing, making artificial asphalt, black varnishes, etc. The coke from the gas retorts serves as fuel. The ammoniacal gas liquors serve as a source of ammonium salts. These liquors are neutralized with sulphuric acid, and the ammonium sulphate so obtained is used as a fertilizer or converted into ammonia water by treatment with lime and absorption of the gas liberated. The coal gas is treated with lime to remove carbon dioxide and sulphides, particularly hydrogen sulphide, which is always present.

In the process of manufacture, coal gas passes from the retort *R* (Fig. 99), through the condensers *C*, in which the tar and ammoniacal liquors are condensed, into the scrubber *S*, where it is washed with water. The gas then goes through layers of lime or oxides of iron, or both, which are contained in the purifiers *P*. This removes the hydrogen sulphide. Finally the gas enters the holder *H*, from which it is distributed through the mains.

Not all illuminating gas is coal gas. Much illuminating gas is made in America from petroleum. By allowing the latter to come into contact with the walls of a chamber lined with fire bricks heated to about 1000° C. the heavy hydrocarbons are

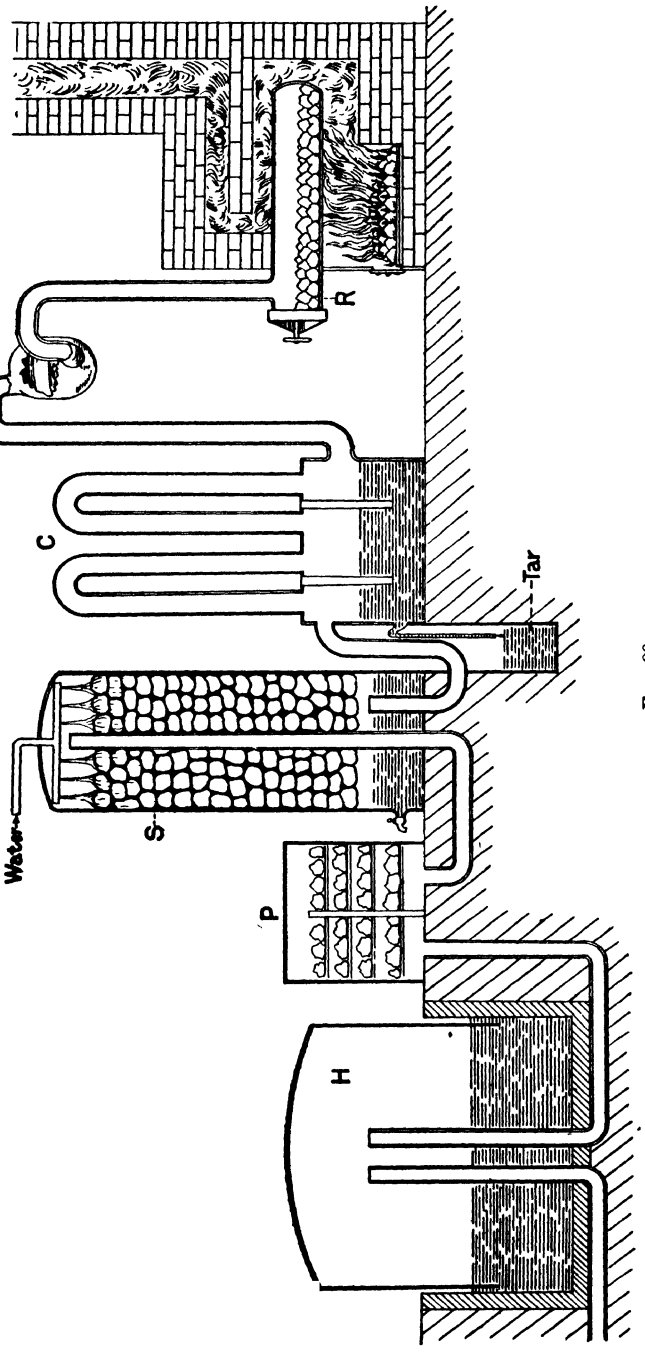


FIG. 99.
Diagram of a plant for the manufacture of coal gas.

decomposed into simple hydrocarbons that contain fewer carbon atoms in the molecule, and are consequently gaseous at ordinary temperatures. This process is called "cracking" the petroleum oils. **Pintsch gas** is made entirely by this process. It has very high illuminating power and is used for lighting railway cars, for which purpose it is compressed, with moderate pressure, in steel cylinders. A special burner must be used with this gas to prevent smoking of the flame. *Oil gas thus made is rich in benzene and the hydrocarbons of the ethylene and acetylene series.* These give it its high illuminating power, and are consequently called **illuminants**. It is now common practice to increase the illuminating power of coal gas by "enriching" the gas by means of petroleum oils added directly to the coal in the retorts, or by adding oil gas to the coal gas. It will be recalled that water gas consists of hydrogen and carbon monoxide, and consequently burns with a flame that is nearly non-luminous. To make it serve for illuminating purposes, it is enriched, or "carbureted," by means of oil gas. To accomplish this the water gas is passed through heated chambers into which petroleum oil is run and *cracked* as above stated, thus furnishing the necessary illuminants. Sometimes the oil gas is made separately and then added to the water gas in proper proportion. Enriched water gas is much used in the large cities of the United States.

Coal gas was first used for house illumination in 1792, by William Murdock in London, where it was employed for street lighting in 1812. Three years later it was also used for this purpose in Paris. However, the fact that a combustible gas is evolved from coal when it is heated, was discovered as early as the year 1680 by Becher.

The illuminating power of a gas is usually expressed in candle power. The gas is burned from a burner consuming 5 cu. ft. per hour, and this light is compared with that of a standard candle by means of a photometer.

The composition of gases used for illuminating purposes varies considerably. A general idea of the composition of illuminating gas may, however, be obtained from the following table, from the reports of the Massachusetts State Gas Inspectors, which presents average results in per cent by volume: —

	Coal Gas	Carburetted Water Gas	Oil Gas
Candle power	17.5	25.	65.
Illuminants	5.0	16.6	45.0
Methane	34.5	19.8	38.8
Hydrogen	49.0	32.1	14.6[1]
Carbon monoxide . . .	7.2	26.1	—
Nitrogen	3.2	2.4	1.1
Oxygen	—	—	—
Carbon dioxide	1.1	3.0	—

Flame. — Flames are produced by burning gases. Whenever a continuous stream of one gas issues into an atmosphere of another gas upon which it acts chemically, producing a sufficient rise of temperature and a certain degree of luminosity, we have at the surface of contact of the gases the phenomenon of flame. Solids like charcoal and coke burn practically without flame. In the kerosene lamp the wick draws up the oil and the latter is converted into gas by heat, and thus it is really the gas that burns in the flame. Similarly in the flame of a candle it is gas that burns; for the wax or tallow is melted by the heat, and the liquid is drawn up by the wick, being converted to gas before it is burned. This is well illustrated by the experiment represented in Fig. 100, in which some of the unconsumed gas from the inner part of the flame is conducted off by means of the glass tube, at the end of which it has been lighted.

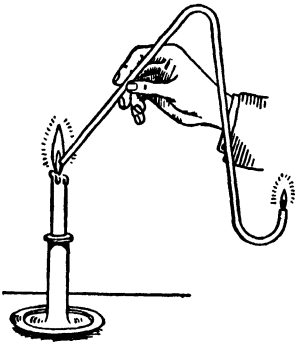


Fig. 100.

Oxygen is said to *support* the combustion of a gas that burns in the air. Obviously, however, *combustion is really the mutual interaction of the two gases.* So, for instance, coal gas can be burned in the form of a flame in the air, or air can be burned in the form of a flame in an atmosphere of coal gas. This is well illustrated by the experiment shown in Figs. 101, 102, and 103.

[1] This figure represents ethane and not hydrogen. The latter is not present in oil gas.

Illuminating gas is passed into the apparatus (Fig. 101), through the tube at the left, and then the gas is ignited at the end of the other tube at the right, as shown. Now the lid on top of the apparatus is opened (Fig. 102), whereupon the draft created causes the flame to strike inward and burn inside of the large tube, as shown in the figure. This is now a jet of air burning in an atmosphere of illuminating gas. The gas issuing from the opening created by removing the lid may be lit as shown, and thus we have the upper flame of illuminating gas burning

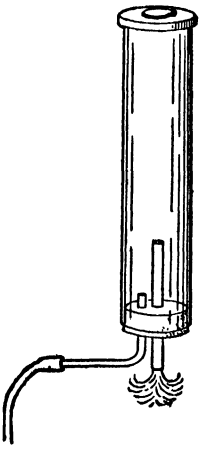


FIG. 101.

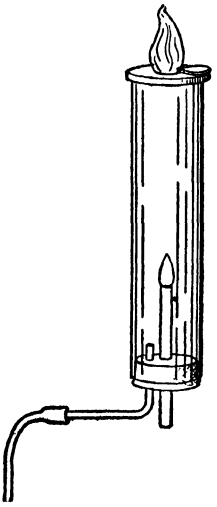


FIG. 102.

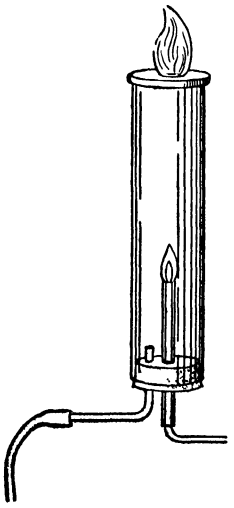


FIG. 103.

in the air, and at the same time the inner flame of air burning in the atmosphere of the gas. This is commonly spoken of as the *reverse flame*. That it is actually air that is burning in the illuminating gas may be demonstrated by passing a small gas flame up into the inside of the flame of air burning in the illuminating gas, as shown in Fig. 103; the small gas jet burns in the inner cone of the flame.

It will be recalled that a jet of hydrogen will burn in oxygen and a jet of oxygen in an atmosphere of hydrogen; and that a jet of chlorine will burn in hydrogen and a jet of hydrogen in an atmosphere of chlorine. These experiments also demonstrate further the relative nature of combustion. The latter experiment further shows that we may have flames due to chemical changes other than oxidation.

The fact that oxygen will burn in coal gas is readily demonstrated by the experiment illustrated in Fig. 104. Chlorate of potassium heated in a deflagrating spoon till oxygen is evolved freely is introduced into the atmosphere of coal gas as shown. The oxygen burns brilliantly, the flame being colored purple by the presence of potassium. The gas should be ignited at the upper orifice, as shown in the figure, before introducing the deflagrating spoon.

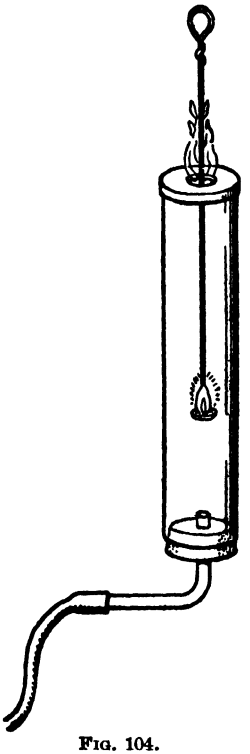


Fig. 104.

Luminosity of Flame. — Flames are either luminous or non-luminous. Thus, hydrogen burns with a non-luminous flame. This may, however, be made luminous by blowing fine solid particles, like soot, for example, into the flame. These fine particles become heated to incandescence and emit light. Similarly, a platinum wire introduced into the hydrogen flame soon becomes hot and gives off light. Carbon monoxide burns with a blue flame, which can readily be made luminous by the introduction of fine particles of carbon. Figure 105 shows a convenient apparatus for accomplishing this. Carbon monoxide is passed through the apparatus, the cock at the left being open, and ignited. We now have the characteristic blue flame. If the cock at the right is then opened and the one at the left closed, thus causing the gas to pass through the cotton saturated with benzene contained in the right limb, the flame becomes luminous, for the heavy hydrocarbon vapors carried into the

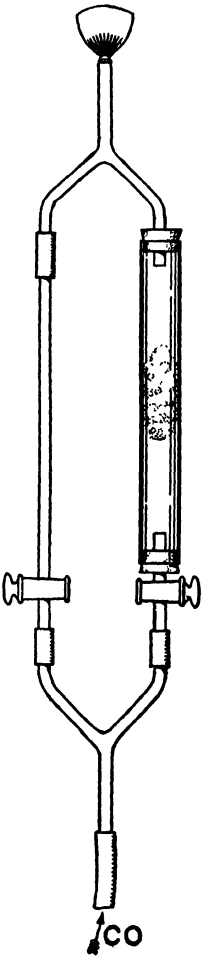


Fig. 105.

flame lose their hydrogen at the high temperature of the flame, thus setting particles of carbon free which are heated to incandescence and so give the flame luminosity. By proper manipulation of the two cocks, the flame may be rendered luminous or non-luminous alternately. That all luminous gas flames, including those of oil lamps and candles, contain carbon particles in suspension is readily demonstrated by the fact that a layer of soot is deposited upon glass or porcelain held in such flames. According to Lewes, acetylene is formed in all luminous flames, and it would seem probable that the luminosity is due to the presence of this gas, which breaks up, yielding carbon particles that then become heated to incandescence. At any rate, it is certain that the luminosity of the flame of illuminating gas is due to the presence of benzene and gases of the ethylene and acetylene series, which are commonly called the illuminants. It is well known that at high temperatures these decompose, yielding acetylene as one of the products.

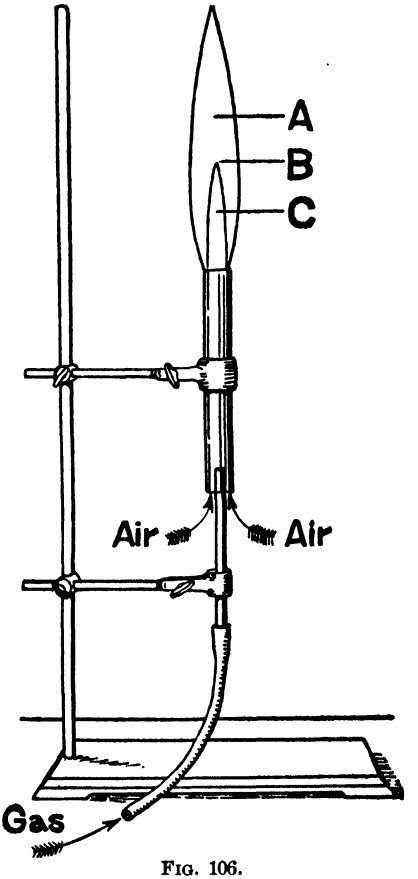


FIG. 106.

When a jet of illuminating gas is mixed with air and then ignited, a non-luminous flame is obtained. This is the principle used in the **Bunsen burner**. Figure 106 shows a simple apparatus for illustrating this principle. Gas issues through the opening of the small tube, over which the larger tube is placed as shown. The gas passing upward creates a current of air which enters the larger tube, as shown by the arrows, and mixes with the gas in the large tube at the end of which the mixture is lighted, yielding

a blue, practically non-luminous flame. It is commonly held that this non-luminosity is due to the oxygen, which causes complete combustion of the carbon particles.

The Bunsen burner is used in various forms in the laboratory. In principle, gas stoves and furnaces are all Bunsen burners. By supplying compressed air by means of a bellows or otherwise, the **blowpipe** or **blast flame** is produced. This additional supply of air insures more rapid and more complete combustion, and consequently a higher temperature is obtained. The ordinary form of blast lamp is similar to the oxyhydrogen lamp, except that coal gas and air are used instead of hydrogen and oxygen.

The flame of an alcohol lamp is non-luminous because alcohol contains some oxygen, and this, together with that supplied by the air, is sufficient to secure complete combustion of the particles of carbon. For similar reasons ether burns with a practically non-luminous flame. As the carbon content of compounds increases, however, the flames with which the compounds burn become luminous, and even sooty.

It will be recalled that when calcium oxide was introduced into the oxyhydrogen flame, the lime was heated to a temperature at which it emitted a brilliant white light. The brilliant light formed when magnesium or phosphorus burn in the air or in oxygen is similarly caused by the incandescence of the particles of MgO and P_2O_5 that are formed during the combustion.

In the **Welsbach light** this principle is used by hanging over the flame of a Bunsen burner a mantle consisting of a network made of 99 per cent thorium dioxide and 1 per cent cerium dioxide. Thus a strong, brilliant, white light is produced with a relatively low consumption of gas. Other oxides will also serve, but they do not yield nearly as good results in practice. The oxides mentioned, when used in the proportion indicated, have been found to give the strongest light.

The Structure of Flame. — Taking as a typical luminous flame that of a candle (Fig. 107), we see that it exhibits three distinct zones. The inner zone *A* is dark and non-luminous. It consists of the gases produced by the decomposition and volatilization of the material of the candle drawn up by the wick, which fact may be demonstrated by the experiment

shown in Fig. 100. This zone is also of relatively low temperature. The next zone *B* is brilliantly luminous. Here partial combustion of the expanding gases is going on. The ethylene and other hydrocarbon gases lose their hydrogen, probably forming at first acetylene, which in turn loses hydrogen and yields carbon particles whose incandescence gives the luminosity to this zone of the flame. Finally, the outer fringe *C* is practically non-luminous, for here more oxygen of the air comes into contact with the hot gases, thus causing more complete combustion. This latter zone is the hottest part of the flame.

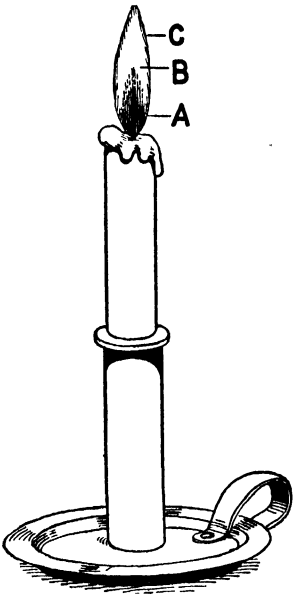


FIG. 107.

In the Bunsen flame (Fig. 106) the luminous zone is absent. We have here only an inner greenish blue cone *C* and an outer practically non-luminous mantle *A*. In the inner cone the essential processes are the combustion of hydrogen to water, and of carbon to carbon monoxide. The inner zone consequently contains an excess of reducing gases and is termed the **reducing flame,** whereas the outer zone contains an excess of oxygen and is called the **oxidizing flame.** Many of the metals are oxidized when introduced into the oxidizing flame. Again, when oxides, like those of lead for instance, are placed in the inner zone they are reduced. Blowpipe flames exhibit the same general structure as the Bunsen flame. That the lower part of the inner cone of the latter is relatively low in temperature is demonstrated by the fact that a match head may be placed in it for some time without taking fire. The outer fringe and the tip of the cone near *B* are the hottest parts of the flame.

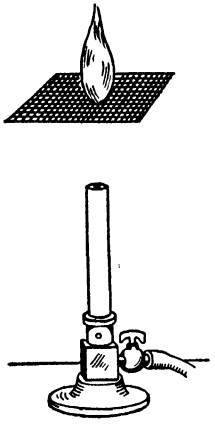


FIG. 108.

Davy Safety Lamp. — When a wire gauze is held over a Bunsen burner, and the gas is then lighted on the upper side of the gauze, the flame burns on that side and does not pass through the gauze to the lower side (Fig. 108). Again, if a wire gauze is pressed down upon a Bunsen flame, the flame does not pass through to the upper side of the netting, but only partially consumed gas makes its appearance there (Fig. 109). These phenomena are due to the fact that the wire netting lowers the temperature of the gases below the kindling point; that is, the temperature at which the gases take fire in the air. If the gauze should become very hot, the flame will pass through, of course.

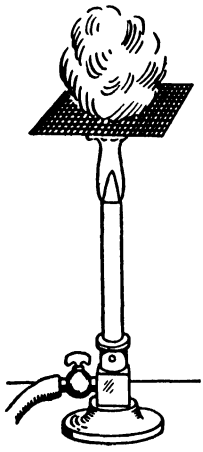


FIG. 109.

Upon the principle that a wire netting is thus able to intercept a flame as explained, Sir Humphry Davy devised the miner's safety lamp (Fig. 110). This consists of an oil lamp having a tight-fitting chimney of wire gauze. When this lamp is lighted and taken into a mine where **fire damp**, methane CH_4, is present, the flame is not communicated through the gauze to the explosive mixture, though to be sure the latter may get into the chimney through the gauze and burn there or cause small, harmless explosions. These serve to warn the miner of the presence of the dangerous gases. The safety lamp is consequently very useful; nevertheless, explosions do still occur in mines because currents of air arising from blasting operations may blow fine coal dust into the lamp and so enable the flame to communicate itself to the fire damp on the outside of the gauze. After such explosions have occurred, the carbon dioxide (called **choke damp** by the miners) formed is dangerous also, because it does not support respiration and so gives rise to suffocation.

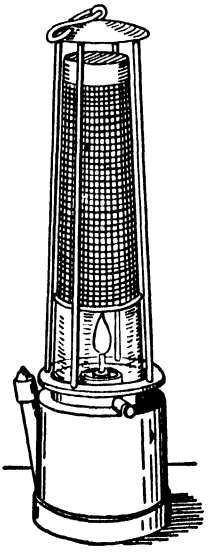


FIG. 110.

REVIEW QUESTIONS

1. What is the difference in composition and method of preparation of water gas and coal gas? What are the products of the coal gas industry?

2. What is a flame? Upon what does the illuminating power of a flame depend? What is meant by the term "enriching a gas"?

3. Explain the principle of a Bunsen burner.

4. What determines the temperature of a flame? Give illustrations substantiating your answer.

5. Explain the principle of the Davy safety lamp. Why do explosions in mines occur in spite of this safety device? What is fire damp? Choke damp?

6. Explain the action of the following when used to extinguish fires: (*a*) water, (*b*) carbon dioxide, (*c*) carbon tetrachloride, (*d*) sand, (*e*) a blanket, (*f*) saleratus.

7. Why should water not be used to extinguish gasoline or oil fires? What would you do to extinguish such fires?

CHAPTER XVII

THERMOCHEMISTRY

General Remarks. — All chemical changes are accompanied by either an evolution or an absorption of heat. In most of the ordinary chemical processes heat is liberated. These are consequently called **exothermic changes**, to distinguish them from **endothermic changes**, or reactions in which heat is absorbed. Endothermic changes are by no means uncommon. In fact many reactions occur with absorption of heat, particularly at higher temperatures. It must be borne in mind that physical changes as well as chemical reactions are generally accompanied by thermal changes. Thus, in melting ice or vaporizing water heat is absorbed, while in freezing water or in condensing vapor heat is liberated. Similarly, whenever a solid is converted into a liquid, or a gas is formed from a solid or liquid, heat is absorbed so far as the physical change is concerned; and heat is liberated when the reverse action takes place. The amount of heat required to convert 1 gram of a given solid into liquid of the same temperature is termed the **latent heat of fusion**. And the amount of heat necessary to change 1 gram of a liquid into vapor of the same temperature is called the **latent heat of vaporization**.

When a piece of zinc is dissolved in hydrochloric acid, the solid zinc disappears and becomes part of the liquid, and simultaneously a gas, hydrogen, is evolved. Both of these processes, the liquefaction of the solid and the liberation of the gas, considered as physical processes, would proceed with absorption of heat. However, the action of hydrochloric acid on zinc proceeds with disengagement of heat, which fact can readily be demonstrated by means of a thermometer placed in the acid. It is therefore evident that the thermal change observed is equal to the heat developed by the chemical interaction, minus the heat required for the liquefaction of the metal and the conversion of the hydrogen into the gaseous state. It is at

present impossible to determine just how much energy the last-named processes represent when they occur at room temperature, and so it is also impossible to tell how much heat the actual chemical part of the change evolves. All chemical changes are similarly accompanied by physical changes of some kind. The thermal effect of the latter must be taken into consideration; or, at any rate, if this effect cannot be evaluated and subtracted, as is frequently the case, the physical state of the substances before and after the reaction must be mentioned.

Calorimeters. — Thermal changes are measured by means of calorimeters. A thermometer is introduced into a known weight of water contained in a cylindrical dish, the calorimeter, which is preferably made of platinum. The apparatus is so arranged that the heat evolved by the chemical reaction is communicated to the calorimeter water. Knowing the initial and final temperature of the latter, and multiplying the weight of the water by the number of degrees of temperature change, the number of calories of heat evolved is obtained. A **large calorie** is the amount of heat necessary to raise 1000 grams of water 1 degree; it is commonly designated by Cal. A **small calorie** is 0.001 of a large calorie and is designated by cal. In technical work in England and America another heat unit known as the British thermal unit is frequently used. A **British thermal unit** is the amount of heat required to raise the temperature of 1 pound of water 1 degree Fahrenheit; it is designated by B. T. U.

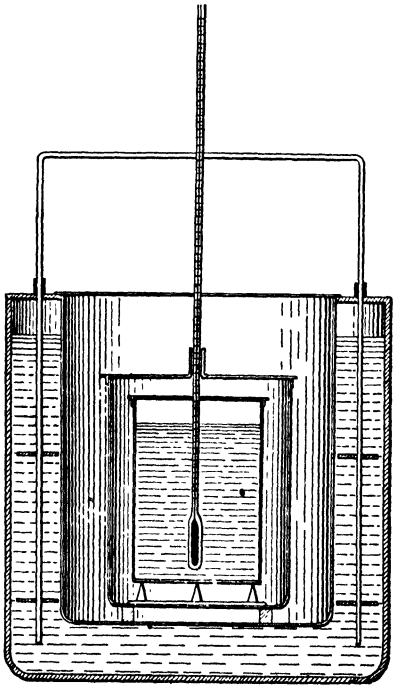


FIG. 111.

During calorimetric measurements care must be taken to prevent loss of heat by radiation, or the exact amount of heat lost

by radiation must be ascertained, and a proper correction made therefor in the final result. Figure 111 shows an ordinary calorimetric apparatus in cross section. The calorimeter itself should not have less than 500 cc. capacity. In Fig. 112 a combustion calorimeter is represented. The substance to be burned is placed in the steel bomb, which is lined with platinum, gold, or porcelain enamel. The bomb is then filled with oxygen under 20 atmospheres pressure and finally immersed in the water of the calorimeter. The ignition is effected by means of a small wire in the bomb, heated by an electric current. Thus the combustion proceeds almost instantaneously, and the heat is communicated to the calorimeter water and measured in the usual way.

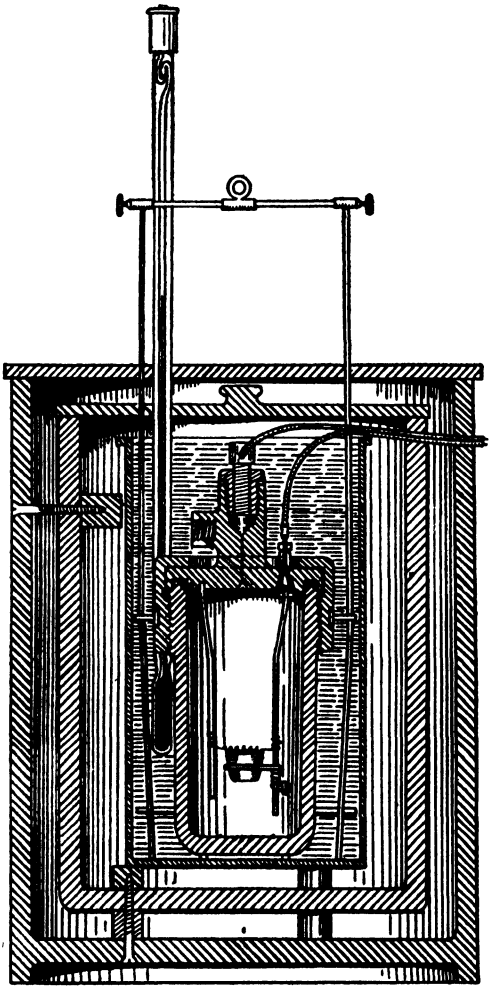


FIG. 112.

Laws of Thermochemistry.— Inasmuch as energy can neither be created nor destroyed, it is evident that *if no heat be lost, the heat evolved during a chemical change is always exactly equal to the heat that is absorbed when the reaction is reversed.* This law was pointed out in 1783 by Lavoisier and Laplace, who regarded it as self-evident.

In 1840 G. H. Hess, professor at the University of St. Peters-

burg, showed that the *thermal change accompanying any chemical reaction depends on the initial and final condition of the substances involved, and is independent of the intermediate changes that may occur during the reaction.* Thus the total amount of heat evolved when a gram of carbon is burned to CO_2 is the same whether the combustion proceeds in one step, or whether CO is first formed, and this is then oxidized to CO_2. This **law of Hess** really follows from the law of conservation of energy. It is of great importance in thermochemical measurements, for it enables many determinations to be made indirectly that could not be carried out by direct means. So it is practically impossible to determine the amount of heat evolved when carbon is burned to CO, for some CO_2 always forms when this is attempted. But it is quite possible to find the heat developed when carbon is burned to CO_2, and also that evolved when CO is burned to CO_2; and the difference between these two experimental results is the heat evolved when carbon is burned to CO. Thus: —

$$\begin{aligned} C(\text{solid}) + O_2(\text{gas}) &= CO_2(\text{gas}) + \quad 97.65 \text{ Cal.} \\ CO(\text{gas}) + O(\text{gas}) &= CO_2(\text{gas}) + \quad 68. \quad \text{Cal.} \\ \hline \text{Therefore, } C(\text{solid}) + O(\text{gas}) &= CO(\text{gas}) + 29.65 \text{ Cal.} \end{aligned}$$

These are typical **thermochemical equations.** For instance, the first one states that when 12 grams of carbon and 32 grams of oxygen unite, 44 grams of carbon dioxide are formed and 97.65 Cal. of heat are liberated. All other thermochemical equations are interpreted similarly. According to the law of Lavoisier and Laplace, it is evident that if carbon dioxide is to be decomposed into carbon and oxygen, energy to the amount of 97.65 Cal. is absorbed during the process per every 44 grams of CO_2. At first it appears peculiar that the combustion of carbon to CO yields but 29.65 Cal., whereas the combustion of CO to CO_2 evolves 68 Cal. But it must be remembered that in the first step, when solid carbon passes into CO, much energy is absorbed in the process of vaporizing the carbon, which doubtless accounts for the fact that we get but 29.65 Cal. when carbon is burned to CO. It is evident that when furnaces are run so that fuel is but partially burned, *i.e.* so that a considerable proportion of the carbon is merely oxidized to monoxide, a

large proportion of the energy that might have been gained as heat is wasted.

The development of the subject of thermochemistry is mainly due to the work of Julius Thomsen, who was professor at the University of Copenhagen, and Marcellin Berthelot, who was professor at the University of Paris. In 1853 the former stated that *every simple or complex change of a purely chemical nature is accompanied by an evolution of heat;* and in 1879 Berthelot announced that *every change accomplished without the intervention of extraneous energy tends to produce a substance or substances in the formation of which the greatest amount of heat is disengaged.* This is now commonly termed Berthelot's **law of maximum work.** It is true that under ordinary conditions those reactions generally take place that evolve the greatest amount of heat; so in dissolving metals in acids, in neutralizing the latter with bases, in displacing one metal by another in solution, in the combustion of carbonaceous substances, etc., heat is evolved. Nevertheless, Berthelot's law, for which he contended strongly, does not hold rigidly; for, as already remarked, at very high temperatures many endothermic reactions proceed readily. Furthermore, at ordinary temperatures many changes like the interaction of ice and salt proceed spontaneously with absorption of heat; though here doubtless the amount of heat required for the liquefaction of the ice and salt is greater than that evolved by the action of the salt on the ice, whence the cooling effect observed.

Thermochemical Equations. — As already stated, it is customary to express the thermal accompaniment of a chemical change for the molecular weight in grams of the substances involved. Thus in making lead iodide from lead and iodine we have: —

$$[Pb] + 2[I] = [PbI_2] + 39.8 \text{ Cal.}$$

indicating that when 207.1 grams of lead and 2×126.92 grams of iodine unite, 460.94 grams lead iodide are formed and 39.8 Cal. are simultaneously liberated. The brackets indicate that the substances are in the solid state. When liquids come into consideration parentheses are used, and in the case of gases, both brackets and parentheses are omitted. Thus, —

$$[P] \text{ yellow} + 3\ Cl = (PCl_3) + 76.6 \text{ Cal.},$$

means that when 31 grams of solid yellow phosphorus react with 3×35.46 grams of gaseous chlorine to form 137.38 grams of liquid phosphorus chloride, 76.6 Cal. are liberated. Thermochemical equations must not be confounded with the ordinary chemical equations. The latter indicate the direction the chemical change takes and specify the nature and amounts of the substances formed, whereas thermochemical equations are energy equations. For example the last equation states that the energy represented in 31 grams of solid phosphorus plus the energy in 106.38 grams of gaseous chlorine is equal to the energy in 137.38 grams of liquid phosphorus trichloride plus 76.6 Cal., at room temperature, *i.e.* about 18° C. All other thermochemical equations are to be interpreted similarly. It should be stated that the use of brackets and parentheses to indicate solids and liquids respectively has been proposed but recently. It is a simple form of designation which will probably be generally adopted.

Different allotropic forms of an element contain different amounts of energy. Thus when 31 grams of red phosphorus are converted into phosphorus trichloride, we have: —

$$[P] \text{ red} + 3\ Cl = (PCl_3) + 49.34 \text{ Cal.};$$

therefore from the last two equations it follows that the conversion of yellow phosphorus to red proceeds with liberation of 27.26 Cal. thus: —

$$[P] \text{ yellow} = [P] \text{ red} + 27.26 \text{ Cal.}$$

Since thermochemical equations are energy equations, they may be transformed like any algebraic equation, for instance: —

(1) $(Hg) + 2\ Cl = [HgCl_2] + 53.3$ Cal.

(2) $(Hg) + 2\ Cl - 53.3$ Cal. $= [HgCl_2]$.

(3) $(Hg) + 2\ Cl - [HgCl_2] = 53.3$ Cal.

(4) $(Hg) + 2\ Cl - [HgCl_2] - 53.3$ Cal. $=$ zero.

Equation (1) indicates that when liquid mercury and gaseous chlorine unite to form solid mercuric chloride, 53.3 Cal. are liberated. Equation (2) indicates that if solid mercuric chloride were transformed into liquid mercury and gaseous chlorine, 53.3 Cal. would be absorbed. Equation (3) states that the energy in 200 grams mercury plus that in 2×35.46 grams

chlorine is greater than that contained in mercuric chloride by 53.3 Cal., and equation (4) expresses the same fact.

The **total energy** contained in any substance is an unknown quantity, for we have no way of robbing a substance of all of its energy and measuring the same. A certain quantity of energy may, however, be obtained from substances; this is the **available or free energy.** It varies according to the nature of the changes to which a substance is subjected. So by burning phosphorus in excess of oxygen more heat is developed than by burning it in excess of chlorine: —

$$2[P] + 5\,O = [P_2O_5] + 370 \text{ Cal.}$$
$$2[P] + 10\,Cl = 2[PCl_5] + 218.4 \text{ Cal.}$$

It is clear that thermochemistry can deal only with available energy.

Definitions. — The **heat of solution** is the thermal change accompanying the solution of a substance in so much solvent that the addition of more solvent causes no further appreciable thermal change. The heat of solution is commonly stated per gram-molecule of dissolved substance, thus: —

$$[NaCl] + (aq) = (NaCl\,aq) - 1.3 \text{ Cal.}$$

indicates that when 1 gram-molecule of sodium chloride is dissolved in much water (100 to 400 gram-molecules of water, which is indicated by **aq** in all thermochemical equations) there is formed the dilute solution NaCl aq, and 1.3 Cal. are absorbed.

The **heat of dilution** is the thermal change accompanying the dilution of a given solution with a definite amount of pure solvent, usually so much that the addition of further solvent does not cause any appreciable change of temperature.

The **heat of reaction** is a general term used to express the thermal change that accompanies any chemical reaction. The **heat of formation** of a chemical compound is the thermal change accompanying the formation of that compound from the elements. The term is also sometimes used to indicate the thermal change that accompanies the formation of a compound from other compounds, or from elements and compounds. When so used, it is necessary to specify from what substances the compound whose heat of formation is under consideration has been formed.

The **heat of neutralization** is the heat liberated when an acid is neutralized by a base. The **heat of combustion** is the heat evolved when a substance is completely burned. In all cases the thermal change is computed per gram-molecule.

Thermochemical Data.— These generally consist of tables of heats of formation, solution, neutralization, and combustion. From what has been stated, tables of this kind will readily be understood. The thermochemical data of nearly all of the important substances have been determined by Thomsen and Berthelot.

When the heat of formation of a compound in solution is known, the heat of formation in the anhydrous condition may be found by subtracting the heat of solution, carefully considering the sign of the latter. By making use of the law of Hess, the heat of formation of any compound may be computed from the heat of any reaction involving that compound, providing the heats of formation of the other compounds in the reaction are known. In this way the heat of formation of a compound from the elements may be found indirectly, even though it has not been synthesized. Thus, let the heat of formation of cane sugar be required. Its heat of combustion found experimentally is:—

$$[C_{12}H_{22}O_{11}] + 12\,O_2 = 12\,CO_2 + 11(H_2O) + 1353\text{ Cal.}$$

Again by experiment it has been found that

$$[C] + O_2 = CO_2 + 97.65\text{ Cal., and}$$
$$H_2 + O = (H_2O) + 68.4\text{ Cal.}$$

It is clear then that $12\,CO_2$ when formed from 12 [C] and $12\,O_2$ will liberate 12×97.65 Cal.; and similarly $11\,(H_2O)$ represents a heat of formation of 11×68.4 Cal. Thus, $12\,CO_2$ and $11\,(H_2O)$ together represent a liberation of $12 \times 97.65 + 11 \times 68.4$ or 1924.2 Cal. We may conceive of 12 [C] and $11\,H_2$ as oxidized in one step to $12\,CO_2$ and $11\,(H_2O)$ when 1924.2 Cal. are liberated; or we may think of the operation as going on in two steps: (1) the oxidation of 12 [C] and $11\,H_2$ to sugar (*i.e.* to $[C_{12}H_{22}O_{11}]$), and then (2) the oxidation of the latter to $12\,CO_2$ and $11\,(H_2O)$. Now, since the complete oxidation evolves 1924.2 Cal. and step (2) evolves

1353 Cal., it is evident that step (1), which is the formation of sugar from the elements, proceeds with an evolution of $1924.2 - 1353$ or 571.2 Cal. In this computation 97.65 Cal. represents the heat of combustion of amorphous carbon. The heat of combustion of diamond is 94.3 Cal. If the latter value be employed in the problem selected, the heat of formation from the elements will obviously be $571.2 - 12 \times 3.35$, or 531.3 Cal. The value 3.35 Cal. clearly represents the difference in energy between amorphous carbon and diamond.

From the foregoing illustration, the value of the heats of formation of compounds in computing the thermal accompaniments of chemical changes is evident. The following tables, giving the thermochemical data of a few of the most important compounds, will serve to illustrate how such results are usually presented: —

TABLE 1—HEATS OF FORMATION

VALUES ARE EXPRESSED IN LARGE CALORIES. THE SUBSTANCES NAMED ARE IN THE USUAL STATE AT 15° C.

COMPOUND	FORMED FROM	GASEOUS	LIQUID	SOLID	DISSOLVED
HF	H, F	38.5	45.7	——	50.3
HCl	H, Cl	22.0	——	——	39.3
HBr	H, (Br)	8 6	——	——	28.6
HI	H, [I]	– 6.1	——	——	13.1
H_2O	H_2, O	55.3	68.4	69.8	——
H_2O_2	H_2, O_2	——	——	——	45.3
H_2O_2	(H_2O), O	——	——	——	– 23.1
H_2S	H_2, [S] rhombic	2.7	——	——	7.3
NH_3	N, H_3	12.0	16.6	——	20.4
PH_3	yellow [P], H_3	4.3	——	——	——
AsH_3	cryst. [As], H_3	– 44.1	——	——	——
SbH_3	[Sb], H_3	– 86.8	——	——	——
C_2H_2	diamond [C_2], H_2	– 58.1	——	——	——
C_2H_4	[C_2], H_4	– 14.6	——	——	——
C_2H_6	[C_2], H_6	23.3	——	——	——
CH_4	[C], H_4	17.3	——	——	——
SiH_4	cryst. [Si], H_4	– 6.7	——	——	——
O_3	O_2	– 30.7	——	——	——
HClO	H, Cl, O	——	——	——	31.65
$HClO_3$	H, Cl, O_3	——	——	——	24.0
$HClO_4$	H, Cl, O_4	——	18.3	——	38.6
$HBrO_3$	H, (Br) O_3	——	——	——	12.3
HIO_3	H, [I], O_3	——	——	57.9	55.7
HIO_4	H, [I], O_4	——	——	——	47.6
SO_2	rhombic [S], O_2	71.0	——	——	78.8
SO_3	rhombic [S], O_3	——	——	103.3	142.5
H_2SO_4	H_2, [S], O_4	——	189.9	——	210.9
$H_2S_2O_3$	H_2, [S], O_3	——	——	——	141.7
N_2O	N_2, O	– 17.4	——	——	——
NO	N, O	– 21.5	——	——	——
N_2O_3	N_2, O_3	——	——	——	6.8
NO_2	N, O_2	– 7.7	——	——	——
N_2O_4	N_2, O_4	– 2.6	——	——	——
N_2O_5	N_2, O_5	——	——	13.1	29.8
HNO_3	H, N, O_3	34.4	41.5	42.2	48.8
P_2O_5	yellow [P_2], O_5	——	——	370.0	406.0
H_3PO_4	H_3, [P], O_4	——	——	304.1	306.8
As_2O_3	[As_2], O_3	——	——	154.7	147.0
Sb_2O_3	[Sb_2], O_3	——	——	166.9	——
Bi_2O_3	[Bi_2], O_3	——	——	139.2	——
B_2O_3	amorph. [B_2], O_3	——	——	272.6	——
SiO_2aq	cryst. [Si], O_2, aq.	——	——	179.6	——
CO	amorph. [C], O	29.4	——	——	——
CO	diamond [C], O	26.1	——	——	——
CO_2	amorph. [C], O_2	97.65	——	——	103.25

TABLE 1 — *Continued*

Compound	Formed from	Gaseous	Liquid	Solid	Dissolved
CO_2	diamond [C], O_2	94.3	——	——	99.9
PCl_3	yellow [P], Cl_3	69.3	76.6	——	——
PCl_5	yellow [P], Cl_5	——	——	109.2	——
$AsCl_3$	[As], Cl_3	——	71.7	——	——
$SbCl_3$	[Sb], Cl_3	——	——	91.4	——
$BiCl_3$	[Bi], Cl_3	——	——	96.6	——
CCl_4	diamond [C], Cl_4	68.5	75.7	——	——
$SiCl_4$	cryst. [Si], Cl_4	·121.8	128.1	——	——
$SnCl_4$	[Sn], Cl_4	122.2	129.8	——	——
$(CN)_2$	diamond [C_2], N_2	− 73.9	− 68.5	——	67.1
HCN	diamond H, [C], N	− 30.5	− 24.8	——	24.4
CS_2	diamond [C], [S_2] rhombic	− 25.4	− 19.0	——	——

TABLE 2 — HEATS OF FORMATION OF SOME METALLIC COMPOUNDS AT 15° C.

Values are expressed in Large Calories

Compound	Formed from	Solid	Dissolved	Compound	Formed from	Solid	Dissolved
KOH	[K], O, H	103.2	116.5	NH_4Cl	N, H_4, Cl	75.8	71.9
NaOH	[Na], O, H	101.9	111.8	$CaCl_2$	[Ca], Cl_2	169.8	187.2
LiOH	[Li], O, H	112.3	118.1	$ZnCl_2$	[Zn], Cl_2	97.2	112.8
NH_3 aq	NH_3, $n(H_2O)$	——	20.3	$AlCl_3$	[Al], Cl_3	161.0	237.8
MgO	[Mg], O	143.4	——	$FeCl_2$	[Fe], Cl_2	82.1	100.0
CaO	[Ca], O	131.5	149.6	$NiCl_2$	[Ni], Cl_2	74.5	93.7
$Ca(OH)_2$	[Ca], O_2, H_2	214.9	217.9	$CoCl_2$	[Co], Cl_2	76.5	94.8
SrO	[Sr], O	128.4	157.7	HgCl	(Hg), Cl	31.4	——
BaO	[Ba], O	124.2	158.7	$HgCl_2$	(Hg), Cl_2	53.3	50.0
BaO_2	[Ba], O_2	12.1	——	AgCl	[Ag], Cl	29.4	——
MnO	[Mn], O	90.9	——	AuCl	[Au], Cl	5.8	——
MnO_2	[Mn], O_2	125.3	——	$AuCl_3$	[Au], Cl_3	22.8	27.3
FeO	[Fe], O	65.7	——	$PtCl_4$	[Pt], Cl_4	59.8	79.4
Fe_3O_4	[Fe_3], O_4	270.8	——	NaBr	[Na], (Br)	85.8	83.9
ZnO	[Zn], O	84.8	——	NaI	[Na], [I]	69.1	70.3
CuO	[Cu], O	37.2	——	Na_2CO_3	[Na_2], [C], O_3	269.9	275.4
Cu_2O	[Cu_2], O	40.8	——	$NaHCO_3$	[Na], H, [C], O_3	227.0	223.7
PbO	[Pb], O	50.3	——	Na_2SO_4	[Na_2], [S], O_4	328.4	329.0
PbO_2	[Pb], O_2	63.4	——	$NaHSO_4$	[Na], H, [S], O_4	267.8	266.6
HgO	(Hg), O	20.1	——	KNO_3	[K], N, O_3	119.5	111.0
KSH	[K], [S], H	62.3	63.1	$KClO_3$	[K], Cl, O_3	95.0	85.0
CaS	[Ca], [S]	89.6	——	$KBrO_3$	[K], (Br), O_3	84.1	74.3
SrS	[Sr], [S]	97.4	——	KIO_3	[K], [I], O_3	124.5	117.4
BaS	[Ba], [S]	98.3	——	KCN	[K], [C], N	29.8	26.8
FeS	[Fe], [S]	24.0	——	$KMnO_4$	[K], [Mn], O_4	195.0	184.8
CuS	[Cu], [S]	10.1	——	$AgNO_3$	[Ag], N, O_3	28.7	23.3
Ag_2S	[Ag_2], [S]	3.3	——	$CuSO_4$	[Cu], [S], O_4	182 8	198.4
NaCl	[Na], Cl	105.6	101.2	$BaSO_4$	[Ba], [S], O_4	338.1	——

TABLE 3 — HEATS OF COMBUSTION OF SOME CARBON COMPOUNDS

VALUES ARE GIVEN IN LARGE CALORIES. SUBSTANCES ARE IN THEIR USUAL STATE AT 15° C.

COMPOUND	FORMULA	HEAT OF COMBUSTION	HEAT OF FORMATION DIAMOND = [C]
Methane	CH_4	213.5	16.5
Ethane	C_2H_6	370.5	22.1
Propane	C_3H_8	529.2	25.4
Benzene	C_6H_6	787.8	−9.1
Methyl alcohol	CH_3OH	170.6	61.7
Ethyl alcohol	C_2H_5OH	325.7	69.9
Glycerine	$C_3H_5(OH)_3$	397.2	161.7
Acetic acid	CH_3COOH	209.4	117.2
Oxalic acid	$(COOH)_2$	60.2	196.7
Stearic acid	$C_{18}H_{36}O_2$	2677.8	227.6
Starch	$C_6H_{10}O_5$	684.9	225.9
Dextrine	$C_6H_{10}O_5$	667.2	243.6
Cellulose	$C_6H_{10}O_5$	680.4	230.4
Cane sugar	$C_{12}H_{22}O_{11}$	1353.0	531.3
Milk sugar	$C_{12}H_{22}O_{11}$	1351.4	537.4
Malt sugar	$C_{12}H_{22}O_{11}$	1350.7	538.1
Dextrose	$C_6H_{12}O_6$	677.2	302.6
Lævulose	$C_6H_{12}O_6$	675.9	303.9
Urea	$CO(NH_2)_2$	152.2	77.5

TABLE 4 — HEATS OF COMBUSTION OF VARIOUS OTHER ORGANIC SUBSTANCES

SUBSTANCE	HEAT OF COMBUSTION PER 1 GRAM SUBSTANCE
Butter	9.2 Cal.
Animal or vegetable fats and oils, average	9.5 Cal.
Caseine	5.6 Cal.
White of egg	5.7 Cal.
Egg yolk	8.1 Cal.
Peptone	5.3 Cal.
Gluten	6.0 Cal.
Muscular tissues	5.7 Cal.
Fibrin	5.5 Cal.
Hemoglobin	5.9 Cal.

TABLE 5 — HEATS OF NEUTRALIZATION

VALUES GIVEN IN LARGE CALORIES. (THE SOLUTIONS CONTAINED 1 GRAM EQUIVALENT OF ACID OR BASE IN TWO LITERS. SOME OF THE BASES USED AND SULPHATES FORMED ARE INSOLUBLE.)

BASES	HCl aq	HNO_3 aq	CH_3COOH aq	$\frac{1}{2}H_2SO_4$ aq	HCN aq
KOH aq	13.7	13.8	13.3	15.7	3.0
NaOH aq	13.7	13.7	13.3	15.85	2.9
NH_4OH aq	12.45	12.5	12.0	14.5	1.3
$\frac{1}{2}$ $Ca(OH)_2$ aq	14.0	13.9	13.4	15.6	3.2
$\frac{1}{2}$ $Sr(OH)_2$ aq	14.0	13.9	13.3	15.4	3.1
$\frac{1}{2}$ $Ba(OH)_2$ aq	13.85	13.9	13.4	18.4	3.2
$Mg(OH)_2$ aq	13.8	13.8	—	15.6	—
$\frac{1}{2}$ $Fe(OH)_2$ aq	10.7	—	9.9	12.5	—
$Ni(OH)_2$ aq	11.3	—	—	13.1	—
$\frac{1}{2}$ $Co(OH)_2$ aq	10.6	—	—	13.3	—
$\frac{1}{2}$ $Zn(OH)_2$ aq	9.8	9.8	8.9	11.7	—
$Cu(OH)_2$ aq	7.5	7.5	6.2	9.2	—

Uses of Thermochemical Data. — From Table 1 it appears that the heat of formation of the hydrohalogens diminishes as the atomic weight of the halogens increases, hydriodic acid even having a negative heat of formation. We have seen that the stability of these compounds diminishes in the same way, hydrofluoric acid being the stablest and hydriodic acid the least stable. On the other hand, it will be recalled that iodic and periodic acids are more stable than chloric, bromic, and perchloric acids, and, indeed, Table 1 shows that the heats of formation of iodic and periodic acids are higher than those of the corresponding compounds of the other halogens. Water is a much stabler compound than hydrogen sulphide, as is borne out by the great difference in their heats of formation. Ammonia, phosphine, arsine, and stibine diminish in stability in the order named, which is precisely what one would expect from their heats of formation, which also diminish in the same order. Marsh gas and ethane, it will be observed, have positive heats of formation, whereas the unsaturated compounds ethylene and acetylene are formed with absorption of heat. The formation of ozone from oxygen takes place with absorption of much energy, as the negative heat of formation of ozone indicates. From these illustrations and from others with which Tables 1 and 2

are replete, it appears that thermochemical data offer a means of comparing the relative stability of compounds.

Both Thomsen and Berthelot had hoped that thermochemical data would offer a means of exact measurement of chemical attractions, but this has not been realized. Thermochemical data are complicated by the fact that they also represent the energy concomitants of physical changes which invariably accompany chemical reactions, and which cannot be evaluated, as already explained. Moreover, it must be borne in mind that, *in speaking of the stability of a substance, it is really necessary to specify toward what agencies such stability is being considered.* Thus, a substance A might be much stabler than another substance B towards the decomposing action of heat, whereas towards the action of electricity, light, or the inroads of various reagents, A might be less stable than B. So, for instance, carbon tetrachloride, with its heat of formation +68.5, ought to be less stable than silicon tetrachloride, whose heat of formation is +121.8. While this is substantiated by the fact that silicon tetrachloride may readily be obtained by passing chlorine over hot silicon, whereas carbon tetrachloride cannot be similarly obtained, it must also be borne in mind that when treated with water, silicon tetrachloride is at once decomposed into hydrochloric and silicic acids, whereas carbon tetrachloride remains unchanged under the same treatment. However, here the fact that the heat of formation of silicic acid by far exceeds that of carbonic acid no doubt is a determining factor. By means of the electric current neither $SiCl_4$ nor CCl_4 can be decomposed, whereas common salt, which per gram equivalent has over five times as high a heat of formation as carbon tetrachloride, is nevertheless easily decomposed by electrolysis (which see). Thus it is clear that *great care must be exercised in using thermochemical data in arguing as to the relative stability of compounds.*

The value of fuels depends upon their heat-giving power; that is, their heat of combustion. And so it is clear that the heats of combustion of wood, coal, and various liquid and gaseous fuels is of utmost practical importance. In the animal body the foods consumed are digested, assimilated, and finally slowly oxidized and eliminated in the form of carbon dioxide and water in the case of carbohydrates and fats, and in the form of carbon dioxide, water, urea, and other nitrogenous products

in the case of nitrogenous foods. Therefore the heats of combustion of foodstuffs have sometimes been considered in determining the value of various foods. In such a procedure great care must again be exercised; for foods that have nearly the same heat of combustion are frequently of quite different value, because they are not all digested and assimilated with equal readiness. Compare, for example, the heats of combustion of starch and cellulose in Table 3; the values are nearly the same, and yet the food value of the substances to an animal is very different.

An inspection of the heats of combustion in Table 3 shows that analogous substances of the same carbon and hydrogen content have approximately the same heats of combustion, in spite of their differences in structure. Nevertheless, differences in structure do yield corresponding differences in heats of combustion. This matter has been studied in some detail, especially by Stohmann. Adjacent members of homologous series on the average show a difference of about 158 Cal. for CH_2. The heat of combustion of carbon compounds is approximately an additive property. In Table 4 are given the heats of combustion of a few additional important substances.

It will be observed that the heats of neutralization of different bases by different acids, Table 5, are approximately the same in the case of the strong bases and strong acids. This will be discussed in connection with the subject of electrolytic dissociation. In general, Table 5 shows that when a given acid is neutralized, the heat thus developed by bases that are known to be closely related chemically is approximately the same. So when hydrochloric acid is neutralized by sodium or potassium hydroxide, the heat of neutralization is 13.7 Cal. When the same acid is neutralized by ferrous, cobaltous, or nickelous hydroxide, the heat developed is about 10.8 Cal.

REVIEW QUESTIONS

1. Define the following terms: exothermic change, endothermic change, latent heat of fusion, latent heat of vaporization, calorie, British thermal unit, heat of reaction, heat of combustion.

2. What is the law of Hess? Give an example of the law.

3. How do thermochemical equations differ from ordinary chemical equations? Illustrate by means of a concrete example.

4. What is Berthelot's law of maximum work? Discuss its validity.

5. What is meant by each of the following: heat of solution, heat of dilution, heat of neutralization, heat of formation? Give an illustration in each case.

6. How proceed to find the heat of formation of starch? Explain in detail.

7. Of what use is thermochemistry: (*a*) in the study of the value of fuels, (*b*) in the study of the value of foodstuffs? Illustrate by means of concrete instances.

CHAPTER XVIII

SILICON AND BORON AND THEIR IMPORTANT COMPOUNDS

Occurrence, Preparation, and Properties of Silicon. — Next to oxygen, silicon is the most abundant element found in the earth's crust, constituting more than one fourth of the latter. Silicon does not occur in the free state. It is always found in combination with other elements, especially with oxygen as silica, and with oxygen and various metals as silicates. Quartz, quartzite, flint, and the white sands of the seashore and the deserts are nearly pure silicon dioxide; whereas clays are largely composed of silicates.

Silicon was first prepared in pure form in 1823 by Berzelius, who heated potassium silicofluoride with metallic potassium: —

$$K_2SiF_6 + 4\ K = 6\ KF + Si.$$

The element may also be obtained by heating finely powdered quartz sand with magnesium powder: —

$$SiO_2 + 2\ Mg = 2\ MgO + Si.$$

In this case magnesium silicide Mg_2Si is generally also formed; but by means of hydrochloric acid the silicon can readily be freed from this silicide and also from the oxide of magnesium. Silicon may also be obtained by heating sodium or aluminum in a current of silicon tetrachloride vapor, thus: —

$$SiCl_4 + 4\ Na = 4\ NaCl + Si.$$
$$3\ SiCl_4 + 4\ Al = 4\ AlCl_3 + 3\ Si.$$

On a large scale, silicon is now manufactured at Niagara Falls by heating together quartz sand and coke in the electric furnace, thus: —

$$SiO_2 + 2\ C = 2\ CO + Si.$$

Silicon is run out of the electric furnaces into molds. It thus forms "pigs" that weigh from 600 to 800 pounds. The material varies in purity from 90 to 97 per cent, though silicon

over 99 per cent pure has thus been prepared. Silicon is sold in car lots at about $120 per ton. It is mainly used in the steel industry as a reducing agent. Hundreds of tons of 90 per cent silicon are used annually in manufacturing steel. It is very likely that silicon will be used for many other purposes in the near future.

Silicon is either crystalline, or an amorphous brown powder. In the latter form it is commonly obtained by the first three methods above described. **Amorphous silicon** burns when highly heated in the air, the product being silicon dioxide SiO_2. Since the latter is practically non-volatile, its accumulation hinders the securing of complete oxidation of all the silicon. Under a layer of common salt, amorphous silicon may be melted, and on cooling it becomes crystalline. Silicon may also be obtained in crystalline form by dissolving amorphous silicon in molten zinc; on cooling, silicon separates out in form of crystals. The zinc may be removed with hydrochloric acid. Silicon crystallizes in the isometric system, forming dark gray shining plates or rods, which in reality consist of octahedra that have grown together so as to form twin crystals. The specific gravity of silicon is 2.49. It is so hard that it will scratch glass. The crystalline variety conducts electricity, though rather poorly. The amorphous powder is a non-conductor. Like graphite, **crystalline silicon** is hard to oxidize by heating it in the air or in oxygen. Hydrofluoric acid attacks it but slowly; nitric and hydrofluoric acids act on it more rapidly. Fluorine reacts with silicon even at ordinary temperatures with evolution of light and heat: —

$$Si + 4\ F = SiF_4.$$

Hot solutions of caustic potash dissolve silicon: —

$$2\ KOH + H_2O + Si = K_2SiO_3 + 2\ H_2.$$

The atomic weight of silicon is 28.3. It has been determined by analyzing its compounds with the halogens. Silicon is quadrivalent in all of its compounds, the formulæ of which consequently are analogous to those of the compounds of carbon. Indeed, silicon and carbon bear many resemblances in their chemical behavior, and while carbon is exceedingly important in the organic world, silicon plays a similar rôle in the inorganic realm.

Silicon Dioxide, Silica. — This is by far the most important compound of silicon. Its formula is SiO_2. It is **silicic acid anhydride.** In the form of **quartzite**, it often forms mountains. It is the chief constituent of sandstones, and sand is largely silica. In crystalline form it occurs as **quartz** and **amethyst**, and also, though rarely, as **tridymite.** In the amorphous form it is found as **agate, opal, flint, carnelian,** and **chalcedony**, which frequently contain water in combination. Pure silicon dioxide is colorless, but many of the varieties found in nature are colored by various impurities. Thus smoky quartz is discolored with organic matter, rose quartz with manganese, carnelian with oxide of iron, etc. Quartz crystallizes in the hexagonal system. Its crystals occur in two forms that are non-superposable (Fig. 113); that is, they are to each other as the right hand is to the left. These crystals rotate the plane of polarized light passed through them parallel to the main axis. The degree of rotation is proportional to the thickness of the layer traversed, and the deviation is either dextro or lævo according to the crystal used. This property makes quartz useful in certain kinds of optical instruments, particularly in certain types of polariscopes. Tridymite also crystallizes in the hexagonal system. It usually occurs in prismatic plates (Fig. 114).

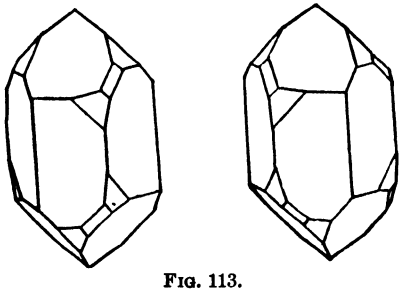


FIG. 113.

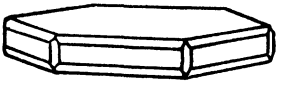


FIG. 114.

Quartz is brittle and very hard. It is consequently used as an abrasive material in grinding glass, metals, etc. Glued on paper, it forms sandpaper. Its specific gravity is 2.6. It requires the temperature of the oxyhydrogen flame to melt quartz. When thus heated, it forms a viscous liquid that can be drawn out and worked like glass. In the electric furnace, the liquid may be boiled and evaporated. In recent years flasks, crucibles, evaporating dishes, and other utensils have been made of **quartz glass.** These have the great advantage that they will not break when subjected to sudden and very great differences

of temperature. This is due to the fact that *quartz changes its volume but very slightly with alterations of temperature.* The coefficient of expansion of quartz between 0° and 1000° is only 0.0000007 on the average, being less than that of any other known substance. A white-hot quartz crucible may be quenched in cold water without injuring the dish.

Silica constitutes about 40 per cent of the ash of the feathers of birds. It is also found in egg albumin, in the hair of animals, and in various crustaceans. Diatomic or **infusorial earth** consists of the siliceous remains of minute organisms called diatoms or infusoria. The stalks of grasses, cereals, field horsetails, bamboo, and other canes contain notable amounts of silica, which is in combination with other elements and aids in giving the stalks stability. Sometimes over half of the ash of these stalks consists of silica.

Besides being used as an abrasive material, silica is employed in the manufacture of glass and in making mortar, cement, and porcelain.

Silicic Acids. — Silicon dioxide is the anhydride of a series of silicic acids. These may all be considered as composed of silica and water in various proportions. They may all be referred to **orthosilicic acid** $Si(OH)_4$, which is well known in the form of salts, though it has not been prepared in the pure state. The acid is probably present in the gelatinous precipitate formed when silicon tetrachloride or tetrabromide is treated with water: —

$$SiCl_4 + 4\ H_2O = 4\ HCl + Si(OH)_4.$$

By losing a molecule of water, orthosilicic acid passes over into **metasilicic acid** H_2SiO_3. From two molecules of orthosilicic acid by elimination of one, two, and three molecules of water the following acids, commonly known as **disilicic acids,** are formed: —

$$H_6Si_2O_7,\ H_4Si_2O_6,\ H_2Si_2O_5.$$

From three molecules of the ortho acid by loss of two and four molecules of water the **trisilicic acids** $H_8Si_3O_{10}$ and $H_4Si_3O_8$ are formed. None of these **polysilicic acids** have been isolated. Their existence is simply vouchsafed by the fact that salts of these acids occur in nature, or have been made in the laboratory. The mineral **olivine** Mg_2SiO_4 (Fig. 70) is a salt of

H_4SiO_4; **sodium silicate**, or water glass, Na_2SiO_3 is a salt of H_2SiO_3; **serpentine** $Mg_3Si_2O_7$ is a salt of $H_6Si_2O_7$; and the feldspars, **orthoclase** $AlKSi_3O_8$ and **albite** $AlNaSi_3O_8$, are salts of $H_4Si_3O_8$.

When silica is fused with sodium carbonate, sodium silicate is formed: —

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

Sodium silicate is soluble in water and is known as **water glass**, as is also the silicate of potassium K_2SiO_3, which may be made similarly. *The silicates of metals other than the alkalies are very slightly soluble in water.* On treating a solution of sodium or potassium silicate with a mineral acid, silicic acid is set free: —

$$Na_2SiO_3 + 2\ HCl = 2\ NaCl + H_2SiO_3.$$

If the solution is concentrated, the silicic acid is precipitated in the form of a jelly. If dilute solutions are used and the water glass is poured into an excess of hydrochloric acid, no precipitate forms. From this clear solution, the sodium chloride and excess of hydrochloric acid may be removed by **dialysis**. The apparatus required for the purpose is called a dialyser, a common form of which is shown in Fig. 115. A parchment paper or animal bladder is securely tied over one end of a cylinder into which the solution is poured. The whole is then immersed in a larger outer dish of water as shown in the figure. The sodium chloride and hydrochloric acid pass through the septum into the outer liquid, while the silicic acid remains behind in the inner vessel. By renewing the water in the outer dish from time to time, practically all of the chlorides can be removed from the inner vessel, which then contains only a solution of silicic acid. This may be concentrated

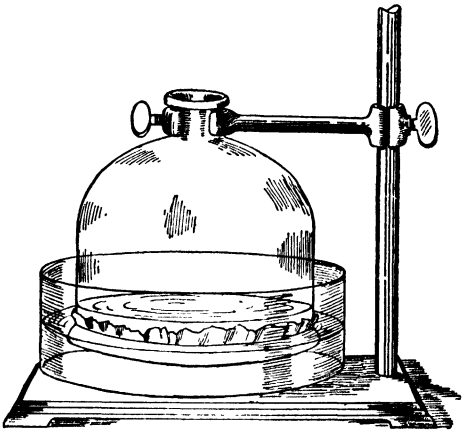


FIG. 115.

by careful evaporation to about 10 per cent, if not quite all of the chlorides have been removed, or to about 1 per cent if practically all the chlorides have been taken out. If attempts are made to concentrate to a greater extent or to preserve the solution for a long time, the silicic acid largely separates out in form of a gelatinous mass, which is termed a **hydrogel**, the clear solution from which the latter has been formed being termed a **hydrosol**. The solution of silicic acid obtained by dialysis as described is also commonly called a **colloidal solution**. This term was introduced by Thomas Graham to denote solutions of non-crystalline bodies which do not pass through membranes used in dialysis experiments. Thus Graham found that, like silicic acid, substances such as glue, gums, albumin, ferric hydroxide, etc., which are non-crystalline, do not pass through parchment or animal membranes as readily as crystalline substances. He consequently made two classes of substances: **colloids**, which do not pass through membranes on dialysis; and **crystalloids**, which do make their way through such septa readily. Though this distinction is still frequently made, it really cannot be held in the light of more recent experiments; for it is quite possible to separate crystalline substances from each other by this process. It is even possible to effect the separation of crystalline from non-crystalline substances by having the *latter* pass through the septum and the crystalline substances remain behind. It all depends upon the nature of the septum chosen and the character of the substances under consideration. So when cane sugar and camphor, both crystalline substances, are dissolved in pyridine, and the solution is separated from pure pyridine by means of a vulcanized caoutchouc membrane, such as the dentists use as "rubber dam," camphor passes through and sugar remains behind. Again, when copper oleate, a non-crystalline substance, and cane sugar together in pyridine solution are similarly subjected to dialysis, the copper oleate passes through the rubber membrane, and the crystalline sugar remains behind. Finally, if to a solution of collodion in alcohol and ether, copper oleate is added and this solution is then (by means of a rubber membrane) separated from a mixture of alcohol and ether such as is used in making up the collodion copper oleate solution, the copper oleate passes through the septum and the nitrocellulose remains behind.

As both copper oleate and nitrocellulose are non-crystalline in character, we have here a case of the separation of two non-crystalloids, that is, in Graham's language, of two colloids, by dialysis.

On drying gelatinous silicic acid, it loses water and finally forms a white amorphous powder which must be heated in the blast to expel all traces of moisture.

Action of Water on Silicates. — Silicates are difficultly soluble in water, yet the earth's crust is continually being worn away by the solvent action of rain water upon the siliceous geological deposits. Rocks like granite, gneiss, schists, shales, and slates are continually being washed away by the solvent action of water, slight though it be. Thus a gradual leveling process is going on which is aided by the action of wind and the disintegrating effects of alternate freezing and thawing. So the silicates are gradually dissolved, and the more resistant quartz grains remain behind as sand. This, however, finds its way into the sea and other depressions filled with water, where the sand grains are frequently gradually cemented together with calcium carbonate or oxides of iron, thus forming so-called **sandstones**. As silicic acid is a very weak acid, which is evident from the fact that its solutions neither react toward litmus nor have any taste, we should expect solutions of silicates to contain these salts, largely in a state of hydrolytic decomposition; and such is actually the case.

Decomposition of Silicates in the Laboratory. — This is effected by fusing the pulverized silicate with sodium carbonate or a mixture of this salt and potassium carbonate. In this way sodium silicate is formed which is soluble in water. The other bases present may generally be readily dissolved with the aid of hydrochloric acid. Silicates may also be decomposed with hydrofluoric acid, or with this and hydrochloric or sulphuric acid. Thus the silicon is volatilized in form of SiF_4, and the bases remain as chlorides or sulphates. Silicates may further be decomposed by heating with calcium carbonate and ammonium chloride and then extracting the mass with water. In the latter process calcium silicate is formed, and the bases are converted into chlorides.

Hydrogen Silicide. — When magnesium silicide Mg_2Si is

treated with hydrochloric acid, hydrogen silicide or **silicomethane** SiH_4 is formed: —

$$Mg_2Si + 4\ HCl = 2\ MgCl_2 + SiH_4.$$

The colorless gas so obtained always contains hydrogen and some **silicoethane** Si_2H_6. Pure SiH_4 does not take fire in the air except under diminished pressure. Silicoethane, however, ignites spontaneously on exposure to the air, and it is this gas whose presence causes SiH_4 to burn in contact with air at ordinary pressure. Silicon tetrahydride may be liquefied at $-11°$ under a pressure of 50 atmospheres. In chlorine gas SiH_4 takes fire. On burning silicon hydride in the air, the products formed are water and silica; the latter forms white smoke. Silicoethane Si_2H_6 boils at $+52°$.

Compounds of Silicon with the Halogens. — **Silicon tetrafluoride** SiF_4 is formed by treating silicon with fluorine, or more readily by treating silica with hydrofluoric acid or a mixture of fluorspar CaF_2 and sulphuric acid, thus: —

$$CaF_2 + H_2SO_4 = 2\ HF + CaSO_4, \text{ and}$$
$$SiO_2 + 4\ HF = 2\ H_2O + SiF_4; \text{ or}$$
$$2\ CaF_2 + SiO_2 + 2\ H_2SO_4 = 2\ CaSO_4 + 2\ H_2O + SiF_4.$$

Silicon tetrafluoride is a colorless gas of very pungent odor. It boils at $-65°$, and the solid melts at $-77°$. The tetrafluoride is always formed when hydrofluoric acid acts on silicates, and it is consequently produced when that acid is used in etching glass.

Water decomposes silicon tetrafluoride: —

$$3\ H_2O + 3\ SiF_4 = H_2SiO_3 + 2\ H_2SiF_6.$$

The silicic acid formed separates out as a gelatinous precipitate, while the hydrofluosilicic acid H_2SiF_6 remains in solution. The latter may be concentrated to some extent by evaporation. The concentration must be carried on in a platinum dish, because hydrogen fluoride is formed during the process, and so glass or porcelain dishes would be attacked. Pure H_2SiF_6 is not known, for on attempting to concentrate its solutions beyond a certain point the acid breaks up, yielding hydrogen fluoride and silicon tetrafluoride. In making fluosilicic acid the silicon tetra-

fluoride generated in a flask by the reaction above mentioned is conducted into water by means of a tube whose lower end dips in mercury (Fig. 116), so that the gelatinous silicic acid formed will not stop the end of the tube. As the gas rises from the mercury, clouds of silicic acid are formed in the water.

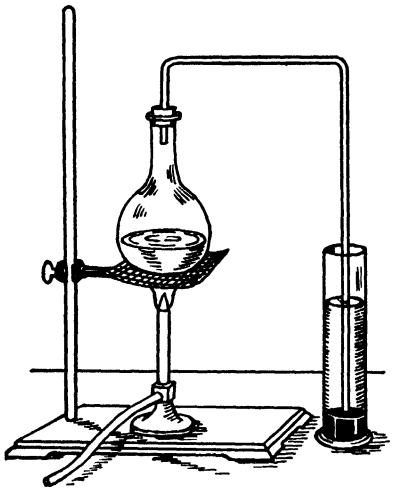


FIG. 116.

Hydrofluosilicic acid is a strong acid. It readily decomposes carbonates and hydroxides of the metals, forming the **fluosilicates.** The latter are decomposed by heat, yielding fluorides of the metals and silicon tetrafluoride. The silicofluorides are commonly soluble in water. The barium salt is insoluble, and the potassium salt is sparingly soluble.

Silicon tetrachloride $SiCl_4$ is formed by heating silicon in a current of chlorine, or by passing chlorine over a heated mixture of carbon and silica, thus: —

$$Si + 2\ Cl_2 = SiCl_4, \text{ or}$$
$$SiO_2 + 2\ C + Cl_4 = 2\ CO + SiCl_4.$$

The product is a liquid of pungent odor. It boils at 59°, has a specific gravity of 1.52 at 0°, and solidifies at − 89°. Water at once decomposes it: —

$$SiCl_4 + 4\ H_2O = 4\ HCl + H_4SiO_4.$$

On heating silicon in a current of hydrochloric acid gas, **silicon chloroform** $SiHCl_3$ may be obtained. This boils at 34°, has a specific gravity of 1.3, and, like silicon tetrachloride, it is at once decomposed by water.

Bromine and iodine compounds of silicon, analogous to the chlorine compounds, have been prepared by similar methods. **Silicon tetrabromide** boils at 153° and melts at − 12°, **silicon tetraiodide** SiI_4 forms octahedra that melt at 120° and boil at 290°

Esters of Silicic Acid. — **Methyl silicate** $(CH_3)_4SiO_4$, boiling at 121°, and **ethyl silicate** $(C_2H_5)_4SiO_4$, boiling at 165°, are also known. They are formed by the action of alcohols on silicon tetrachloride, thus: —

$$SiCl_4 + 4\ CH_3OH = 4\ HCl + (CH_3)_4SiO_4.$$

Water decomposes the esters to alcohol and silicic acid.

Silicon Carbide, Carborundum, SiC. — This substance is formed in the electric furnace by heating together silica or quartz sand, carbon, and common salt to about 3500°. The following reaction occurs: —

$$SiO_2 + 3\ C = 2\ CO + SiC.$$

Silicon carbide forms hexagonal plates that commonly have a dark greenish blue color. The substance is not attacked by acids; not even hydrofluoric acid makes inroads upon it. It may readily be decomposed, however, by fusion with caustic alkalies. Carborundum has a specific gravity of 3.2, and is extremely hard, being next to the diamond in hardness. It is consequently used as an abrasive material. Grinding wheels, whetstones, etc., made of carborundum are in common use.

Titanium, Zirconium, and Thorium. — These are quadrivalent metallic elements whose compounds are analogous to those of silicon. The elements are steel-gray, brittle metals.

Titanium (Ti — 48.1) is found in nature as the dioxide TiO_2, in form of rutile, brookite, and anatase. The element is widely distributed, but occurs nowhere in large quantities. It is also met in **titaniferous iron ores,** which are in the main ferrous titanate $FeTiO_3$. It also occurs together with zircon in certain silicates.

Zirconium (Zr — 90.6) is found chiefly in the mineral **zircon,** which forms tetragonal crystals of the composition $ZrSiO_4$, from which Klaproth prepared the dioxide ZrO_2 in 1789. Moissan prepared the metal by heating the oxide with carbon in the electric furnace.

Though in its compounds **cerium** is also more frequently quadrivalent, it will nevertheless be discussed in connection with lanthanum and other rare-earth elements (which see).

Thorium (Th — 232.4) was found in thorite $ThSiO_4 \cdot 2\,H_2O$ by Berzelius, in 1828. Thorium salts are now prepared from

monazite found in North Carolina. Welsbach light mantles consist of 99 per cent thoria ThO_2 and 1 per cent ceria CeO_2 (see under cerium). Thorium compounds are radio-active (see radium).

Occurrence, Preparation, and Properties of Boron. — This element occurs in nature in the form of boric acid and its salts, called borates. Of the latter borax, the sodium salt, and borocalcite and colemanite, which are calcium salts, are the most important.

The methods of preparing boron are analogous to those of making silicon. So boron may be prepared by reduction of its oxide by means of potassium, sodium, magnesium, or aluminum or by passing the vapors of boron chloride over heated sodium. An *amorphous* and a *crystalline* variety of boron are known. The former results when the oxide B_2O_3 is reduced with potassium, or when borax is heated with magnesium powder. Amorphous boron is a brown powder. On being heated in the air it burns, forming the oxide B_2O_3 and the nitride BN. Sulphuric or nitric acid and other oxidizing agents convert boron into boric acid. When fused with caustic alkalies or their carbonates, borates result. Amorphous boron dissolves in molten aluminum, and on cooling it crystallizes out in tetragonal crystals, which are transparent and generally somewhat colored, due to impurities. These crystals are nearly as hard as the diamond. They are less readily attacked by reagents than the amorphous variety.

Boron is trivalent in all of its compounds. Its atomic weight is 11. While boron resembles silicon and carbon in many respects, the formulæ of its compounds, owing to its trivalence, are analogous to those of the compounds of the phosphorus group and to those of aluminum. The latter element and boron really belong to the same family, though aluminum is a pronounced metal and shows but slight acid-forming properties, while just the opposite is true of boron. The latter really occupies a somewhat lone position amongst the chemical elements.

Boric Acid and its Salts. — Boric acid H_3BO_3 occurs in volcanic regions, particularly in Tuscany, where it issues from the earth in jets of steam. These jets, which contain only small amounts of boric acid, are called *soffioni*, whereas the hot

springs from which the jets issue are termed *fumaroles*. The vapors are condensed in small natural or artificial basins surrounding the fumaroles, and the boric acid is finally obtained by evaporation to the point at which the acid crystallizes out, the heat necessary being furnished by the hot springs. The presence of boric acid in these steam jets is due to the fact that boric acid may be volatilized with water vapor. In the Caucasus Mountains and in some of the hot springs of California, boric acid issues from the earth in a similar manner. Much boric acid is also prepared from borax $Na_2B_4O_7 \cdot 10\ H_2O$, particularly in Nevada and California. A hot, concentrated solution of borax is treated with either hydrochloric or sulphuric acid, and on cooling boric acid crystallizes out. The reaction is: —

$$Na_2B_4O_7 + 5\ H_2O + 2\ HCl = 2\ NaCl + 4\ H_3BO_3.$$

Boric acid crystallizes in shining white scales which are "soapy" to the touch. At 18°, 100 parts of water dissolve 3.9 parts of boric acid, whereas at 100°, 33 parts of the acid are thus dissolved. This fact makes it simple to recrystallize boric acid from its aqueous solutions. The acid is quite weak. It affects litmus but slightly, and its taste is not sour but simply astringent, and somewhat bitter. Solutions of boric acid turn turmeric paper reddish brown. To bring out this color the paper must be dried when very dilute solutions are used. This **test for boric acid** is a very delicate one. When the paper reddened by boric acid is treated with caustic alkali, a black stain is produced, which further serves to characterize boric acid. On treating boric acid with alcohol and sulphuric acid, a volatile ester, **ethyl borate**, is formed, which when ignited burns with a characteristic green flame. This also serves as a test for boric acid. Boric acid is often used in medicine and surgery as an antiseptic. It is also employed in making certain glazes for pottery, and it is still sometimes used as a preservative for meat, fresh fish, milk, and other foods. The latter practice is to be condemned, because the substance is injurious to health.

At 100° boric acid loses water and so forms **metaboric acid** HBO_2, which on further heating to 140° passes over into **pyroboric acid** or **tetraboric acid** $H_2B_4O_7$. The latter on igni-

tion forms the trioxide or **boric anhydride** B_2O_3, which fuses at a high temperature and congeals to a glassy mass on cooling. When treated with water it forms boric acid.

Salts of the acid H_3BO_3 are not known, but the **esters** like $(CH_3)_3BO_3$ and $(C_2H_5)_3BO_3$ are well known. **Metaborates** like $NaBO_2$ have been formed, but they are unstable.

By far the most important salt of boric acid is **borax** $Na_2B_4O_7 \cdot 10\,H_2O$. It is the sodium salt of tetraboric acid $H_2B_4O_7$, which may be considered as $4\,H_3BO_3$ minus $5\,H_2O$. Borax is found in the borax lake of California and in certain marshes of that state and Nevada. It also occurs in Thibet, Ceylon, and Bolivia. Large quantities of borax and boric acid are prepared from colemanite $Ca_2B_6O_{11} \cdot 5\,H_2O$, which is found in California and Oregon. The amount of borax produced annually from the deposits in the United States is in the neighborhood of 50,000 tons.

Borax solutions have a slightly alkaline reaction toward indicators, which is explained by the fact that boric acid is weak and its salts are somewhat decomposed by hydrolysis. At 100°, 100 parts of water dissolve 201.4 parts of $Na_2B_4O_7 \cdot 10\,H_2O$, whereas at 10° only 4.6 parts are thus dissolved. Borax crystallizes in large monoclinic prisms from solutions below 50°; above that temperature the crystals formed are octahedra of the composition $Na_2B_4O_7 \cdot 5\,H_2O$. The salt comes in the market in both forms.

When borax is heated, it swells up because of loss of water in the form of steam. A clear liquid is finally obtained which solidifies to **borax glass**. The latter when molten dissolves many metallic oxides, and these solutions have colors characteristic of the metals they contain, a fact that is often used in chemical analysis, and in making glazes and enamels for pottery.

Borax is used in the laundry for softening water, and to increase the gloss of starch in ironing. It is further employed as a flux in welding and brazing metals, as a mordant in dyeing fabrics, as an antiseptic in medicine, and as a preservative. It ought not to be used as a preservative for foods.

Other Compounds of Boron. — **Boron hydride** BH_3 is a gas formed by the action of magnesium boride upon hydrochloric acid.

Boron nitride BN is a white solid formed by the direct union of nitrogen with boron when heated. Water vapor decomposes it at high temperatures, forming boric acid and ammonia.

Boron trifluoride BF_3 is a colorless, pungent gas made by the action of hydrofluoric acid on boron trioxide, or by heating the latter with fluorspar: —

$$3\,CaF_2 + 2\,B_2O_3 = Ca_3B_2O_6 + 2\,BF_3.$$

Boron trichloride BCl_3 is a colorless liquid of pungent odor. It boils at 18.2° and is decomposed by water into hydrochloric and boric acids: —

$$BCl_3 + 3\,H_2O = 3\,HCl + H_3BO_3.$$

Boron carbide B_6C is obtained as an extremely hard solid by heating boron with carbon in the electric furnace.

Boron sulphide B_2S_3 forms small white crystals obtained by heating boron and sulphur together. The sulphide is decomposed by water with violence, thus: —

$$B_2S_3 + 6\,H_2O = 2\,B(OH)_3 + 3\,H_2S.$$

REVIEW QUESTIONS

1. Compare the physical and chemical properties of silicon and carbon.
2. How may silicon be prepared? Give three methods and the chemical equation illustrating each.
3. What practical use is made of silicon?
4. Discuss the occurrence of silica and silicates in nature?
5. What is water glass? Give the reaction showing its preparation. What use is made of water glass?
6. What is quartz? What uses are made of quartz? How is it affected by hydrofluoric acid? Write the equation.
7. Classify the silicic acids. Mention five important silicates that are formed in nature and give their formulas. Mention two different methods by means of which these silicates may be decomposed chemically.
8. Define: dialysis, hydrogel, hydrosol, colloid, crystalloid, and give an example of each.
9. How does water act upon the silicates of the earth's crust?
10. Compare the properties of hydrogen silicide with those of marsh gas.

11. What is carborundum, and how is it made?

12. What other elements are commonly classed with silicon? Why? What use is made of these elements or their compounds?

13. How show that silica has acidic properties? Equation. What compound of silicon is analogous to: (*a*) potassium carbonate, (*b*) carbon dioxide?

14. How may a soluble substance be prepared from silicon dioxide? How may a volatile substance be formed from it?

15. What are the most important forms in which boron is found in nature?

16. How prepare boric acid from borax. Write the equation. Compare this method with that of making: (*a*) silicic acid, (*b*) oleic acid, (*c*) hydrochloric acid, (*d*) nitric acid, (*e*) hydrogen sulphide. Do the reactions involved in all these cases come under the same principle of chemical equilibrium? Explain.

17. What are the uses of borax and boric acid?

18. Give two tests for boric acid.

19. How much pure crystallized borax would be required to prepare 100 pounds of boric acid?

20. Many metallic oxides give characteristic colors to borax beads. Explain the chemical changes involved, and state what practical use is made of them.

21. What color does cupric oxide impart to a borax bead when heated (*a*) in the oxidizing flame, (*b*) in the reducing flame? Explain.

CHAPTER XIX

PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

Occurrence and Preparation of Phosphorus. — Phosphorus does not occur in the free state in nature because of its great affinity for oxygen. It is widely distributed in the form of phosphates, particularly as calcium phosphate $Ca_3(PO_4)_2$, or apatite $3\,Ca_3(PO_4)_2 + Ca(ClF)$, though it is at times also found as wavellite $2\,Al_2(PO_4)_2 + Al_2(OH)_6 + 9\,H_2O$, vivianite $Fe_3(PO_4)_2 + 8\,H_2O$, and pyromorphite $3\,Pb_3(PO_4)_2 + PbCl_2$. In iron ores, phosphorus occurs as phosphates of iron and calcium, and these are obtained from the slags of blast furnaces. Calcium phosphate is found in many rocks and in all fertile soils. Phosphorus is also an essential ingredient of plant and animal tissues. It is specially necessary in the development of the seeds of plants, hence its importance in the soil, from which the phosphates are taken up by the roots of plants. The ash of bones consists of 80.85 per cent calcium phosphate. In the brain, nerves, blood, albumen, and muscles, phosphorus plays an important rôle. It occurs here in complex compounds with carbon, hydrogen, nitrogen, oxygen, and sulphur, the nervous tissues being especially rich in a compound called **lecithine** $C_{44}H_{90}NPO_9$. The urine and excreta of animals always contain phosphates.

Phosphorus was first prepared in 1669 by the alchemist Brandt, in Hamburg, who evaporated urine and heated the residues mixed with sand to high temperatures. The process was kept a secret, but was soon discovered by Boyle in England and Kunkel in Germany. Gahn showed that calcium phosphate is abundant in bones (1769), and two years later Scheele developed a method for preparing phosphorus from bone ash. Thus calcium sulphate and phosphoric acid are formed by means of the following reaction : —

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 = 3\,CaSO_4 + 2\,H_3PO_4.$$

The calcium sulphate is insoluble, while the phosphoric acid remains in solution and is drained off. This solution is evapo-

rated to dryness after coke, charcoal, or sawdust have been added, and the mass is then transferred to retorts and heated. In this way water is driven off first, finally carbon monoxide, hydrogen, and phosphorus are formed, the latter being condensed and collected under water. An older process consists of first forming **monocalcium phosphate**, which under the name of **superphosphate** is used as a fertilizer, thus: —

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = 2\,CaSO_4 + CaH_4(PO_4)_2.$$

This is then heated to form **calcium metaphosphate** $Ca(PO_3)_2$: —

$$CaH_4(PO_4)_2 = 2\,H_2O + Ca(PO_3)_2.$$

Finally, by mixing the calcium metaphosphate with sand and coke or charcoal, and heating the mixture in earthenware retorts, of which a number are placed in a furnace, the phosphorus is obtained and condensed as before. The reaction is: —

$$2\,Ca(PO_3)_2 + 2\,SiO_2 + 10\,C = 2\,CaSiO_3 + 10\,CO + 4\,P.$$

Figure 117 shows an arrangement of retorts for making phosphorus.

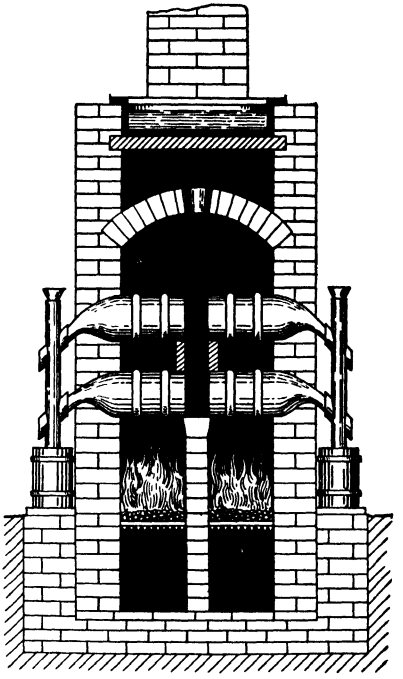


FIG. 117.

By using the electric furnace, phosphorus is now being prepared in a simpler way, the process being a continuous one. Calcium phosphate is thoroughly mixed with carbon and silica in pulverized form, and this mixture is heated to a high temperature in the electric furnace. Figure 118 shows the arrangement. The charge is fed in continuously on top by the conveyor, the calcium silicate slag is tapped off at the bottom, and the phosphorus vapors issue from the pipe in the upper part of the furnace and are condensed under water. The reaction is: —

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C = 3\,CaSiO_3 + 5\,CO + 2\,P.$$

Thus the silica lays hold of the calcium oxide as it were, forming calcium silicate, and the oxygen is taken away from the phosphorus by the carbon at the high temperature, carbon monoxide being formed. Phosphorus when first condensed as described is contaminated with sand, carbon, and other matter, from which it must be freed. This is accomplished by melting it under water and straining it, also under water, of course, through canvas sacks. It is then redistilled from retorts made of iron, and cast into sticks in glass or tin molds kept in cold water. These sticks are commonly half an inch in diameter and 7.5 inches long, so that nine sticks make approximately a pound of phosphorus. Phosphorus is shipped immersed in water in tin cans.

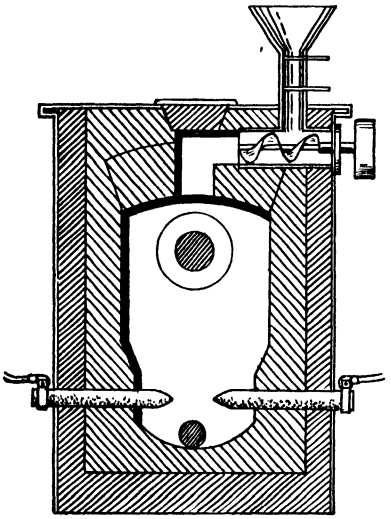


FIG. 118.

Properties and Allotropic Forms of Phosphorus. — The phosphorus obtained by the methods above described is known as **yellow or white phosphorus.** It is a pale yellow, translucent, waxlike solid, which in a high state of purity is nearly colorless. In the cold it is brittle, somewhat above room temperatures it has the consistency of wax, at 44° it melts under water, and at 269° it boils under atmospheric pressure. Yellow phosphorus is practically insoluble in water, but it may be dissolved to some extent in alcohol, ether, benzene, and various ethereal oils and fats. It is copiously soluble in carbon disulphide, from which it may be obtained in rhombic dodecahedra of the isometric system (Fig. 46) by evaporating off the solvent out of contact with the air.

When exposed to the air, phosphorus slowly oxidizes, during which process the oxidation products form fumes, and emit a faint light that is visible in the dark. From the latter phenomenon phosphorus derives its name. By such slow oxidation phosphorus gradually forms a solution of hypophosphoric

acid which has reducing properties. During this oxidation at room temperatures, ozone and ammonium nitrite are also formed from the air. At about 35° phosphorus catches fire in the air. It must consequently be kept under water. If a little of the solution of phosphorus in carbon disulphide is poured upon filter paper and allowed to evaporate, the finely divided phosphorus remaining on the paper takes fire spontaneously. **Phosphorus is very poisonous**, 0.1 gram being a fatal dose for adults. Employees in match factories are apt to suffer from phosphorus poisoning, which manifests itself in enlargement of the liver and necrosis of the jawbones. **Phosphorus should always be handled with a forceps and with great care, for phosphorus burns are dangerous and very slow to heal.**

When yellow phosphorus is heated from 250° to 300° in closed vessels out of contact of the air, it is gradually converted into **red phosphorus**, an allotropic form of phosphorus which was discovered by Schrötter in 1845. The reaction is accompanied with evolution of heat, and is never quite complete, being reversible. When red phosphorus is heated to 260° in a current of carbon dioxide or nitrogen, and the vapors are condensed under water, the yellow variety is again obtained. Light acting on yellow phosphorus slowly produces some of the red variety, so that ordinary sticks of phosphorus often have a reddish brown outer appearance. Red phosphorus is also called *amorphous;* it does not emit light in the dark. It may be heated to about 200° in the air without taking fire and consequently need not be kept under water. It is insoluble in carbon disulphide and other solvents that dissolve yellow phosphorus. Moreover, red phosphorus is not poisonous; and, in general, it is much less active than yellow phosphorus, which contains more energy. The specific gravity of red phosphorus is 2.25. By careful heating, it may be sublimed. The atomic weight of phosphorus is 31. Its valence is either three or five. The vapors of red and yellow phosphorus are identical. The density of the vapor corresponds to the formula P_4.

Uses of Phosphorus, Matches. — A small portion of the phosphorus produced is used for poisoning rats and other vermin. Most of it is used in making matches. The annual production of phosphorus amounts to over 3000 tons. Flint, steel, and tinder were still used to light fires at the beginning of the nine-

teenth century. In 1812 the first matches made their appearance. They were invented by Chancel, and consisted of sticks dipped in molten sulphur which was afterwards covered with sugar mixed with potassium chlorate. To light such a match its head was brought in contact with concentrated sulphuric acid, which was commonly absorbed in asbestus and kept in a bottle. Thus chloric acid was liberated, and this set the sulphur and sugar on fire. In 1827 **friction or lucifer matches** came into use. These had a head consisting of potassium chlorate, antimony sulphide, and glue. They were set on fire by rubbing them vigorously on sandpaper. Phosphorus matches appeared in the market in 1832. They contained a little phosphorus in place of the sulphide of antimony, which caused them to ignite more readily. Soon potassium nitrate came into use in matches in place of potassium chlorate, which is apt to cause explosions. At present the oxidizing agents in matches are red lead Pb_3O_4, lead peroxide PbO_2, or manganese peroxide MnO_2. In making matches the ends of the well-dried sticks are first dipped into paraffine. Afterwards they are dipped into the igniting mixture, consisting of phosphorus stirred into a solution of glue or dextrine, to which the oxidizing agents are added, together with some coloring matter like lamp-black, chalk, or ultramarine to form a paste of proper consistency. **Safety matches** were invented by Böttger in 1848. They had a head of potassium chlorate and antimony trisulphide like the lucifer matches, but it contained enough glue so that the match ignited with great difficulty on ordinary surfaces. However, by rubbing these matches on a surface containing red phosphorus, which was glued on the box, they would ignite very readily. These safety matches, which are often called Swedish matches, for they were first placed on the market in large quantities in Sweden, are now in common use. The use of the ordinary match that will ignite by friction on any surface is prohibited by law in some countries. The modern safety matches commonly have a head consisting of potassium chlorate, potassium bichromate, powdered glass, and glue or dextrine; and the friction surface on the box contains antimony trisulphide, red phosphorus, manganese dioxide, and glue. The purpose of the powdered glass in the head is to increase the friction, the heat from which raises

the temperature so that the phosphorus unites vigorously with the oxygen of the oxidizing agents, thus setting the match on fire.

Compounds of Phosphorus with Hydrogen.—Three compounds of phosphorus and hydrogen are known. They are called **phosphines or phosphureted hydrogen.** Their composition corresponds to the formulæ: —

PH_3, a gas; P_2H_4, a liquid; and P_4H_2, a solid.

Gaseous phosphine PH_3 is prepared by heating phosphorus in a concentrated solution of caustic potash out of contact with the air. The reaction is: —

$$P_4 + 3\,KOH + 3\,H_2O = 3\,KH_2PO_2 + PH_3.$$

In addition, there is always some hydrogen and P_2H_4 formed. The vapors of the latter are spontaneously inflammable in the air. The experiment is conducted with the apparatus shown in Fig. 119. The small flask is filled half full of caustic potash

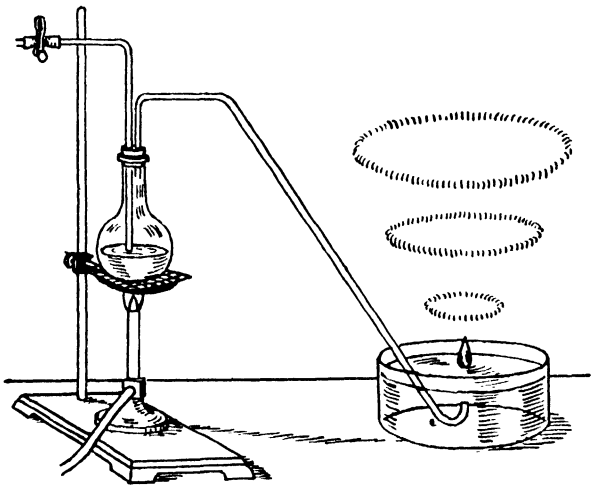


FIG. 119.

solution, and the remaining air is displaced by conducting in illuminating gas or hydrogen through the small tube at the left, which is then closed. On applying heat, phosphine forms and catches fire, forming white smoke rings as it issues from the mouth of the delivery tube, which is kept *under warm* water

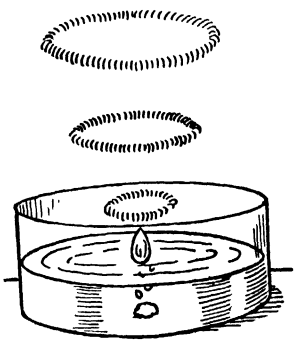


FIG. 120.

to prevent its clogging by phosphorus that might distill over and solidify in the end of the tube. If the phosphine formed is first passed through alcohol or hydrochloric acid, the P_2H_4 is removed and the gas PH_3 is then no longer spontaneously inflammable in the air. In a simpler manner, phosphine may be obtained by treating calcium phosphide with water or dilute hydrochloric acid (Fig. 120) thus: —

$$Ca_3P_2 + 6\,H_2O = 3\,Ca(OH)_2 + 2\,PH_3, \text{ or}$$
$$Ca_3P_2 + 6\,HCl = 3\,CaCl_2 + 2\,PH_3.$$

In these reactions, smaller amounts of the solid and liquid hydrides of phosphorus, P_4H_2 and P_2H_4, are also obtained by secondary reactions. Phosphides of magnesium, zinc, and iron similarly yield phosphine with hydrochloric acid.

By heating phosphorous or hypophosphorous acid, phosphine is produced, thus: —

$$\underset{\text{phosphorous acid}}{4\,H_3PO_3} = \underset{\text{phosphoric acid}}{3\,H_3PO_4} + PH_3, \text{ or}$$
$$\underset{\text{hypophosphorous acid}}{2\,H_3PO_2} = \underset{\text{phosphoric acid}}{H_3PO_4} + PH_3.$$

When phosphonium iodide PH_4I is treated with caustic alkalies, phosphine is formed, thus: —

$$PH_4I + NaOH = NaI + H_2O + PH_3.$$

Water also decomposes phosphonium iodide: —

$$PH_4I + H_2O = HI + H_2O + PH_3.$$

Gaseous phosphine is colorless. It boils at $-85°$ and solidifies at 133°. The gas has the odor of rotten fish and is *very poisonous*. Heated to about 100° in the air it burns and forms water and phosphoric acid. Phosphine is but slightly soluble in water. Alcohol dissolves it more copiously.

With the hydrohalogens phosphine forms **phosphonium compounds**, which are analogous to ammonium salts. **Phosphonium iodide**, the best known of the phosphonium compounds, is prepared by the following reaction: —

$$PH_3 + HI = PH_4I; \text{ which is analogous to}$$
$$NH_3 + HI = NH_4I.$$

Phosphonium iodide is a very unstable, colorless, crystalline salt, which is decomposed by water into phosphine and hydriodic acid, as stated above. Oxygen acids do not form phosphonium salts with phosphine.

Liquid phosphine P_2H_4 is analogous to hydrazine N_2H_4. It is a colorless liquid of specific gravity 1.01 at 15°. It boils at 57° and is insoluble in water.

Solid phosphine P_4H_2 is a yellow, flocculent powder which is devoid of odor and taste. It does not dissolve in water. At about 160° it takes fire in the air.

Compounds of Phosphorus with the Halogens. — Phosphorus forms compounds with all of the halogens. These have the general formulæ PX_3 and PX_5. The chlorides PCl_3 and PCl_5 are the most important.

Phosphorus trichloride PCl_3 is formed when chlorine is passed upon phosphorus in a retort. The action proceeds readily with liberation of heat, the product being a colorless liquid of pungent odor. In the pure state phosphorus trichloride boils at 76° and solidifies at − 115°. Its specific gravity is 1.613 at 0°. Water decomposes it: —

$$PCl_3 + 3\ H_2O = 3\ HCl + P(OH)_3.$$

Phosphorus pentachloride PCl_5 is formed by treating phosphorus trichloride with chlorine, or by passing an excess of chlorine upon phosphorus in a retort: —

$$PCl_3 + Cl_2 = PCl_5, \text{ or}$$
$$P_4 + 10\ Cl_2 = 4\ PCl_5.$$

The product is a light yellow, finely crystalline solid which cannot be melted under atmospheric pressure, for the temperature at which its vapor tension equals atmospheric pressure lies below the melting point of the compound. Under the pressure of its own vapor in a sealed tube, phosphorus pentachloride may be melted at 148°. When heated, phosphorus pentachloride decomposes into phosphorus trichloride and chlorine: —

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

At 300° this dissociation is nearly complete. The action is reversible, as indicated. It is quite similar to the dissociation of ammonium chloride by means of heat: —

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

With water, phosphorus pentachloride forms hydrochloric acid and phosphorus oxychloride: —

$$PCl_5 + H_2O = 2\,HCl + POCl_3.$$

The latter is a colorless liquid of specific gravity 1.712 at 0°. It boils at 107.5° and melts at 1.8°. On further treatment with water, the oxychloride also decomposes, yielding hydrochloric acid and phosphoric acid: —

$$POCl_3 + 3\,H_2O = 3\,HCl + H_3PO_4.$$

Phosphorus trifluoride PF_3 is a colorless gas. It boils at − 95° and congeals at − 160°. The **pentafluoride** PF_5 melts at − 83° and boils at − 75°. These compounds are decomposed by water like the analogous chlorides, but more slowly. **Phosphorus oxyfluoride** POF_3 is a gas which may be liquefied at − 50°.

Phosphorus tribromide PBr_3 is a colorless liquid boiling at 172°. Its specific gravity is 2.925 at 0°. **Phosphorus pentabromide** PBr_5 forms yellow crystals, which on heating dissociate into bromine and phosphorus tribromide.

Phosphorus triodide PI_3 forms dark red, prismatic crystals melting at 61°. Phosphorus pentaiodide is not known, but a **diphosphorus tetraiodide** P_2I_4 is known. It forms orange-yellow crystals which melt at 110°.

On treatment with water, both the bromides and iodides of phosphorus are decomposed into the hydrohalogen acids and oxygen acids of phosphorus. From phosphorus pentabromide, **phosphorus oxybromide** $POBr_3$ may be obtained in a manner analogous to the formation of $POCl_3$. *The treatment of phosphorus tribromide or triodide with water affords excellent methods for making pure hydrobromic and hydriodic acids*, as already stated.

Oxides and Acids of Phosphorus. — The following oxides of phosphorus are well known: phosphorus trioxide P_2O_3; phosphorus tetroxide P_2O_4; and phosphorus pentoxide P_2O_5. Of these the latter is the most important by far. The trioxide is a white crystalline solid melting at 22.5°. It is obtained together with the pentoxide by burning phosphorus in an insufficient amount of oxygen. The tetroxide is a white solid formed, together with red phosphorus, by heating the trioxide

in a sealed tube to 440°. **Phosphorus pentoxide** P_2O_5 is formed when phosphorus is burned in the air or in oxygen. It is a light white powder which unites with water with great avidity, forming metaphosphoric acid, thus:—

$$P_2O_5 + H_2O = 2\,HPO_3.$$

Phosphorus pentoxide is the best drying agent known. Its action on water is accompanied with evolution of much heat and a hissing noise resembling that accompanying the quenching of hot iron.

In union with different amounts of water, phosphorus pentoxide forms three acids, thus. —

$$P_2O_5 + H_2O = 2\,HPO_3 \text{ (metaphosphoric acid)},$$
$$P_2O_5 + 2\,H_2O = H_4P_2O_7 \text{ (pyrophosphoric acid)},$$
$$P_2O_5 + 3\,H_2O = 2\,H_3PO_4 \text{ (orthophosphoric acid)}.$$

By union with two or six molecules of water phosphorus trioxide forms two acids, thus: —

$$2\,P_2O_3 + 2\,H_2O = 4\,HPO_2 \text{ (metaphosphorous acid)},$$
$$2\,P_2O_3 + 6\,H_2O = 4\,H_3PO_3 \text{ (phosphorous acid)}.$$

There are also known **hypophosphoric acid** $H_4P_2O_6$ and **hypophosphorous acid** H_3PO_2. The former is prepared by allowing sticks of phosphorus to oxidize slowly in contact with moist air, under which conditions phosphoric and phosphorous acids are also formed to some extent. The acid is tetrabasic, and consequently is able to form four kinds of salts by successive replacement of the hydrogen atoms. Hypophosphorous acid H_3PO_2 may be liberated from its barium salt by action of sulphuric acid, thus: —

$$8\,P + 3\,Ba(OH)_2 + 6\,H_2O = 2\,PH_3 + 3\,Ba(H_2PO_2)_2, \text{ and}$$
$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2\,H_3PO_2.$$

It is a monobasic acid, forming crystals that melt at 17.4°. It is a strong reducing agent. On being heated, it yields phosphine and phosphoric acid.

Orthophosphoric Acid. — This compound is also called simply **phosphoric acid**. Its composition is expressed by the formula H_3PO_4. It may be considered as derived from the hypothetical pentahydroxide of phosphorus $P(OH)_5$ by loss of one molecule of water. Pure phosphoric acid is prepared by action

of phosphorus pentoxide on water or by the oxidation of phosphorus by means of nitric acid. Phosphoric acid is also made by the action of sulphuric acid upon calcium phosphate. The calcium sulphate formed simultaneously, being insoluble, is readily removed and the clear solution containing the phosphoric acid is then evaporated. It commonly still contains some calcium salts which may be precipitated by means of alcohol. Solutions of pure phosphoric acid may be evaporated to a thick, colorless sirup of specific gravity 1.88, from which upon cooling a crystalline mass is obtained, which melts at 42°. The crystals are deliquescent and dissolve in water with great readiness. The solutions are strongly acidic in character. The acid is not poisonous. *Phosphoric acid is tribasic and consequently is able to form three classes of salts, the primary, secondary, and tertiary phosphates*, for instance : —

$$H_3PO_4 + KOH = KH_2PO_4 + H_2O.$$
$$H_3PO_4 + 2\,KOH = K_2HPO_4 + 2\,H_2O.$$
$$H_3PO_4 + 3\,KOH = K_3PO_4 + 3\,H_2O.$$

The tertiary phosphates are the normal or neutral salts ; whereas the secondary and primary salts still contain one and two hydrogen atoms respectively in the molecule. The hydrogen atoms need not all be replaced by the same metal or radical. Thus we have sodium ammonium hydrogen phosphate $NaNH_4HPO_4$, which is also known as **microcosmic salt.** **Magnesium ammonium phosphate** $MgNH_4PO_4$ forms white insoluble crystals ; it is of importance in analytical chemistry. Solutions of the secondary salts have an alkaline reaction, being to some extent decomposed by hydrolysis. The tertiary salts are much more hydrolyzed by water; indeed they are stable only as solids, and are obtained by evaporating the acid to dryness with the proper amount of alkali. These salts are not decomposed by heat, whereas both the secondary and primary phosphates lose water on being heated : so, for instance : —

$$2\,Na_2HPO_4 \rightleftarrows \underset{\text{sodium pyrophosphate}}{Na_4P_2O_7} + H_2O \text{ ; and}$$

$$NaH_2PO_4 \rightleftarrows \underset{\text{sodium metaphosphate}}{NaPO_3} + H_2O.$$

Thus secondary phosphates yield pyrophosphates, and primary phosphates yield metaphosphates, on heating. Conversely, on treatment with water the pyrophosphates gradually pass back into secondary phosphates, and the metaphosphates into primary phosphates. Microcosmic salt and magnesium ammonium phosphate lose ammonia as well as water on being heated, thus:—

$$NaNH_4HPO_4 = H_2O + NH_3 + NaPO_3.$$
$$2\,MgNH_4PO_4 = H_2O + 2\,NH_3 + Mg_2P_2O_7.$$

Pyrophosphoric acid $H_4P_2O_7$ is formed by heating phosphoric acid to about 250° till a sample neutralized with ammonia and tested with silver nitrate solution yields a white precipitate. The white precipitate is **silver pyrophosphate** $Ag_4P_2O_7$, whereas the phosphate of silver Ag_3PO_4 is yellow. The formation of pyrophosphoric acid takes place thus:—

$$2\,H_3PO_4 = H_4P_2O_7 + H_2O.$$

The aqueous solutions of pyrophosphoric acid are fairly stable, the acid passing over into orthophosphoric acid but slowly. The presence of sulphuric or nitric acids hastens the change. Though the molecule of pyrophosphoric acid contains four hydrogen atoms, but two kinds of pyrophosphates are known. These correspond to the types $K_4P_2O_7$ and $K_2H_2P_2O_7$.

By the color of the silver salt, pyrophosphoric acid is readily distinguished from orthophosphoric acid. From metaphosphoric acid, pyrophosphoric acid is distinguished by the fact that it does not coagulate albumen like the former.

Metaphosphoric acid HPO_3 is made by heating phosphoric acid to 400°:

$$H_3PO_4 = H_2O + HPO_3;$$

or by treating phosphorus pentoxide with water;

$$P_2O_5 + H_2O = 2\,HPO_3;$$

or by heating ammonium phosphate;

$$(NH_4)_2HPO_4 = 2\,NH_3 + H_2O + HPO_3.$$

The acid is a glassy, semitransparent mass which is also called **glacial phosphoric acid.** In contact with water, it slowly passes over into phosphoric acid, the action being hastened by boiling. The acid is monobasic and is analogous to nitric, chloric, and

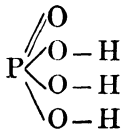
bromic acids. Solutions of glacial phosphoric acid coagulate albumen and give white precipitates with the chlorides of barium or calcium, which behavior is different from that of solutions of pyrophosphoric acid.

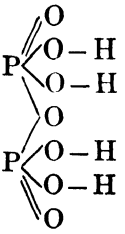
Phosphorous acid H_3PO_3 forms as one of the products of the slow oxidation of phosphorus in moist air. It is best prepared by treating phosphorus trichloride with water and driving off the hydrochloric acid formed simultaneously, by heating to 180°. The acid forms very hygroscopic crystals that melt at 70°. On heating, it decomposes into phosphoric acid and phosphine: —

$$4\,H_3PO_3 = 3\,H_3PO_4 + PH_3.$$

At the high temperature at which the reaction takes place, the phosphoric acid formed passes over into metaphosphoric acid, and the phosphine burns with a green flame. Though phosphorous acid has three hydrogen atoms in the molecule, it is only dibasic. Its salts correspond to the type Na_2HPO_3, the third hydrogen atom not being replaceable by a metal.

Formulæ of the Acids of Phosphorus. — The following structural formulæ of the oxy-acids of phosphorus will serve to impress their relationships further: — .


orthophosphoric acid.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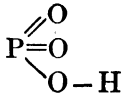
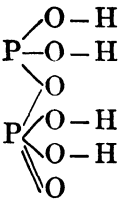
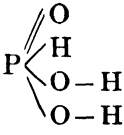
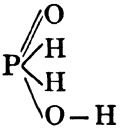

metaphosphoric acid.


hypophosphoric acid.


phosphorous acid.


hypophosphorous acid.

It will be seen that the dibasic character of phosphorous acid is expressed by connecting the non-replaceable hydrogen atom directly with the phosphorus. Similarly the monobasic character of hypophosphorous acid is indicated by connecting the two non-replaceable hydrogen atoms directly with phosphorus.

Compounds of Phosphorus with Sulphur. — With sulphur, phosphorus unites directly, forming a series of compounds: P_4S_3, P_2S_3, P_3S_6, and P_2S_5. The action of yellow phosphorus upon hot sulphur is violent; the sulphides are consequently made by using red phosphorus. **Phosphorus pentasulphide** P_2S_5 forms yellow crystals which melt at 275°. The liquid boils at 518°. With **potassium sulphide** it forms **potassium sulphophosphate**: —

$$P_2S_5 + 3\,K_2S = 2\,K_3PS_4.$$

With phosphorus pentachloride **phosphorus sulphochloride** $PSCl_3$ results: —

$$P_2S_5 + 3\,PCl_5 = 5\,PSCl_3.$$

The latter compound is a colorless liquid of specific gravity 1.168 at 0°. It boils at 125°, and decomposes upon treatment with water: —

$$PSCl_3 + 4\,H_2O = 3\,HCl + H_2S + H_3PO_4.$$

Occurrence, Preparation, and Properties of Arsenic. — Arsenic is very widely distributed in nature in minute quantities. It rarely occurs in the uncombined state, being found in larger quantities in combination with sulphur, as in realgar As_2S_2 and orpiment As_2S_3. It is also found combined with oxygen, as in arsenolite As_2O_3, and with iron and sulphur and cobalt and sulphur, as in arsenical pyrites or mispickel FeAsS and cobaltite CoAsS.

Arsenic is commonly prepared by heating mispickel or by reducing arsenolite with carbon. The reactions are: —

$$FeAsS = FeS + As.$$
$$2\,As_2O_3 + 6\,C = As_4 + 6\,CO.$$

Arsenic is volatile; it sublimes, and is readily condensed.

Arsenic is steel-gray in color, has a bright metallic luster, and is very brittle. Its specific gravity is 5.73 at 15°. On heating, it volatilizes without melting; but under pressure it may be melted at about 480°. At 450° its vapor tension equals

atmospheric pressure. Heated in the air, it burns, the fumes having a garlic-like odor and the flame a pale lavender color; these are characteristic of arsenic. *Between* 560° *and* 860° *the vapor of arsenic is about* 150 *times as heavy as hydrogen. Hence the molecular weight is approximately* 300; *and since the atomic weight of arsenic is* 75 *as determined from the analysis of the chloride, the molecular formula of arsenic is* As_4. Between 1600° and 1700°, Victor Meyer found the vapor of arsenic to be only 75 times as heavy as hydrogen, which leads to the molecular formula As_2. The valence of arsenic is either three or five, and the formulæ of its compounds are consequently analogous to those of nitrogen and phosphorus.

Arsenic burns to As_2O_3 in the air when heated to 180°. It combines directly with many elements like chlorine, bromine, sulphur, and some of the metals. When boiled with nitric acid or aqua regia, arsenic is oxidized to arsenic acid H_3AsO_4.

Besides the metallic form of arsenic above described, this element may be obtained as yellow crystals by rapidly cooling its vapor. The crystals resemble ordinary phosphorus in that they dissolve in carbon bisulphide. Arsenic itself does not act as a poison, for it is not taken up by the animal system. Its insoluble sulphides also are not especially toxic in character. However, all other *compounds of arsenic, notably arsine* AsH_3, *arsenious oxide* As_2O_3, *halogen compounds, and salts of arsenious and arsenic acids are* **very poisonous**. From 0.1 to 0.4 gram of arsenious oxide is sufficient to cause death. The antidote for arsenic is freshly precipitated ferric hydroxide.

Arsine, Arseniureted Hydrogen, AsH_3. — Arsine is a colorless gas. It was discovered by Scheele in 1755. It melts at $-113.5°$ and boils at $-55°$. It is analogous to ammonia NH_3 and phosphine PH_3. It is commonly prepared (1) by the action of hydrochloric or sulphuric acid upon the arsenide of zinc or sodium, or (2) by introducing compounds of arsenic in a flask containing zinc and hydrochloric or sulphuric acid. The reactions involved in these processes are typified by the following equations: —

$$(1)\quad Zn_3As_2 + 6\,HCl = 3\,ZnCl_2 + 2\,AsH_3.$$

$$AsNa_3 + 3\,H_2SO_4 = 3\,NaHSO_4 + AsH_3.$$

$$(2)\quad As_2O_3 + 12\,H = 3\,H_2O + 2\,AsH_3.$$

The odor of arsine is very disagreeable, resembling that of garlic. *Arsine is* **extremely poisonous** *and great care must consequently be exercised in experimenting with it.* Arsine does not unite with water or with acids; it thus exhibits much less basic properties than ammonia or phosphine. Ignited in the air, arsine burns with a pale lavender flame, forming water and arsenious oxide: —

$$2\,AsH_3 + 3\,O_2 = 3\,H_2O + As_2O_3.$$

On being heated, the gas readily dissociates into arsenic and hydrogen: —

$$4\,AsH_3 = As_4 + 6\,H_2.$$

So when dry arsine is passed through a tube heated to dull redness, the reaction just given takes place, the arsenic condensing in form of a metallic mirror in the colder parts of the tube. Since solutions of all arsenic compounds when introduced into a flask containing zinc and hydrochloric or sulphuric acid yield arsine, a simple and very efficient method of testing arsenic, known as **Marsh's test**, has been devised. The apparatus is shown in Fig. 121. Pure zinc and hydrochloric acid are

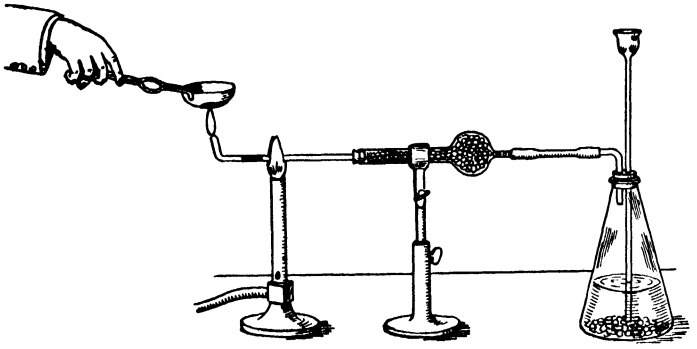


FIG. 121.

introduced into the flask. The calcium chloride in the tube serves to dry the gases evolved. After all air has been expelled, the hydrogen is lighted and the solution to be tested for arsenic is poured down the funnel tube. If arsenic is present, the flame will acquire the characteristic pale lavender color, and dark spots of metallic arsenic will be deposited upon a white porcelain dish held in the flame. If the tube, which should be of hard glass, is heated as shown, a mirror of metallic

arsenic will deposit on the sides of the tube just beyond the flame. Both the mirror and the spots are soluble in sodium hypochlorite or bleaching powder solution. It is to be noted that compounds of antimony under like treatment yield similar spots and mirrors; these are, however, *not* soluble in hypochlorites. Moreover, the arsenical mirror is more volatile than that of antimony. The former may be converted into yellow sulphide of arsenic and the latter into red sulphide of antimony by means of hydrogen sulphide.

When conducted into a solution of silver nitrate, arsine precipitates metallic silver, thus: —

$$2\,AsH_3 + 12\,AgNO_3 + 3\,H_2O = As_2O_3 + 12\,HNO_3 + 12\,Ag.$$

Since the corresponding antimony hydride, stibine SbH_3, does not reduce silver nitrate solutions thus, this reaction may be used to distinguish between arsine and stibine.

Compounds of Arsenic with the Halogens. — Of these compounds **arsenic trichloride** $AsCl_3$ is the most important. There are also known: the trifluoride AsF_3, boiling at 63° and melting at −8.5°; the tribromide $AsBr_3$, melting at 31° and boiling at 221°; the triodide AsI_3, melting at 140°, as well as iodides of the formulæ AsI_2 and AsI_5.

Arsenic trichloride is formed by conducting chlorine upon powdered arsenic contained in a retort, or by the action of hydrochloric acid upon arsenic trioxide. It is a colorless, fuming liquid of specific gravity 2.205 at 0°. It boils at 129° and solidifies to a crystalline mass at −18°. *It is very poisonous.* Water decomposes it: —

$$2\,AsCl_3 + 3\,H_2O = As_2O_3 + 6\,HCl.$$

By addition of concentrated hydrochloric acid, the hydrolysis may be reversed. It will be recalled that this cannot be done in the case of the analogous chloride of phosphorus.

Oxides and Oxy-acids of Arsenic. — Two oxides, the trioxide As_2O_3 and the pentoxide As_2O_5, are known; and the corresponding acids, arsenious acid H_3AsO_3 and arsenic acid H_3AsO_4, are of importance.

Arsenic trioxide As_2O_3, *also called "white arsenic," or commonly simply "arsenic," is the commonest, and by far the most important, of all the compounds of arsenic.* It is found in nature

and is formed when arsenic burns in the air or in oxygen. Arsenic trioxide is manufactured on a commercial scale by roasting arsenical pyrites in the air. In this process iron oxide remains as a non-volatile residue, sulphur dioxide escapes, and the arsenious oxide condenses as a white powder upon the brick walls of the chambers. It is purified by resublimation. Each year approximately 4000 tons of arsenious oxide are produced in the United States. From two to three times this amount is annually produced in Europe. On heating arsenic trioxide, it gradually forms an amorphous glassy mass, which after a time becomes white, crystalline, and opaque. Below 200° the crystals formed are octahedra of the regular system, whereas above that temperature crystallization in monoclinic forms takes place. At 800° the vapor density of arsenious oxide corresponds to the formula $(As_2O_3)_2$, whereas at about 1800° the density of the gas leads to the simple formula As_2O_3, the double molecules having been dissociated. Arsenic trioxide is readily reduced to arsenic by heating it with carbon, or cyanide of potassium. Its conversion to arsine has already been mentioned. In water it dissolves but slightly. Hydrochloric acid dissolves it, forming arsenic trichloride.

The trioxide has a sweetish, disagreeable taste. It is a strong poison. It is used as rat poison, also in taxidermy, in calico printing, in the manufacture of certain kinds of glass, in the preparation of many other compounds of arsenic, and in medicine. Freshly precipitated ferric hydroxide forms an insoluble compound with arsenious oxide and is consequently used as an antidote in cases of poisoning.

Arsenious acid H_3AsO_3 has not been isolated. It probably exists in the aqueous solutions of arsenious oxide. Its salts, the **arsenites**, are known. Among these may here be mentioned silver arsenite Ag_3AsO_3 and copper hydrogen arsenite, or **Scheele's green**, $CuHAsO_3$. Salts of meta-arsenious acid $HAsO_2$ are also known, like $KAsO_2$ and $Pb(AsO_2)_2$. **Paris green**, also called **Schweinfurt green**, is a double salt of cupric arsenite and cupric acetate $Cu_3As_2O_6 \cdot Cu(C_2H_3O_2)_2$. It is used as a poison for potato bugs and other insects.

Arsenic acid H_3AsO_4 is readily produced by oxidation of arsenious acid. Scheele prepared arsenic acid in 1775 by passing chlorine into arsenic trioxide suspended in

water; nitric acid or a mixture of nitric and hydrochloric acids serves equally well. The reaction in the former case is: —

$$As_2O_3 + 2\,Cl_2 + 5\,H_2O = 2\,H_3AsO_4 + 4\,HCl.$$

The acid forms rhombic, deliquescent prisms or plates of the composition $2\,H_3AsO_4 + H_2O$. At 100° the water of crystallization passes off. At about 180° the acid loses water, passing over into **pyroarsenic acid** $H_4As_2O_7$, which on being heated still further again loses water, forming **meta-arsenic acid** $HAsO_3$. So far then the behavior is entirely similar to that of phosphoric acid, though in contact with water pyro- and meta-arsenic acids *at once* form arsenic acid. On further ignition of meta-arsenic acid, water is again split off and **arsenic pentoxide** As_2O_5 is formed, thus: —

$$2\,HAsO_3 = H_2O + As_2O_5.$$

It will be recalled that metaphosphoric acid cannot thus be decomposed into P_2O_5 and water. Furthermore, phosphorus pentoxide is very stable when heated, whereas arsenic pentoxide decomposes upon ignition into arsenic trioxide and oxygen: —

$$As_2O_5 = As_2O_3 + O_2.$$

The salts of arsenic acid are quite analogous to those of phosphoric acid. Thus, *there are primary, secondary, and tertiary arsenates, also pyroarsenates and meta-arsenates.* In contact with water, however, all the salts form orthoarsenates at once.

Sulphides of Arsenic. — Three sulphides of arsenic are known, namely: the disulphide As_2S_2, the trisulphide As_2S_3, and the pentasulphide As_2S_5.

Arsenic disulphide As_2S_2 occurs in nature as **realgar**, in red monoclinic prisms. It is also manufactured by fusing sulphur and arsenic together. Thus made, it forms a dark red, glassy substance, which in pulverized condition is sometimes used as a pigment in paints. A mixture of 1 part arsenic disulphide, 12 parts saltpeter, and 3.5 parts sulphur when ignited makes white Bengal fire.

Arsenic trisulphide As_2S_3 occurs in nature in short rhombic prisms as orpiment. It was formerly used as a pigment. It is readily obtained as a lemon-yellow precipitate by passing

hydrogen sulphide into a solution of arsenic trioxide in hydrochloric acid : —

$$2\,AsCl_3 + 3\,H_2S = As_2S_3 + 6\,HCl.$$

On heating the precipitate with concentrated hydrochloric acid, it may be redissolved; that is, the reaction just given may be reversed. Arsenic trisulphide may also be obtained by fusing sulphur and arsenic together in the right proportions. In ammonium sulphide, arsenic trisulphide is soluble, forming **ammonium sulpharsenite** $(NH_4)_3AsS_3$: —

$$As_2S_3 + 3\,(NH_4)_2S = 2\,(NH_4)_3AsS_3.$$

In solution of yellow ammonium sulphide, that is, in ammonium sulphide containing an excess of sulphur, arsenic trisulphide dissolves as **ammonium sulpharsenate** $(NH_4)_3AsS_4$: —

$$As_2S_3 + 3\,(NH_4)_2S + 2\,S = 2\,(NH_4)_3AsS_4.$$

On treatment with hydrochloric acid the sulpharsenites and sulpharsenates are decomposed : —

$$2\,(NH_4)_3AsS_3 + 6\,HCl = As_2S_3 + 6\,NH_4Cl + 3\,H_2S.$$
$$2\,(NH_4)_3AsS_4 + 6\,HCl = As_2S_5 + 6\,NH_4Cl + 3\,H_2S.$$

Arsenic pentasulphide As_2S_5, made by means of the reaction just given or by melting together sulphur and arsenic in proper proportions, is a yellow solid which may be sublimed when heated out of contact with the air.

Occurrence, Preparation, and Properties of Antimony. — Antimony (stibium) is sometimes, though rarely, found in nature in the uncombined state. When thus found, it occurs in rhombohedral crystals. The mineral **stibnite** Sb_2S_3, found in Hungary and Japan, is the chief source of antimony, though the latter also occurs combined with sulphur in many native sulphides of lead, copper, silver, iron, and arsenic. Native oxide of antimony, senarmontite Sb_2O_3, forming white octahedra of the regular system, is also known. Stibnite was known in ancient times. The Chaldeans manufactured various articles out of metallic antimony, and the alchemists frequently used the metal.

Antimony is prepared by heating stibnite with iron, thus : —

$$Sb_2S_3 + 3\,Fe = 3\,FeS + 2\,Sb.$$

It is also made by roasting stibnite in the air, and reducing the tetroxide thus formed, by means of carbon. The reactions are as follows: —

$$Sb_2S_3 + 5\,O_2 = 3\,SO_2 + Sb_2O_4.$$
$$Sb_2O_4 + 4\,C = 4\,CO + 2\,Sb.$$

To free the antimony "regulus" so obtained from iron, lead, copper, etc., it is fused with a little sulphur or saltpeter. Thus the impurities are converted to sulphides or oxides, which float on top and can be removed. Antimony free from arsenic and other metals may be obtained by reducing pure sodium metantimoniate $NaSbO_3$.

Antimony is a hard, brittle, silvery-white metal having a high metallic luster. It can readily be ground to powder. At 625° it melts, and on cooling it forms rhombohedral crystals. Its boiling point is approximately 1400°, and its specific gravity is 6.75. In the air it remains practically unchanged, but when strongly heated it burns with a bluish white flame to Sb_2O_3 or Sb_2O_4. Introduced into an atmosphere of chlorine, it takes fire and burns to $SbCl_5$. It dissolves in hot concentrated sulphuric acid, also in aqua regia, but nitric acid converts it into Sb_2O_3 or antimonic acid H_3SbO_4. Hydrochloric acid acts slowly on antimony, liberating hydrogen. The latter gas is also formed by the action of steam on antimony at high temperatures.

The atomic weight of antimony is 120.2. The vapor density leads to a molecular weight of approximately 290, which represents a formula lying between Sb_2 and Sb_3. The valence of antimony is either three or five. Its compounds consequently have formulæ analogous to those of nitrogen, phosphorus, and arsenic. The latter is a close relative of antimony.

Metallic antimony is much used in alloys, particularly in **type metal** and **britannia metal**. Type metal consists of approximately 25 per cent antimony, 25 per cent tin, and 50 per cent lead. The presence of antimony in alloys makes them hard. Furthermore, antimony expands as it congeals (resembling water in this behavior) and consequently fills molds perfectly, thus yielding sharply defined castings.

Hydrogen Antimonide, Stibine, SbH_3. — This compound is analogous to ammonia, phosphine, and arsine. It is quite similar to the latter and is prepared by similar methods. So, for

instance, by treating an alloy of magnesium and antimony or zinc and antimony with dilute hydrochloric or sulphuric acid, stibine is formed. Again, by introducing a solution of any antimony compound into a flask in which zinc is being acted upon by hydrochloric or sulphuric acid, stibine results, which in this case is mixed with hydrogen.

Stibine is a colorless gas of peculiar odor, reminding one somewhat of that of hydrogen sulphide. The odor is distinctly different from that of arsine. Stibine melts at $-88°$ and boils at $-17°$. The gas readily dissociates into antimony and hydrogen, thus: —

$$2\,SbH_3 = 2\,Sb + 3\,H_2.$$

The change begins at 150°. Even when diluted with hydrogen, stibine is largely decomposed when passed through a tube heated to 150°, yielding a deposit of antimony in the form of a mirror, which is insoluble in hypochlorites. Thus, in the apparatus used for making Marsh's test for arsenic, antimony compounds would yield a similar mirror; but the latter is readily distinguished from arsenic by the method described under arsine. The dissociation of stibine is practically complete at 200°, at which temperature arsine remains unchanged. Stibine is moderately poisonous. Water dissolves about four times its own volume of the gas at room temperature. In the air or in oxygen, when ignited, stibine burns with a bluish white flame, forming water and Sb_2O_3. Conducted into a silver nitrate solution, stibine is decomposed, the antimony being precipitated as silver antimonide $SbAg_3$. When pure or when diluted with hydrogen, stibine may be kept unchanged; but the presence of even small amounts of oxygen in the gas leads to the deposition of some of the antimony.

Compounds of Antimony with the Halogens. — Of these, antimony trichloride $SbCl_3$ and antimony pentachloride $SbCl_5$ are of most importance.

Antimony trichloride is formed by the action of chlorine on antimony or of hydrochloric acid on antimony sulphide: —

$$2\,Sb + 3\,Cl_2 = 2\,SbCl_3.$$
$$Sb_2S_3 + 6\,HCl = 3\,H_2S + 2\,SbCl_3.$$

The antimony trichloride is purified by distillation. It is a colorless crystalline mass which at ordinary temperatures is

soft, reminding one of the consistency of butter, hence it goes by the name of **butter of antimony**. It melts at 73° and boils at 223°. At 26° its specific gravity is 3.064. Its vapor is 229 times as heavy as hydrogen, which fact leads to the formula $SbCl_3$. It is deliquescent and has caustic properties. Antimony trichloride is used as a mordant, also in medicine and in burnishing metals, notably gun barrels, to which it imparts a brown hue. Antimony trichloride may be dissolved in water containing hydrochloric acid. But when treated with water alone, antimony trichloride is decomposed into hydrochloric acid and insoluble oxychlorides, the composition of which varies according to the temperature and relative amount of water used. Two **oxychlorides of antimony**, SbOCl and $(SbOCl)_2 \cdot Sb_2O_3$, are well known as white crystalline powders. They are formed thus: —

$$(1) \quad SbCl_3 + H_2O = SbOCl + 2\,HCl.$$

$$(2) \quad 4\,SbCl_3 + 5\,H_2O = (SbOCl)_2 \cdot Sb_2O_3 + 10\,HCl.$$

The second reaction takes place in hot solutions. The compound $(SbOCl)_2 \cdot Sb_2O_3$, or $Sb_4O_5Cl_2$, was used by the Italian physician Victor Algarotus, and is consequently known as the **powder of algaroth**.

Antimony pentachloride is prepared by burning antimony in an excess of chlorine or by conducting chlorine upon antimony trichloride. It is a fuming liquid of yellow color. At − 6° its crystals melt. It can only be distilled in a partial vacuum, for on heating it readily dissociates into chlorine and the trichloride. With water it forms crystalline hydrates, $SbCl_5 \cdot H_2O$ and $SbCl_5 \cdot 4\,H_2O$. Antimony pentachloride is decomposed by hot water. It readily gives off part of its chlorine, and is consequently used in organic chemistry in chlorinating substances. It will be observed that while antimony pentachloride forms crystalline hydrates with water, the latter decomposes the chlorides of phosphorus at once.

Antimony trifluoride SbF_3 forms deliquescent rhombic crystals that are not decomposed by cold water. With ammonium sulphate it forms a compound that is used as a mordant.

Antimony pentafluoride SbF_5 is an amorphous gummy mass. It readily enters into the formation of double salts.

Antimony tribromide $SbBr_3$ forms white rhombic crystals that melt at 94°. The salt boils at 275°, and is decomposed by water.

Antimony triiodide SbI_3 forms three different varieties of crystals. The common red crystals melt at 171°. The boiling point is 430°.

Antimony pentiodide SbI_5 is a dark brown, crystalline mass of melting point 79°. It is unstable.

Oxides and Oxy-acids of Antimony. — There are three oxides of antimony: antimony trioxide Sb_2O_3, antimony tetroxide Sb_2O_4, and antimony pentoxide Sb_2O_5. The trioxide acts mainly as a base, though toward very strong bases, like caustic potash and soda, it is also able to act as an acid. The tetroxide exhibits neither acid nor basic properties, whereas the pentoxide acts solely in an acid-forming capacity.

Antimony trioxide is found in nature as senarmontite. It is formed by burning antimony in the air or by oxidizing the metal with nitric acid. The oxide is white and may be sublimed. It crystallizes in octahedra or rhombic prisms, being dimorphous. At 1560° the density of its vapor corresponds to the formula Sb_4O_6, nevertheless it is commonly called the trioxide. It is possible that at higher temperatures it would dissociate into Sb_2O_3 like the corresponding oxide of arsenic. In water and nitric or sulphuric acid, antimony trioxide is practically insoluble, while in hydrochloric or tartaric acid, or in acid potassium tartrate or caustic alkalies, it dissolves, thus: —

$$Sb_2O_3 + 6\,HCl = 2\,SbCl_3 + 3\,H_2O.$$

$$Sb_2O_3 + 2\,KOH = 2\,KSbO_2 + H_2O.$$

$$Sb_2O_3 + 2\,(C_4H_4O_6)HK = 2\,(C_4H_4O_6)SbO\cdot K + H_2O.$$

The salt $KSbO_2$ is **potassium metantimonite.** It is plainly a salt of **metantimonious acid** $HSbO_2$, which may be considered as derived from **antimonious acid** H_3SbO_3 by loss of a molecule of water. The salt $(C_4H_4O_6)\cdot SbO\cdot K$ is **potassium antimonyl tartrate** or **tartar emetic.** It contains the univalent **antimonyl group,** $-Sb=O$, which is frequently found in other antimony salts. Tartar emetic has been known for a long time. The salt crystallizes with half a molecule of crystal water, a part of which escapes on exposure to the air. The salt is still some-

times used in medicine. Antimony salts were formerly frequently prescribed by physicians. These compounds gained in prominence through the work of Basil Valentine, who in the fifteenth century, published his book on "The Triumphal Chariot of Antimonium." The compounds $(C_4H_4O_6)\cdot AsO\cdot K$ **potassium arsenyl tartrate** and $(C_4H_4O_6)\cdot BO\cdot K$ **potassium boryl tartrate** are analogous to tartar emetic.

On treating tartar emetic with dilute sulphuric acid, the hydrate H_3SbO_3 separates out as a precipitate, which, however, loses water and forms metantimonious acid $HSbO_2$, *i.e.* $SbO\cdot OH$.

The basic properties of antimony are shown in its salts, in which either $Sb(OH)_3$ or $SbO\cdot OH$ act as bases. Thus, there are known **antimony nitrate** $Sb(NO_3)_3$, **antimony sulphate** $Sb_2(SO_4)_3$, and the halogen salts like $SbCl_3$; further, when these salts are acted upon by water, oxy-salts or basic salts are produced, which may be considered as derived from $SbO\cdot OH$. So **antimonyl nitrate** $SbO\cdot NO_3$ and **antimonyl sulphate** $(SbO)_2SO_4$ are known, and antimony oxychloride and tartar emetic, already mentioned, belong in this category.

Antimony tetroxide is a white powder obtained by burning antimony in oxygen or by heating the trioxide in the air. In water it is insoluble, while boiled with cream of tartar it is converted into tartar emetic and metantimonic acid, thus: —

$$Sb_2O_4 + (C_4H_4O_6)HK = (C_4H_4O_6)SbO\cdot K + HSbO_3.$$

The tetroxide is also obtained on igniting antimony pentoxide: —

$$Sb_2O_5 = Sb_2O_4 + O.$$

Antimony tetroxide may be regarded as the antimonyl salt of metantimonic acid, which is $HSbO_3$. The antimonyl salt would have the formula $(SbO)\cdot SbO_3$.

Antimonic acid H_3SbO_4 is formed as an insoluble white powder by the action of concentrated nitric acid upon antimony, or by the action of water on antimony pentachloride. Salts of this acid and also of its dehydration products, **pyro-** and **metantimonic acids** are known. So on fusing antimony with potassium nitrate, there is formed with explosive violence **potassium metantimonate** $KSbO_3$, which on being heated with water passes into solution as **potassium antimonate** KH_2SbO_4. On fusing

potassium metantimonate with caustic potash, the pyroantimonate $K_4Sb_2O_7$ results: —

$$2\,KSbO_3 + 2\,KOH = K_4Sb_2O_7 + H_2O.$$

Potassium pyroantimonate is decomposed by water: —

$$K_4Sb_2O_7 + 2\,H_2O = 2\,KOH + K_2H_2Sb_2O_7.$$

When the latter salt is added to a solution of a sodium salt, **sodium pyroantimonate** $Na_2H_2Sb_2O_7$ is precipitated. This is practically the only sodium salt known that does not dissolve in water readily.

Antimonic acid and its dehydration products are then quite analogous to those of the corresponding phosphorus and arsenic compounds.

Antimony pentoxide Sb_2O_5 is a yellow powder obtained by heating antimonic acid to 275°. At higher temperatures it is decomposed, yielding the tetroxide and oxygen. With strong bases it forms salts. It is soluble in hydrochloric acid.

Compounds of Antimony with Sulphur. — It has already been mentioned that antimony trisulphide Sb_2S_3 is found in nature as stibnite. Precipitated from solutions of antimony salts by means of hydrogen sulphide, **antimony trisulphide** is an orange-red powder, which is insoluble in dilute hydrochloric acid, but soluble in concentrated hydrochloric acid, with concomitant evolution of hydrogen sulphide. In ammonium sulphide it dissolves, yielding **ammonium sulphantimonite**, thus: —

$$Sb_2S_3 + 3\,(NH_4)_2S = 2\,(NH_4)_3SbS_3.$$

The latter is decomposed by hydrochloric acid: —

$$2\,(NH_4)_3SbS_3 + 6\,HCl = 6\,NH_4Cl + Sb_2S_3 + 3\,H_2S.$$

In yellow ammonium sulphide, antimony trisulphide dissolves more readily, yielding **ammonium sulphantimonate**: —

$$Sb_2S_3 + 3\,(NH_4)_2S + S_2 = 2\,(NH_4)_3SbS_4.$$

On treating the latter with hydrochloric acid, **antimony pentasulphide** Sb_2S_5 is obtained: —

$$2\,(NH_4)_3SbS_4 + 6\,HCl = 6\,NH_4Cl + Sb_2S_5 + 3\,H_2S.$$

Antimony pentasulphide may also be obtained by treating antimonic acid with hydrogen sulphide, thus: —

$$2\,H_3SbO_4 + 5\,H_2S = Sb_2S_5 + 8\,H_2O.$$

It is a powder of golden yellow color, hence it is called *sulphur auratum*. On being heated, it gives off sulphur and forms the trisulphide. In soluble sulphides of the metals it dissolves, forming sulphantimonates. Thus with sodium sulphide it forms $Na_3SbS_4 + 9\,H_2O$, which is known as "Schlippe's salt."

Antimony pentasulphide is used in making red vulcanized caoutchouc. The trisulphide is used in making matches, also as a pigment. Antimony cinnabar, **kermes mineral**, a mixture of the trisulphide and trioxide of antimony, is used in medicine.

Occurrence, Preparation, and Properties of Bismuth. — This element, though not abundant or widely distributed in nature, has been known since the fifteenth century, when it was referred to by Basil Valentine, who, on account of its brittleness, regarded it as a half metal. Bismuth generally occurs in the free state in nature, and is almost always fairly pure. Sometimes it is found as the sulphide, bismuth glance Bi_2S_3, more rarely as the oxide, bismuth ocher Bi_2O_3. The sulphide is roasted to oxide, which is then reduced with charcoal. The bismuth so obtained, or the native bismuth, is refined by fusing it with saltpeter or soda plus a little potassium chlorate. Thus, arsenic and other impurities, consisting mainly of lead, iron, antimony, copper, sulphur, etc., are oxidized and removed as a slag that floats on the surface.

Bismuth is a white, brittle metal having a high metallic luster and a slightly reddish sheen, which readily distinguishes it from antimony. Bismuth is crystalline. Its crystals belong to the rhombohedral division of the hexagonal system. Its specific gravity is 9.82. It melts at 269°, and may be distilled in a vacuum at about 995°. It is a rather poor conductor of heat and electricity, as compared with other metals. The atomic weight of bismuth is 208, and its valence is commonly either three or five; so that the formulæ of its compounds are analogous to those of nitrogen, phosphorus, arsenic, and antimony. Nevertheless, bismuth is more pronouncedly basic in character than these, and consequently it is to be grouped with the metals.

In the air bismuth remains practically unchanged. On ignition in the air it burns with a bluish-white flame; the product formed is a yellow powder, the trioxide, Bi_2O_3. In nitric acid, bismuth may readily be dissolved, forming the nitrate

$Bi(NO_3)_3$; likewise when the metal is treated with sulphuric acid, the sulphate, $Bi_2(SO_4)_3$, is formed. Hydrochloric acid scarcely attacks bismuth. The latter does not combine with hydrogen.

Bismuth is used in pharmaceutical preparations. It is also used in making alloys that have a low melting point. Of these the following are frequently used: **Rose's metal**, consisting of 1 part tin, 1 part lead, and 2 parts bismuth, melts at 93.8°; **Newton's metal**, consisting of 3 parts tin, 5 parts lead, and 8 parts bismuth, melts at 94.5°; and **Wood's metal**, which consists of 1 part tin, 2 parts lead, 1 part cadmium, and 4 parts bismuth, melts at 60.5°. On changing from the liquid to the solid state bismuth expands even more than antimony. It is consequently also employed, like the latter, in alloys for stereotyping and other purposes where castings of sharp outline are required.

Halogen Compounds of Bismuth. — In these compounds bismuth is always trivalent. **Bismuth chloride** $BiCl_3$ is made by the action of chlorine upon bismuth, or by dissolving the latter in nitro-hydrochloric acid. It may also be obtained by dissolving the trioxide, Bi_2O_3, in hydrochloric acid. The salt consists of white crystals melting at 227°, and boiling at about 445°. It is soluble in hydrochloric acid solutions, from which it is precipitated in the form of **bismuth oxychloride** BiOCl: —

$$BiCl_3 + H_2O = BiOCl + 2\,HCl.$$

Bismuth fluoride BiF_3 is a grayish powder formed by the action of hydrofluoric acid on bismuth trioxide. On treatment with much water, **bismuth oxyfluoride** BiOF is formed. **Bismuth bromide** $BiBr_3$ forms orange-colored crystals melting at 215° and boiling at 453°. With water they yield **bismuth oxybromide** BiOBr. **Bismuth iodide** BiI_3 consists of dark brown or black crystals of metallic luster, melting at 439°. On boiling with water they are decomposed, yielding red crystals of **bismuth oxyiodide** BiOI.

Halogen compounds of bismuth in which the element has a valence of five have not been prepared, but a dichloride of the formula $(BiCl_2)_2$ has been described as a white powder formed by heating bismuth with mercurous chloride.

Oxides of Bismuth. — **Bismuth trioxide** Bi_2O_3, which is formed as a yellow powder when the metal is burned in the air, is the

most important of the oxides. It acts only as a base, forming salts which may be considered as derived from either $Bi(OH)_3$ or $BiO \cdot OH$.

Bismuth dioxide Bi_2O_2 is obtained as a dark brown precipitate by pouring a solution containing stannous chloride and bismuth chloride into caustic potash solution.

Bismuth tetroxide Bi_2O_4 is a reddish yellow powder formed by heating the pentoxide to about 165°.

Bismuth pentoxide Bi_2O_5 is an unstable brown powder obtained by passing chlorine into caustic potash solution containing bismuth trioxide in suspension. On being heated, it forms the tetroxide. With hydrochloric acid it forms bismuth trichloride and chlorine: —

$$Bi_2O_5 + 10\,HCl = 5\,H_2O + 2\,BiCl_3 + 2\,Cl_2.$$

Bismuth Salts of Oxy-acids. — The salts of bismuth with the halogens have already been described. With sulphuric acid bismuth forms bismuth sulphate $Bi_2(SO_4)_3$, which on treatment with water yields the oxysulphate or **bismuthyl sulphate** $(BiO)_2SO_4$, thus: —

$$Bi_2(SO_4)_3 + 4\,H_2O = (BiO)_2SO_4 + 2\,H_2SO_4 + 2\,H_2O.$$

With nitric acid, bismuth forms the nitrate $Bi(NO_3)_3$, which crystallizes in triclinic forms with five molecules of water. The salt is decomposed into basic nitrates by treatment with water. The composition of these basic nitrates varies with the temperature and the relative amounts of water and normal nitrate used in preparing them. Thus a white powder, **bismuth oxynitrate** $BiO \cdot NO_3$, is known. On boiling this salt with water, a more basic salt of approximately the composition $BiO \cdot NO_3 + BiO \cdot OH$ is obtained which is used as a cosmetic and antiseptic under the name **bismuth subnitrate**. Furthermore, it is very often prescribed in medicine in cases of dysentery and other disturbances of the digestive tract. In the treatment of diseases of the skin, particularly in cases of acute inflammations, it is also frequently employed.

All salts of bismuth may be regarded as derived from the two basic hydroxides $Bi(OH)_3$ *and* $BiO \cdot OH$. The univalent radical $-Bi=O$, bismuthyl, is analogous to the antimonyl radical $-Sb=O$. The tendency to form oxy-salts or basic salts is very characteristic of bismuth and also of antimony.

Bismuth Trisulphide Bi_2S_3 occurs in nature as bismuth glance. It may also be obtained as a very dark brown or black precipitate by passing hydrogen sulphide into a solution of a salt of bismuth: —

$$2\,BiCl_3 + 3\,H_2S = 6\,HCl + Bi_2S_3.$$

It is *insoluble in ammonium sulphide solution*, also in solutions of the sulphides of the alkalies. This behavior distinguishes it from the sulphides of arsenic and antimony, which readily dissolve in alkali sulphides as sulpho-salts. On heating a precipitate of bismuth trisulphide suspended in a solution of an alkali sulphide to 200°, the compound becomes crystalline. Bismuth trisulphide may also be obtained by melting together sulphur and bismuth in proper proportions.

A compound of the composition Bi_2S_2, **bismuth disulphide**, has also been described as consisting of steel-gray needles formed by melting sulphur and bismuth together in the proportions represented by the formula.

General Considerations of the Group. Nitrogen, phosphorus, arsenic, antimony, and bismuth form another natural group of elements. Their atomic weights increase in the order named, and their physical properties show a corresponding gradation of changes, as is evident from the following table: —

Element	Atomic Weight	Color	Specific Gravity	Melting Point	Boiling Point
Nitrogen, N	14.01	colorless	0.885 (liquid)	−210.5°	−194.4°
Phosphorus, P	31.0	yellow or red	1.8–2.3	+44.4°	+278.0°
Arsenic, As	75.0	gray, lustrous	5.7	500° (approx.)	450° (approx.)
Antimony, Sb	120.2	white, lustrous	6.8	625°	1500° (approx.)
Bismuth, Bi	208.0	reddish white	9.8	268°	1600° (approx.)

The chemical properties of the members of the group also present an interesting series of changes as the atomic weight increases. The compounds with hydrogen have the formula RH_3. So we have ammonia NH_3, phosphine PH_3, arsine AsH_3,

and stibine SbH_3. The stability of these compounds diminishes in the order named, a hydride of bismuth being unknown. Ammonia has strong basic properties; these are also exhibited by phosphine, but to a lesser degree, in the phosphonium salts. But arsine and stibine are no longer able to unite with acids to form salts. Hydrazine $(NH_2)_2$ has its analogue in liquid phosphine $(PH_2)_2$, while analogous hydrides of arsenic and antimony are unknown. Furthermore, hydrazoic acid HN_3 and solid phosphine P_4H_2 stand alone, no analogous compounds of the group being known.

In general, *as the atomic weight of the elements of this group increases, the affinity for hydrogen decreases.*

Just the reverse is true of the affinity of nitrogen, phosphorus, arsenic, antimony, and bismuth for the halogens. The halogen compounds have the general types $\overset{III}{R}X_3$ and $\overset{V}{R}X_5$. Thus, we have the following series of the halogen compounds: —

HALOGEN COMPOUNDS OF THE NITROGEN GROUP

NF_3 (?)	——	NCl_3	——	NBr_3	——	——	$NI_3 + NH_3$	——
PF_3	PF_5	PCl_3	PCl_5	PBr_3	PBr_5	P_2I_4	PI_3	——
AsF_3	——	$AsCl_3$	——	$AsBr_3$	——	As_2I_4	AsI_3	——
SbF_3	SbF_5	$SbCl_3$	$SbCl_5$	$SbBr_3$	——	——	SbI_3	SbI_5
BiF_3	——	$BiCl_3$	——	$BiBr_3$	——	——	BiI_3	——

While the halogen compounds of nitrogen are so unstable as to be explosive in character, the phosphorus halides possess a considerable degree of stability, which increases as we pass to corresponding compounds of arsenic, antimony, and bismuth in the order named. The phosphorus halides are at once decomposed by water completely. The arsenic halides suffer such hydrolysis more slowly, and even incompletely if but little water is used, while the halides of antimony and bismuth are but partially decomposed by water, forming oxy-salts that are fairly stable. These oxy-salts generally have the formula $\overset{III}{R}O\overset{V}{X}$, like SbOCl, etc., though on treatment with boiling water they form more basic salts because of further hydrolysis.

The affinity of the elements of this group toward oxygen and sulphur also diminishes as the atomic weight increases. With oxygen we have the following compounds: —

N_2O	NO	N_2O_3	(NO_2)	N_2O_5
——	——	P_2O_3	$(PO_2)_2$	P_2O_5
——	——	As_2O_3	——	As_2O_5
——	——	Sb_2O_3	$(SbO_2)_2$	Sb_2O_5
——	$(BiO)_2$	Bi_2O_3	$(BiO_2)_2$	Bi_2O_5

The oxy-acids are as follows, those in parentheses being known only in the form of salts: —

$H_2N_2O_2$	HNO_2	——	——	——	——	HNO_3
——	——	H_3PO_2	H_3PO_3	H_3PO_4	$H_4P_2O_7$	HPO_3
——	$(HAsO_2)$	——	H_3AsO_3	H_3AsO_4	$H_4As_2O_7$	$HAsO_3$
——	$HSbO_2$	——	H_3SbO_3	H_3SbO_4	$H_4Sb_2O_7$	$HSbO_3$
——	——	——	——	——	——	$(HBiO_3)$

The sulphides are commonly of the general type $\overset{III}{R}_2S_3$ or $\overset{V}{R}_2S_5$. They are given in the following table: —

$(N_2S_2)_2$	——	N_2S_5
——	P_2S_3	P_2S_5
As_2S_2	As_2S_3	As_2S_5
——	Sb_2S_3	Sb_2S_5
Bi_2S_2	Bi_2S_3	——

The sulphides of arsenic and antimony unite with ammonium sulphide and other alkaline sulphides to form sulpho-salts, while the sulphide of bismuth does not do this.

Bismuth is already a fairly pronounced metal. It is, after all, not very closely related to the other members of the group. Nitrogen, too, it must be admitted, stands rather remotely related to the other members of the group. Its relation to the latter is more like that of fluorine toward the other halogens, or like oxygen toward sulphur, selenium, and tellurium.

Vanadium, Columbium, and Tantalum. — These are rare metallic elements which form compounds that are analogous to those of the phosphorus group, though in some respects these three elements are also similar to aluminum, iron, chromium, and tungsten.

Vanadium (V — 51.0) was discovered by Del Rio in 1801 in vanadinite $PbCl_2 \cdot 3\,Pb_3(VO_4)_4$, but was characterized defi-

nitely as an element in 1830 by Sefström. In 1867 Roscoe prepared vanadium by heating its dichloride, VCl_2, in a current of hydrogen. Thus made, vanadium is a crystalline, grayish powder of specific gravity 5.8, which readily burns to V_2O_5 in oxygen. Other oxides are V_2O, V_2O_2, V_2O_3, V_2O_4. The chlorides are VCl_2, VCl_3, $VOCl_3$, VCl_4. The **vanadates** are salts of **vanadic acid** H_3VO_4. As in the case of the phosphates, there are ortho-, meta-, and pyrovanadates; of these the metavanadates, like $NaVO_3$, are met most frequently.

Columbium (Cb — 93.5) is also called **niobium**, Nb. It occurs together with tantalum (Ta — 181.0) in **columbites** and **tantalites**. These metals may be prepared like vanadium. Moissan prepared tantalum by reduction of its oxide Ta_2O_5 with carbon in the electric furnace. **Tantalum** is a steel-gray, malleable metal which melts at about 2300°. It is now being used to make filaments for incandescent electric lamps. As the metal conducts better than carbon, tantalum filaments must be made longer than carbon filaments to obtain the necessary amount of electrical resistance.

REVIEW QUESTIONS

1. From what sources is phosphorus obtained?
2. Mention the allotropic forms of phosphorus, stating their characteristics.
3. How may yellow phosphorus be prepared from phosphate rock? Give the equations.
4. Explain the chemistry of: (*a*) friction matches, (*b*) safety matches.
5. What compounds does phosphorus form with hydrogen? When these compounds are burned in oxygen, what products result?
6. What compound of phosphorus is analogous to: (*a*) ammonia, (*b*) nitric acid, (*c*) nitrogen chloride, (*d*) nitric acid anhydride?
7. How may the halides of phosphorus be prepared? Write the equations. How does water act on these halides? Equations.
8. What is the formula of ortho phosphoric acid? How much of this can be prepared from 50 kilograms of normal calcium phosphate?
9. Define the following and give an example of each, writing the appropriate formula: phosphate, phosphite, pyrophosphate, metaphosphate, hypophosphite.
10. What is microcosmic salt? What changes does it undergo on heating? Equation.
11. What is bone ash? What is it used for?

12. By means of structural formulas show the relation between: ortho, meta and pyro phosphoric acids; ortho and meta boric acids; ortho and meta silicic acids.

13. What is the commonest and most important compound of arsenic? Describe its properties and mention its uses.

14. What property have all arsenic compounds in common? Describe arsenic and state how it may be prepared, writing the equation.

15. What is Paris green? How may it be prepared and what is it used for?

16. Write the names and formulas of the hydrogen compounds of phosphorus, arsenic, and antimony that are analogous to ammonia. How may these compounds be prepared? Discuss the relative stability of these compounds.

17. Write the names and formulas of the chlorides of nitrogen, phosphorus, arsenic, antimony, and bismuth, and compare their properties.

18. Give the names of the following compounds and also the names and formulas of the corresponding compounds of phosphorus: As_2O_3, $SbCl_5$, H_3AsO_4, $HSbO_3$, As_2S_3, Sb_2S_5, $(NH_4)_3AsS_4$, $(NH_4)_3SbS_3$.

19. By means of chemical equations, show that antimonious oxide may act either as an acid or a base.

20. Write the equations expressing the successive steps that take place when a suspension of white arsenic in water is subjected to the Marsh test.

21. How distinguish between arsenic and antimony mirrors resulting from the Marsh test?

22. Mention some of the uses of the metals antimony and bismuth. Why are they sometimes called half-metals?

23. Explain the solubility of the sulphides of arsenic and antimony in yellow ammonium sulphide. Write the equations. Why does the sulphide of bismuth not dissolve in yellow ammonium sulphide?

24. What is bismuth subnitrate? What use is made of it? Given 500 grams of metallic bismuth, how much bismuth subnitrate could you prepare from it? Write all the equations.

25. What rare elements belong to the phosphorus group? Why?

26. How many liters of hydrogen would be required to make 60 liters of arsine, measured under the same standard conditions of temperature and pressure? How much zinc would be necessary to prepare this hydrogen?

27. Give the valence of each element in each of the following compounds: $KClO_4$, Na_2HPO_4, HPO_3, H_3PO_3, Bi_2S_3, $KSbO_2$, $PbSiO_3$, $NaHCO_3$, KIO_3, $(NH_4)_3AsS_4$, $SbOCl$, $POCl_3$.

CHAPTER XX

CLASSIFICATION OF THE ELEMENTS

The Periodic System

We have already seen that the chemical elements may be divided into metals and non-metals, although a sharp line of division between these two groups does not exist. It would be natural to classify the elements according to their physical and chemical properties. Experience has shown that the properties of the elements are closely related to their atomic weights. As early as 1817 Döbereiner called attention to the fact that the atomic weight of strontium, 87.62, is approximately the arithmetical mean of the atomic weights of barium, 137.37, and calcium, 40.09. These three metals are very similar in character, forming the group of the alkaline earth metals. A number of other elements that are closely related also form similar groups of three, or so-called **triads**, which is evident from the following cases: —

Chlorine, 35.46; Bromine, 79.92; Iodine, 126.92.

$$\frac{35.46 + 126.92}{2} = 81.19.$$

Sulphur, 32.07; Selenium, 79.2; Tellurium, 127.5.

$$\frac{32.07 + 127.5}{2} = 79.78.$$

Phosphorus, 31.0; Arsenic, 75.0; Antimony, 120.2.

$$\frac{31.0 + 120.2}{2} = 75.6.$$

Lithium, 6.94; Sodium, 23.00; Potassium, 39.10.

$$\frac{6.94 + 39.10}{2} = 23.02.$$

In 1875 Lenssen attempted to arrange all the elements known in such groups of three.

In 1864 Newlands pointed out a relation which he termed the **law of octaves.** He arranged the elements in the order of the magnitude of their atomic weights, and thus found that the eighth element has properties similar to the first, no matter from which element we begin to count. He did not work out a complete classification, however.

In 1869 Dimitri Mendeléeff, and practically simultaneously Lothar Meyer, arranged all of the elements in a table which is known as the **periodic system of the elements.** In slightly modified form, this table has remained the best classification of the elements to the present day. Referring to the table on page 339 it will be noted that the elements are arranged horizontally in the order of magnitude of their atomic weights, in nine groups, which are numbered from zero to VIII. The symbols in the horizontal series are so written that similar elements appear in the same vertical column.

At the head of each column is indicated the valence of the elements towards oxygen and also towards hydrogen. So from left to right the maximum valence of the elements towards oxygen increases from zero to eight, while the valence towards hydrogen is greatest in group IV, *i.e.* in the middle of the table.

Beginning with lithium and passing horizontally to fluorine, the elements show a gradation from powerfully basic to strongly acidic properties. The second horizontal series, beginning with sodium and ending with chlorine, also shows the same phenomenon. The first and second series are consequently two complete **short periods.** In the third horizontal series, beginning with potassium and ending with manganese, iron, nickel, and cobalt, we do not have a complete change from strongly basic to strongly acidic properties; but by continuing in the fourth horizontal series from copper to the right we do pass from the more basic elements to the acidic bromine. Consequently the third and fourth horizontal series together are said to form one **long period.** Again, taking the fifth series, beginning with the basic element rubidium and ending with the metals ruthenium, rhodium, and palladium, and then continuing in the sixth series from silver to iodine, we have a complete change from strongly basic to markedly acidic properties. For this reason, the fifth and sixth horizontal series together are a second long period.

PERIODIC SYSTEM OF THE ELEMENTS

Periods	Series	0	I	II	III	IV	V	VI	VII	VIII		
		— / —	R_2O / —	RO / —	R_2O_3 / —	RO_2 / RH_4	R_2O_5 / RH_3	RO_3 / RH_2	R_2O_7 / RH	RO_4 / — ← Oxides / Hydrides		
1	1	He 4	Li 7	Gl 9.1	B 11	C 12	N 14	O 16	F 19	—		
2	2	Ne 20	Na 23	Mg 24.3	Al 27.1	Si 28.3	P 31.0	S 32.1	Cl 35.5	—		
3	3	A 39.9	K 39.1	Ca 40	Sc 44.1	Ti 48.1	V 51.2	Cr 52.1	Mn 55	Fe 55.8	Ni 58.7	Co 59
	4	—	Cu 63.6	Zn 65.5	Ga 70	Ge 72.5	As 75	Se 79.2	Br 80	—		
4	5	Kr 82	Rb 85.5	Sr 87.6	Y 89	Zr 90.6	Cb 93.5	Mo 96	—	Ru 101.7	Rh 103	Pd 106.7
	6	—	Ag 107.9	Cd 112.4	In 114.8	Sn 119	Sb 120.2	Te 127.5	I 126.9	—		
5	7	X 128	Cs 133	Ba 137.4	La 139	Ce 140.2, etc.	—	—	—	—		
	8	—	—	—	—	—	—	—	—	—		
	9	—	—	—	Yb 172	—	Ta 181	W 184	—	Os 191	Ir 193	Pt 195
	10	—	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	—	—	—		
6	11	—	—	Ra 226	—	Th 232	—	U 238.5	—	—		

In this table approximate atomic weights are used, and some of the rare-earth elements have not been located.

The seventh, eighth, ninth, and tenth horizontal series taken together are sometimes considered as the fifth period, and the eleventh series as a sixth period. These latter periods, to be sure, are incomplete.

When helium, neon, argon, krypton, and xenon were discovered, the question as to their place in the periodic system arose. As these gases do not combine with anything, their valence is zero, and so these elements have been placed in a zero group at the head of the system.

It will be noted that the periodic system contains many blank spaces. These represent elements yet to be discovered. When Mendeléeff first published his table, the spaces now occupied by the elements scandium, gallium, and germanium were vacant. He boldly predicted that these metals would be found; and from the known characteristics of the neighboring elements in the table, he foretold the approximate atomic weights and also described in some detail what the physical and chemical properties of these metals would be. He called the elements ekaboron, ekaaluminium, and ekasilicon. When some years later scandium, gallium, and germanium were discovered, their atomic weights and other properties proved to be those of the metals foretold by Mendeléeff. This brilliant achievement of the great Russian chemist attracted special attention to the value of the periodic system, which has since served to stimulate inquiry in various lines.

Some of the elements did not seem to fit properly into the table and so the question arose whether their atomic weights had really been correctly determined. This led to more accurate atomic weight determinations of a number of elements.

It will be noted that according to the size of their atomic weights tellurium and iodine ought to change places in the table; and this ought also to occur in the case of argon and potassium. Considering the properties of these elements, however, such changes are not to be thought of for a moment, for it would take iodine from the column of the halogens, in which it certainly belongs, and place it in the sixth group with oxygen and sulphur. Similarly, potassium must remain in group I with the other alkali metals. Redeterminations of the atomic weight of tellurium have shown that this element, indeed, has a slightly higher atomic weight than iodine; and so the anomalies

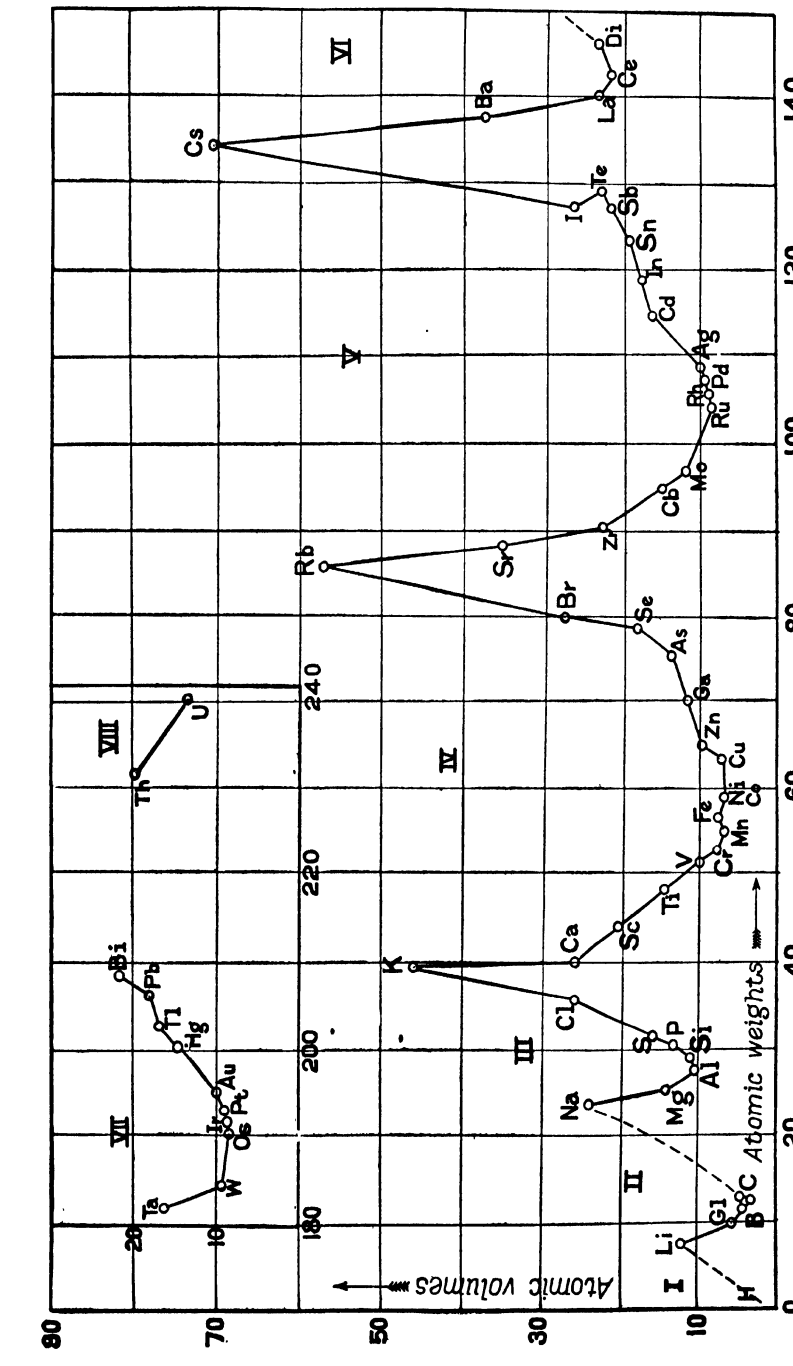


FIG. 122. — Lothar Meyer's Curve.

mentioned remain unexplained. The position of hydrogen in the system is also uncertain. This element does not seem to fit into the table. Furthermore, group VIII is peculiar as compared with the other groups. It contains three groups of three elements each, though to be sure the elements in each of these groups have approximately the same atomic weight. A number of the rare-earth elements (which see) have atomic weights that are not widely different from one another, and for these there do not appear to be suitable places in the system.

Stated in words, the so-called **periodic law** is that *the physical and chemical properties of the elements are periodic functions of their atomic weights.* An illustration of this is given in Fig. 122, in which the atomic weights are represented as abscissas and the atomic volumes (*i.e.* the atomic weights divided by the specific gravities) are represented as ordinates. The trend of the curve shows the periodicity, similar elements appearing in similar positions on the curve, which was first published by Lothar Meyer.

The periodic system does not represent a sharp quantitative relationship between the atomic weights and the properties of the elements. Some of its anomalies have already been mentioned. In spite of these imperfections, the periodic system offers a useful means of classifying the elements, which will in our further considerations be grouped accordingly. It will be noted that in considering the non-metals the natural families that have been studied really represent the essential elements of certain groups of the periodic system. The reader will comprehend the significance of the periodic system much better after having studied the physical and chemical peculiarities of the metals which still remain to be considered.

REVIEW QUESTIONS

1. What relation exists between the atomic weights of chlorine, bromine, and iodine? Mention three other groups of three elements each which also exemplify this relation.
2. What is the law of octaves? Who discovered it?
3. What is the first complete classification of the chemical elements called?
4. State the so-called periodic law in words. Mention the names of the two men who discovered this law.

5. How many vertical columns are there in the periodic system of the elements and what do the numbers of these columns correspond to? What is meant by a complete short period? By a complete long period?

6. Given a chart of the periodic system, point out the complete short periods, also the complete long periods.

7. Criticize the position of the following elements in the periodic system: manganese, iodine, tellurium, argon, nickel, hydrogen.

8. Of what use has the periodic system been in the advancement of chemistry?

CHAPTER XXI

THE ALKALI METALS

THE alkali metals are potassium, sodium, lithium, rubidium, and cæsium. Of these potassium and sodium are by far the most abundant and important. Lithium is also found in fair quantities, but rubidium and cæsium occur only in very small amounts, and they will consequently receive less consideration here. None of the metals of this group are found in the free state in nature. They always occur in the form of salts, which is due to the fact that their affinity for oxygen, the halogens, sulphur, and other non-metals is very great. The compounds which the alkali metals form with the non-metals are in general simple, very stable, and well characterized. These metals are univalent in all of their salts, hydroxides, and oxides. *The hydroxides of the alkali metals are the most powerful bases known.* The solutions of the hydroxides are very alkaline and caustic, so that they are commonly called the **caustic alkalies.** These alkalies are non-volatile, and are consequently termed the **fixed alkalies,** in contradistinction to ammonium and other very basic groups which may under proper conditions be volatilized. So far as its general chemical behavior is concerned, ammonium (NH_4) is closely allied to the alkali metals, and it will consequently be advantageous to refer to the chemistry of the ammonium compounds in this chapter.

Occurrence, Preparation, and Properties of Potassium. — Potassium is very widely distributed as a constituent of silicates like potassium feldspar and certain forms of mica. Inasmuch as soils are produced by the disintegration of rocks by the process of weathering, all soils contain potassium in the feldspathic constituents they have derived from rocks. Plants take up potassium salts from the soil, and in the ashes of plants the potassium is found as potassium carbonate, commonly called **potash.** By treating ashes with water and filtering, the potas-

sium carbonate is obtained by evaporating the filtrate. Since human beings and animals get their food supply directly or indirectly from plants, it is not strange that potassium is found in all animal tissues and secretions, like muscles, bones, blood, urine, albumen, eggs, milk, etc. Oceanic water contains about 0.04 per cent potassium, while the earth's crust contains about 2.45 per cent of the element. Though potassium is thus widely distributed, it occurs in large quantities in but few places. *The chief deposits of potassium salts are found in Germany, notably at Stassfurt*, where they occur as layers twenty to thirty meters thick, covering strata of native common salt. Potassium occurs here mainly as **carnallite** $KCl \cdot MgCl_2 \cdot 6\ H_2O$ and **kainite** $MgSO_4 \cdot KCl \cdot 3\ H_2O$, but also as **sylvite** KCl. Associated with sodium nitrate, potassium nitrate is found to some extent in Peru and Chili.

Metallic potassium was first prepared by Sir Humphry Davy, who in 1807 electrolyzed molten caustic potash. At present it is prepared commercially by electrolysis of either potassium chloride or potassium hydroxide, though formerly it was largely made by heating potassium carbonate with carbon: —

$$K_2CO_3 + 2\ C = 2\ K + 3\ CO.$$

In this process the potassium passes off as vapor which is condensed and kept under petroleum oils.

Potassium is a silvery white metal, which has a bright metallic luster, and is soft as wax at ordinary temperatures. Below 0° it becomes hard and brittle. Its specific gravity is 0.865 at 15°. It melts at 62.5° and boils at 667°. Its vapors are green. The atomic weight of potassium is 39.10; and its molecular weight is the same, the vapors being about twenty times as heavy as hydrogen. Potassium reacts vigorously with water, evolving hydrogen and forming potassium hydroxide. The heat generated during the action is generally so great as to set the hydrogen and some of the potassium on fire, thus giving rise to explosions. A freshly cut surface of potassium at once becomes blurred because of reaction with the moisture of the air. The metal is consequently kept under petroleum oils.

Potassium hydride KH is formed by passing hydrogen over potassium at 360°. It consists of white needlelike crystals, that catch fire on exposure to the air. Water decomposes

the compound, forming potassium hydroxide and hydrogen, thus: —

$$2\,KH + 2\,H_2O = 2\,KOH + 2\,H_2.$$

With carbon dioxide it readily forms potassium formate: —

$$KH + CO_2 = HCOOK.$$

Compounds of Potassium with the Halogens. — Of these salts **potassium chloride** KCl is the commonest. In nature it occurs as sylvite KCl, and also in carnallite $MgCl_2 \cdot KCl \cdot 6\,H_2O$, as already stated. Potassium chloride crystallizes in cubes which melt at 730°; at higher temperatures it is converted into vapor. With many other salts it unites to form double salts, examples of which we have in carnallite and kainite. Water dissolves potassium chloride readily. The salt is not soluble in *liquid* hydrochloric acid; hence the addition of hydrochloric acid to a concentrated aqueous solution of potassium chloride causes a precipitate of the latter to form.

Potassium bromide KBr is made by the action of bromine on potassium hydroxide: —

$$6\,KOH + 3\,Br_2 = KBrO_3 + 5\,KBr + 3\,H_2O.$$

The potassium bromate simultaneously formed is reduced by heating the product with carbon. Potassium bromide forms cubical crystals that melt at 715°. It is used in medicine and in the process of preparing silver bromide for photographic plates.

Potassium iodide KI is prepared by the action of iodine upon potassium hydroxide, the process being analogous to that described for making the bromide. The following method is also used for making the iodide: Iodine is mixed with iron filings under water, when a solution of a compound Fe_3I_8 (that is, $FeI_2 + 2\,FeI_3$) is formed. This when treated with potassium carbonate yields potassium iodide, which remains dissolved, and an hydroxide of iron which is insoluble and can be filtered off. Carbon dioxide gas is also given off during the change, which is: —

$$Fe_3I_8 + 4\,K_2CO_3 + 4\,H_2O = 8\,KI + Fe_3(OH)_8 + 4\,CO_2.$$

Potassium iodide crystallizes in cubes, on evaporation of the filtrate. The salt melts at 625°. It is more copiously soluble

in water than the bromide. Its aqueous solutions readily acquire a yellow color, due to the separation of free iodine formed by the action of oxygen and carbon dioxide of the air upon the salt. Solutions of potassium iodide readily dissolve additional iodine. These solutions are frequently employed in analytical chemistry. Potassium iodide is often used in medicine, also in photography.

Potassium fluoride KF is formed by treating potassium hydroxide or carbonate with hydrofluoric acid. With the latter it readily forms the double compound $KF \cdot HF$. Potassium fluoride is a deliquescent white salt, forming cubical crystals of the composition $KF + 2\,H_2O$. The solutions attack glass.

All of the halides of the alkali metals form double salts with salts of many other metals.

The halides of the alkalies may all be prepared by the action of the caustic alkalies upon the hydrohalogen acids, or by the direct union of the metals with the free halogens. The methods employed in preparing the bromide and iodide of potassium, as above described, are used because of the difficulty of making pure hydrobromic and hydriodic acids, to which fact attention has already been called.

Potassium Hydroxide KOH. — This compound is also called **caustic potash** and **potassium hydrate.** It is prepared by treating potassium carbonate with slaked lime in vessels of iron or silver, for caustic alkalies attack glass or porcelain. The reaction is : —

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2\,KOH.$$

The calcium carbonate is insoluble, which fact really forms the basis of the process. On evaporating the clear filtrate, caustic potash is obtained. The latter is also made in large quantities by the electrolysis of solutions of potassium chloride. In this process the electric current enters the solution by a carbon plate dipping into it, and leaves the solution by a mercury surface also submerged in it, but not in contact with the carbon. Thus as the current passes, chlorine is liberated on the carbon and is conducted off in pipes and used for making bleaching powder; at the same time, potassium is liberated on the mercury, in which it dissolves. This solution of potassium in

mercury is called **potassium amalgam.** Water acts on it slowly, forming potassium hydroxide and hydrogen, leaving the mercury behind. The aqueous solution on evaporation yields solid caustic potash. The essential reactions of the process are, first, by electrolysis,

$$2\,KCl = 2\,K + Cl_2;$$

and when the amalgam is acted upon by water,

$$2\,K + 2\,H_2O = 2\,KOH + H_2.$$

Potassium hydroxide is a hard, brittle, white solid, which is deliquescent and very soluble in water with evolution of heat. The solution is very caustic, having a corrosive and disintegrating action upon animal and vegetable tissues. It is the most powerful of the ordinary bases, and consequently generally decomposes the salts of other bases. Caustic potash commonly comes into the market cast in sticks which contain about 80 per cent of the compound KOH and 20 per cent water. Caustic potash readily absorbs carbon dioxide, forming potassium carbonate. As a drying agent and an absorbent for carbon dioxide, potassium hydroxide is much used in chemical laboratories, though sodium hydroxide, which is cheaper, is often employed in its place when it will do just as well. Caustic potash is used in making soft soaps.

Potassium Oxide K_2O may be prepared (1) by melting potassium and potassium hydroxide together, or (2) by heating potassium nitrate with potassium; the reactions are: —

$$(1)\quad 2\,KOH + 2\,K = 2\,K_2O + H_2.$$
$$(2)\quad 2\,KNO_3 + 10\,K = 6\,K_2O + N_2.$$

The oxide is a white, unstable powder. With water it unites, yielding potassium hydroxide. Exposed to the air, it absorbs oxygen, forming **potassium peroxide** KO_2, which is a yellow powder. With water this yields oxygen, hydrogen peroxide, and potassium hydroxide: —

$$4\,KO_2 + 6\,H_2O = 4\,KOH + 4\,H_2O_2 + O_2.$$

Peroxide of potassium is also formed together with the oxide when potassium is burned in the air or in oxygen.

Potassium Chlorate $KClO_3$ may be obtained by passing chlorine into a hot solution of potassium hydroxide, as already

described. By electrolyzing a solution of potassium chloride, chlorine and potassium hydroxide form at the opposite electrodes; and by stirring the hot solution, the chlorate thus forms and crystallizes out. Often solutions of the more soluble sodium chlorate are thus prepared, by means of which potassium chlorate is precipitated from potassium chloride solutions. *Nearly all the potassium chlorate of commerce is now made electrolytically.*

Potassium chlorate crystallizes in the monoclinic system. About six parts of it dissolve in 100 parts of water at room temperature. The salt melts at 350° and yields oxygen at a slightly higher temperature. It is used for making oxygen, also in manufacturing matches, fireworks, and explosives. The ease with which the salt gives up oxygen is shown by mixing two or three grains of it with a grain of sulphur or of red phosphorus in a mortar. As the substances are pressed together by means of the pestle, there is an explosion. By heating the chlorate, **potassium perchlorate** $KClO_4$ is produced as a first decomposition product, thus: —

$$8\,KClO_3 = 5\,KClO_4 + 3\,KCl + 2\,O_2.$$

It forms rhombic crystals and is less soluble than either the chlorate or chloride, and consequently it may readily be separated from these by fractional crystallization. At 400° the perchlorate decomposes into chloride and oxygen:

$$KClO_4 = KCl + 2\,O_2.$$

Potassium bromate $KBrO_3$ and **potassium iodate** KIO_3 are analogous to the chlorate. The methods of their preparation have already been mentioned under potassium bromide and iodide.

Potassium Nitrate KNO_3, also called **saltpeter**, is widely distributed in soils in small quantities, being formed wherever organic substances decay. It was formerly produced on a large scale by allowing refuse of nitrogenous organic bodies to decay in presence of potassium salts. At present potassium nitrate is made by treating hot, saturated solutions of Chili saltpeter $NaNO_3$ with potassium chloride, thus: —

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

The sodium chloride formed, being far less soluble than potassium nitrate, is precipitated, and from the clear supernatant solution potassium nitrate is readily obtained in form of crystals on cooling. The product is further purified by recrystallizing. At 0°, 100 parts of water dissolve 13 parts of KNO_3, while at 100°, 247 parts of the salt are dissolved.

Potassium nitrate crystallizes in rhombic prisms, which change into rhombohedra at about the melting point of the salt, 339°. When heated above its melting point, potassium nitrate gives off oxygen, forming **potassium nitrite** KNO_2. The latter salt is more readily formed by heating the nitrate with lead or iron, which take up the oxygen, forming oxides.

Potassium nitrate is used as a fertilizer, as a preservative for meat, as an oxidizing agent in the laboratory, and as an ingredient of fireworks and gunpowder. Most of it is used in making **gunpowder**, which consists of a mixture of 75 parts saltpeter, 13 parts charcoal, and 12 parts sulphur. When it is ignited, the following reaction takes place: —

$$2\,KNO_3 + S + 3\,C = K_2S + 3\,CO_2 + N_2.$$

Thus a large volume of gas is suddenly liberated, and this causes the explosion. The pressure of the gases produced at 2200°, the temperature of the discharge, is about 96,000 pounds per square inch. When discharged under pressure, as in a gun, the chemical reaction is somewhat more complicated than the one above given, potassium carbonate, sulphate, and thiosulphate being also produced in notable amounts. Besides this, products of partial combustion remain suspended in the air in a finely divided state, as smoke, after the discharge. *Black powder*, as it is called, is being displaced more and more by *smokeless powder*, which see.

Potassium Cyanide KCN has already been mentioned in connection with cyanogen. Besides being made as there described, it is prepared on a large scale by heating potassium ferrocyanide $K_4Fe(CN)_6$ with potassium carbonate: —

$$K_4Fe(CN)_6 + K_2CO_3 = 5\,KCN + KCNO + Fe + CO_2.$$

The potassium cyanide thus prepared always contains some **potassium cyanate** KCNO, which, in case a pure product is required, is reduced by means of charcoal or zinc. On evapo-

ration of the clear solution, potassium cyanide is obtained in white deliquescent lumps that readily dissolve in water. Moisture decomposes the salt somewhat, yielding caustic potash and hydrocyanic acid. In presence of carbon dioxide, potassium carbonate is formed together with hydrocyanic acid. Hence the odor of the latter is ever present with potassium cyanide. *This salt is extremely poisonous.* It is a powerful reducing agent, readily passing over into the cyanate, a white salt which also dissolves in water. Potassium cyanide also unites with sulphur to form **potassium sulphocyanate** KCNS, as already mentioned. This salt is crystalline, deliquescent, and consequently readily soluble in water.

Potassium cyanide is used in very large quantities for extracting gold from its ores. It is also employed in photography and in gold and silver electroplating, which see.

Potassium Carbonate K_2CO_3 was formerly prepared as **potash** by leaching out wood ashes. The molasses residues of the beet sugar industry and the fat of sheep's wool also contain potassium salts, from which potash is obtained. *The bulk of the potassium carbonate on the market is made from potassium sulphate and chloride obtained from the Stassfurt deposits.* The method employed is analogous to the Le Blanc process for making sodium carbonate (which see). In addition, however, potassium carbonate is now made at Neustassfurt by passing carbon dioxide into magnesium carbonate $MgCO_3 \cdot 3\,H_2O$ suspended in a solution of potassium chloride, thus : —

$$2\,KCl + 3(MgCO_3 \cdot 3\,H_2O) + CO_2 = 2(MgCO_3 \cdot KHCO_3 \cdot 4\,H_2O) + MgCl_2.$$

When the double carbonate thus formed is properly heated, magnesium carbonate and potassium carbonate are obtained; the former, being insoluble, is filtered off, and the filtrate, upon evaporation, yields potassium carbonate. The latter melts at about 840°. At 0°, 100 parts of water dissolve 83 parts of the salt, while at 20°, 112 parts of the salt are thus dissolved. From concentrated solutions, monoclinic crystals, $2\,K_2CO_3 + 3\,H_2O$, may be obtained. The solutions have a strongly alkaline reaction, for the salt is one of a weak acid with a powerful base, and is consequently appreciably hydrolyzed. In the market, potassium carbonate is often called **pearlash.** It is used

in making hard glass (potash glass), soft soap, and many salts of potassium.

By passing carbon dioxide into solutions of potassium carbonate, **potassium bicarbonate** $KHCO_3$ is formed. It is less soluble than the carbonate, but more so than sodium bicarbonate, and hence cannot, like the latter, be obtained by the Solvay process (which see). Heating potassium bicarbonate, even in aqueous solutions, decomposes it, yielding the carbonate, carbon dioxide, and water.

Potassium Silicate K_2SiO_3 is made by fusing silica with the carbonate: —

$$K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2.$$

Thus a glassy, deliquescent mass is obtained, which dissolves in water, yielding a thick sirupy solution popularly called **potassium water glass.** The solutions commonly contain other potassium silicates besides K_2SiO_3. Its uses are the same as those of the cheaper sodium water glass (which see).

Potassium Fluosilicate K_2SiF_6 is formed as an amorphous, translucent precipitate, when solutions of a potassium salt are treated with hydrofluosilicic acid. It is soluble in about 800 parts of water at 20°.

Potassium Phosphates. —The existence of three phosphates, the primary, KH_2PO_4, the secondary, K_2HPO_4, and the tertiary, K_3PO_4, has already been mentioned. They are white salts, readily soluble in water. Their general characteristics have been sufficiently described.

Potassium Sulphate K_2SO_4 is found at Stassfurt in **schönite** $K_2SO_4 \cdot MgSO_4 \cdot 3\,H_2O$, from which it is obtained by treatment with potassium chloride in solutions, thus: —

$$K_2SO_4 \cdot MgSO_4 + 2\,KCl = 2\,K_2SO_4 + MgCl_2.$$

The magnesium chloride is very soluble and hence remains in solution, while the less soluble potassium sulphate is precipitated. Potassium sulphate is also obtained by the action of sulphuric acid on potassium chloride. It crystallizes in rhombic forms without water of crystallization. Its melting point is 1080°. At room temperature 10 parts of the salt dissolve in 100 parts of water. It is used as a fertilizer, also in making potassium alum, hard glass, and potassium carbonate.

On treating potassium sulphate with sulphuric acid, **acid potassium sulphate** $KHSO_4$ is formed. This is very soluble in water and melts at about 200°, forming water and **potassium pyrosulphate** $K_2S_2O_7$, which, on further heating, decomposes into the normal sulphate and sulphur trioxide. The latter at higher temperatures readily unites with many metallic oxides; hence the practice of fusing refractory metallic oxides and many minerals with **potassium bisulphate** $KHSO_4$ to convert the bases into soluble sulphates.

Potassium Sulphite K_2SO_3 is formed by passing sulphur dioxide into a solution of potassium carbonate till carbon dioxide is no longer formed. The salt crystallizes in monoclinic prisms with two molecules of water.

On saturating a solution of potassium carbonate or sulphite with sulphur dioxide, **acid potassium sulphite** or **potassium bisulphite** $KHSO_3$, crystallizing in needles, is obtained.

Sulphides of Potassium. —**Potassium sulphide** K_2S is made by fusing potassium sulphate with charcoal: —

$$K_2SO_4 + 4\,C = K_2S + 4\,CO.$$

It is a flesh-colored, crystalline mass that readily dissolves in water. The oxygen of the air acts on the solutions, gradually forming **potassium thiosulphate** $K_2S_2O_3$, thus: —

$$2\,K_2S + H_2O + 2\,O_2 = 2\,KOH + K_2S_2O_3.$$

By saturating a caustic potash solution with hydrogen sulphide, **potassium sulphydrate** KSH is formed: —

$$KOH + H_2S = KSH + H_2O.$$

Its solutions are alkaline, and upon evaporation with caustic potash they yield potassium sulphide: —

$$KSH + KOH = K_2S + H_2O.$$

Solutions of K_2S or KSH will readily dissolve sulphur, forming a series of compounds known as **polysulphides**. Thus K_2S_3, K_2S_4, and K_2S_5 have been obtained. On treatment with acids the polysulphides yield hydrogen sulphide and sulphur. By fusing potash with sulphur out of contact with air, a mass of liver-brown color, known as **liver of sulphur**, is obtained. It consists of a mixture of polysulphides of potassium together with potassium sulphate and thiosulphate.

Tests for Potassium. — To detect the presence of potassium in small quantities, the spectroscope (which see) is employed. In addition, the fact that acid potassium tartrate $KHC_4H_4O_6$, potassium silicofluoride K_2SiF_6, and potassium platinic chloride K_2PtCl_6 are difficultly soluble in water serves to determine whether potassium salts are present in a given solution or not. The reactions involved, written for potassium chloride, are as follows: —

$$KCl + H_2C_4H_4O_6 = KH \cdot C_4H_4O_6 + HCl.$$
$$2\,KCl + H_2SiF_6 = K_2SiF_6 + 2\,HCl.$$
$$2\,KCl + PtCl_4 = K_2PtCl_6.$$

Potassium platinic chloride is soluble in about 100 parts of water; but its solubility is much less in alcoholic solutions, of which fact the analytical chemist avails himself.

Rubidium and Cæsium. — These metals have the atomic weights 85.45 and 132.81 respectively. They were discovered in 1860 by Robert Bunsen by means of the spectroscope, in the residues obtained by evaporating Dürkheim mineral water. The spectrum of rubidium contains certain characteristic red lines, while that of cæsium exhibits striking blue lines. Hence Bunsen named the elements rubidium (red) and cæsium (blue); their symbols are Rb and Cs. Salts of both of these metals occur widely distributed in nature, though in extremely minute quantities; they are commonly associated with salts of potassium. Carnallite contains about 0.025 per cent of rubidium, and it has been estimated that from the Stassfurt salts that are used as fertilizers more than 200 tons of rubidium are distributed annually over the soils, from which plants absorb it. Thus in the ash of sugar beets, tobacco, coffee, and tea, rubidium is frequently met. The methods that are used for preparing potassium also serve for making rubidium. The chief source of rubidium salts is the Stassfurt deposit. Cæsium is much rarer than rubidium. The mineral **pollux** found on the island of Elba is a silicate of aluminum and cæsium. It contains about 34 per cent of cæsium oxide.

Metallic cæsium was first prepared in 1881 by Setterberg, who electrolyzed the cyanide CsCN. Cæsium may also be obtained by heating its oxide or carbonate with magnesium.

The salts of both rubidium and cæsium are in general analogous

to those of potassium, with the exception that the former elements are also able to form halides containing three or five halogen atoms. In such compounds rubidium and cæsium consequently exhibit valences of three and five, respectively. The hydroxide of rubidium is a stronger base than that of potassium, while the hydroxide of cæsium is the most powerful base known.

Occurrence, Preparation, and Properties of Sodium. — The chief compound of sodium is sodium chloride, which is widely distributed in nature in large quantities. Thus, it occurs in oceanic waters, while many salt seas and lakes are practically saturated solutions of common salt. Mineral springs are often rich in sodium salts, which also occur in huge deposits as chloride, nitrate, and borate, in various parts of the globe. Cryolite, an aluminum sodium fluoride, is found in Greenland, and albite or soda feldspar, a silicate of sodium and aluminum, is widely distributed in nature. *Just as land plants contain potassium, so sea plants contain sodium, which is found in their ashes as carbonate.* From the soil, sodium gets into plants and then into animal organisms, where it occurs in the blood and the various tissues and secretions.

Metallic sodium was first prepared by Sir Humphry Davy in 1807 by electrolysis of molten sodium hydroxide. In this way it is now prepared on a large scale. Thus, sodium is deposited at one pole, and the hydroxyl liberated at the opposite pole at once decomposes, yielding water and oxygen. The yield is only about 40 per cent, for some of the metal continually reacts with the water, liberating hydrogen and forming sodium hydroxide. *The methods described for making potassium may also be used for preparing sodium.*

Sodium has properties similar to those of potassium. At room temperature the metal is soft like wax, while at $-20°$ it is hard. It has a bright, silvery luster. Its melting point is 95.5°, and its boiling point 742°. The vapor of sodium is colorless, though in thick layers it appears violet. The vapor is 12 times as heavy as hydrogen, whence the molecular weight is 24. The atomic weight is 23, and the valence is one. The molecules of sodium, like those of potassium, consist of but one atom. Sodium decomposes water, like potassium, but the action is not as violent as in the case of the latter. The specific gravity of sodium is 0.974 at 15°. The metal is used in making sodium cyanide and

sodium peroxide, also in the manufacture of complex organic compounds. In the laboratory, it is frequently employed as a reducing agent. Like potassium, it is kept under petroleum oil; but sodium is also shipped in tightly soldered tinned iron boxes.

Sodium dissolves in mercury, forming **sodium amalgam**, which when treated with water yields mercury, sodium hydroxide, and hydrogen. The latter is liberated much less rapidly than when sodium alone acts on water, hence the amalgam is often employed in effecting reductions that are to proceed slowly. With potassium, sodium forms alloys, 1 part sodium to 2 to 10 of potassium, that are liquid at room temperature and have the appearance of mercury. If but little potassium is alloyed with much sodium, that is, if the proportions mentioned are reversed, the alloys formed are brittle solids. With hydrogen, sodium forms **sodium hydride** NaH, which is similar to the hydride of potassium.

Sodium Chloride NaCl, *common salt, is the chief source of sodium and its compounds.* Large deposits are found at Stassfurt and Reichenhall, in Germany, at Wieliczka in Galicia, at Cheshire in England, at Syracuse in New York, in Michigan, Kansas, Texas, Utah, California, as well as in Asia and Africa. In some localities the salt is mined in solid form, and again it is frequently obtained from brines by evaporation. When the brine is dilute, as in case of sea water, it is concentrated by allowing it to trickle over a large surface of twigs, thus giving better opportunity for evaporation to take place. The concentrated solution thus obtained is then generally evaporated by means of artificial heat; though in hot climates, solar heat is often relied upon entirely. Brine is also evaporated in shallow basins either by means of artificial heat or the heat of the sun. Again, so-called vacuum pans, in which brines are evaporated under diminished pressure, are frequently employed. Ordinary salt is not pure. It contains small amounts of sodium sulphate and chlorides of calcium and magnesium. The latter are deliquescent, and their presence in common salt causes it to attract moisture from the air. Pure common salt is obtained by conducting hydrochloric acid gas into a saturated solution of common salt. The latter is thus thrown out of solution, for it is less soluble in hydrochloric acid than in water.

Each year the United States produces about 5,000,000 tons of sodium chloride, which is approximately one fourth of the world's annual output.

Sodium chloride crystallizes in cubes, which when obtained from aqueous solutions form groups of hollow pyramids, that is, are hopper-shaped (Fig. 123). They contain occluded water which escapes on heating, causing the salt to decrepitate. At $-10°$, sodium chloride crystallizes with two molecules of water, forming monoclinic prisms. Sodium chloride melts at about 800°, at which temperature it also volatilizes appreciably. At room temperature, 100 parts of water dissolve 36 parts of salt, and at 100°, 39 parts. The salt is therefore about as soluble in hot as in cold water. *In practically all solvents other than water, common salt is insoluble.*

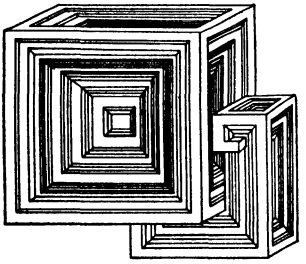


FIG. 123.

Human beings and many animals cannot live without sodium chloride, which is found distributed throughout their systems in small amounts, though its function is not known. It has been estimated that the quantity of salt used annually by a human being amounts to about one tenth of his weight.

Common salt is used in enormous quantities in making hydrochloric acid, chlorine, and nearly all of the sodium compounds.

Sodium bromide NaBr and **sodium iodide** NaI are more soluble in water than the chloride; they are also more volatile. In general, these halides and **sodium fluoride** are much like the corresponding salts of potassium.

Oxides and Hydroxide of Sodium. — When sodium is burned in oxygen, a mixture of the two oxides, Na_2O and Na_2O_2 is formed.

Sodium oxide Na_2O is also obtained as a gray mass by heating the hydroxide with sodium. When treated with water, it dissolves, forming a solution of the hydroxide.

Sodium peroxide Na_2O_2 is a white powder formed by prolonged heating of sodium or sodium oxide in oxygen or in the air at about 300°. At high temperatures it decomposes into the oxide and oxygen. With water it yields sodium hydroxide and oxygen, though in the cold it may in part be dissolved.

With dilute acids it yields hydrogen peroxide; hence it may be regarded as the latter substance whose hydrogen atoms are replaced by sodium. Sodium peroxide is prepared on a large scale as an oxidizing and bleaching agent. It is shipped in air-tight tin cans.

Sodium hydroxide NaOH, **caustic soda**, is made by the same methods as caustic potash, namely, by treating the carbonate with slaked lime or by electrolysis of solutions of the chloride, using a mercury cathode. It is also made by the **Acker process**, which consists of electrolyzing fused sodium chloride, using a

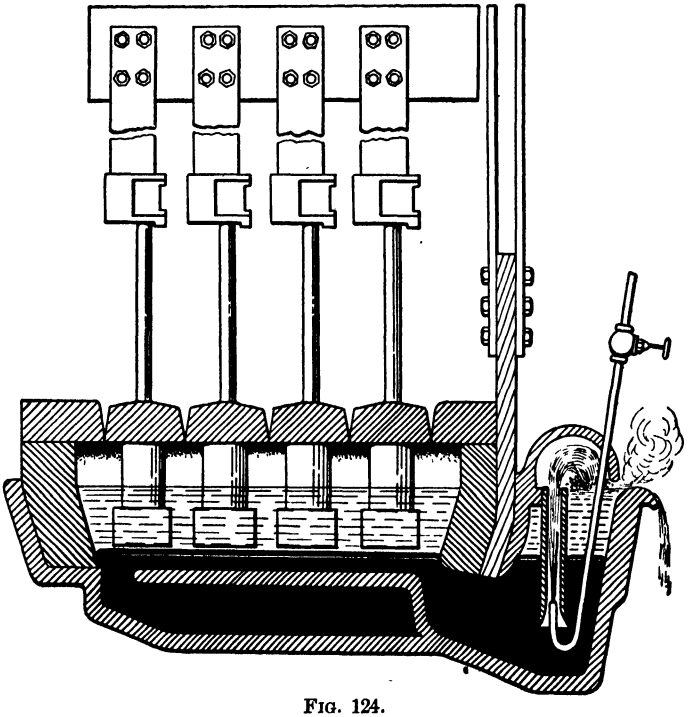


FIG. 124.

carbon anode and a cathode of molten lead. The chlorine is conducted off and used in making bleaching powder, while the sodium forms an alloy with the lead. A jet of steam directed on this alloy reacts with the sodium, forming hydrogen, which burns at once, and sodium hydroxide, which, being molten, is drawn off into proper containers. Figure 124 shows the essential features of the apparatus.

The properties of sodium hydroxide are much like those of potassium hydroxide. The former is much cheaper, however, and is used in place of potassium hydroxide whenever possible.

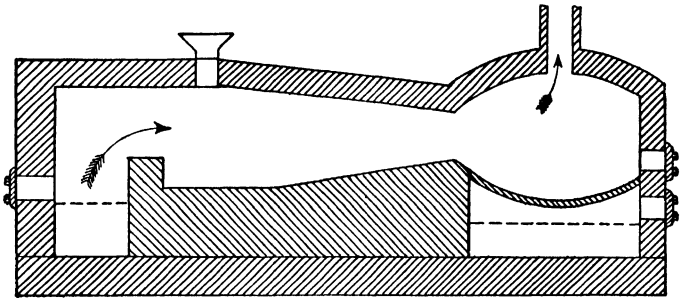


FIG. 125.

Large quantities of sodium hydroxide are used in making soap and in "softening water." It is also used in the paper industry and in making carbolic acid, oxalic acids, and many other products.

Sodium Carbonate Na_2CO_3, popularly called **soda** or sal soda, is manufactured from common salt on a very large scale, for it is essential in making glass, soap, caustic soda, and other sodium compounds. Sodium carbonate is found in nature in Wyoming, California, Mexico, Egypt, and in the ashes of marine plants. It is manufactured by the Le Blanc process, the Solvay process, and the electrolytic process.

The **Le Blanc soda process** was introduced in France by Le Blanc in 1791. It is based upon three chemical reactions. *First*, common salt is treated with sulphuric acid in equivalent quantity; thus hydrochloric acid and "salt cake," consisting of sodium chloride and sodium acid sulphate, are formed: —

$$2\,NaCl + H_2SO_4 = NaCl + NaHSO_4 + HCl.$$

This salt cake is then transferred to the hearth of a furnace, (Fig. 125) and heated; thus sodium sulphate and more hydrochloric acid are produced: —

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The hydrochloric acid formed is absorbed in water and placed on the market. The *second step* consists in mixing the sodium sulphate formed with charcoal and calcium carbonate, and heating

the mixture in a rotating cylindrical furnace (Fig. 126) which has a central flue through which the hot gases of the furnace pass. Thus sodium sulphate is reduced to sulphide : —

$$Na_2SO_4 + 4\,C = Na_2S + 4\,CO;$$

and sodium sulphide reacts with calcium carbonate, yielding sodium carbonate and calcium sulphide : —

$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

The *third step* consists in treating the mixture of calcium sulphide and sodium carbonate, called **black ash**, with water. Thus sodium carbonate dissolves and calcium sulphide remains behind, as an insoluble residue. By evaporation of the clear solution

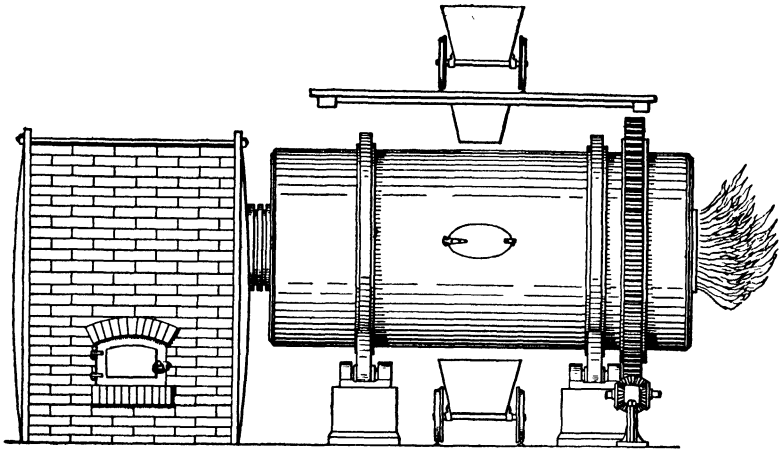


Fig. 126.

crystals of the composition $Na_2CO_3 \cdot H_2O$ are obtained, which are heated to drive off the water, thus forming Na_2CO_3, **calcined soda.** When this is recrystallized from water at room temperatures, crystals of the composition $Na_2CO_3 \cdot 10\,H_2O$ are formed. This is the **washing soda** or **crystallized soda** of commerce. Sodium carbonate made by the Le Blanc process generally contains small amounts of chloride, sulphate, and sulphite.

The sulphur contained in the calcium sulphide, also called **tank waste,** is recovered by a process developed in 1888 by Chance in England. It consists of diluting the waste with water and arranging it in a series of cylinders through which carbon

dioxide from a limekiln is run. There is first formed calcium carbonate and calcium sulphydrate, thus :—

$$2\,CaS + CO_2 + H_2O = CaCO_3 + Ca(SH)_2.$$

By further action of carbon dioxide, this sulphydrate is decomposed, yielding hydrogen sulphide : —

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2\,H_2S.$$

The hydrogen sulphide set free in one cylinder reacts with the material in the next, and so on through the series of cylinders; thus,

$$CaS + H_2S = Ca(SH)_2.$$

Finally, the hydrogen sulphide is burned to water and sulphur, thus,

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S;$$

or it is burned completely to water and sulphur dioxide, and then made into sulphuric acid. About 90 per cent of the sulphur in the tank wastes may be recovered.

The **Solvay process**, also called the **ammonia soda process**, was perfected by the Belgian chemist Solvay in 1863. It is based upon the fact that sodium bicarbonate $NaHCO_3$ is relatively sparingly soluble in water. The process consists of conducting ammonia and carbon dioxide into a cold, saturated solution of common salt. In this way ammonium bicarbonate is formed, which reacts with sodium chloride, causing a precipitate of sodium bicarbonate to separate out : —

$$NaCl + NH_4HCO_3 = NH_4Cl + NaHCO_3.$$

The sodium bicarbonate is placed on the market as such, or it is heated and thus converted into carbonate,

$$2\,NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The ammonium chloride remains in solution, from which, by heating with lime or magnesia, ammonia is again regenerated. Thus, the waste products are chlorides of calcium or magnesium. On heating magnesium chloride, magnesium oxide and hydrochloric acid are formed : —

$$MgCl_2 + H_2O = MgO + 2\,HCl.$$

In this way the magnesia can be recovered and used over again. In Germany and the United States most of the sodium carbonate is made by the Solvay process, while in England the Le Blanc process still predominates. It is evident that a purer product is obtained by the Solvay process.

The **electrolytic process** consists of making caustic soda by one of the electrolytic methods described and then treating the solution with carbon dioxide.

At ordinary temperatures sodium carbonate crystallizes in monoclinic prisms of the composition $Na_2CO_3 \cdot 10\,H_2O$, which effloresce. At 60° this compound melts in its crystal water and on continued heating it yields a deposit of the composition $Na_2CO_3 \cdot 2\,H_2O$, which when dried in the air readily forms $Na_2CO_3 \cdot H_2O$. At 100° the salt may be completely dehydrated. At 15°, 100 parts of water dissolve 55 parts of Na_2CO_3, at 38°, 138 parts, and at 100°, 100 parts. The solution deposits $Na_2CO_3 \cdot 7\,H_2O$ at 50°. Solutions of sodium carbonate have a strong alkaline reaction; for, like potassium carbonate, the salt is hydrolyzed. Sodium carbonate melts at red heat, forming a clear liquid.

Sodium bicarbonate $NaHCO_3$, or sodium acid carbonate, is soluble in about 10 parts of water at 20°. Its solutions have an alkaline reaction, for the salt is decomposed by hydrolysis to a slight extent. When warmed, the solutions give off carbon dioxide, the carbonate being formed. Sodium bicarbonate is used in medicine, in baking powder, as **saleratus**, and in making soda water and other effervescent beverages.

Sodium Nitrate $NaNO_3$ occurs in large quantities in Chili and Peru as **Chili saltpeter**, which also contains other salts of sodium, notably the iodate, sulphate, and chloride. The salt crystallizes in the rhombohedral division of the hexagonal system and melts at 318°. In general, its chemical behavior is like that of potassium nitrate. Sodium nitrate is used as a fertilizer, also in the manufacture of potassium nitrate and nitric acid. The salt is somewhat hygroscopic, which unfits it for use in gunpowder.

By heating sodium nitrate with lead or iron, **sodium nitrite** $NaNO_2$ is formed. This salt is much used in the coal-tar dyestuff industry.

Phosphates of Sodium. — The most important of these is the secondary or **disodium phosphate** $Na_2HPO_4 \cdot 12\,H_2O$. This is

commonly called simply **sodium phosphate.** It is prepared by the action of phosphoric acid on sodium hydroxide or carbonate. The crystals effloresce. At 20°, 100 parts of water dissolve 9.3 parts of the salt. The solution has a slightly alkaline reaction. On adding another equivalent of caustic soda to disodium phosphate solution and evaporating to dryness, the **tertiary sodium phosphate** $Na_3PO_4 \cdot 12\ H_2O$ is obtained. In aqueous solution, this does not exist, being hydrolyzed into disodium phosphate and sodium hydroxide. **Primary sodium phosphate** $NaH_2PO_4 \cdot H_2O$

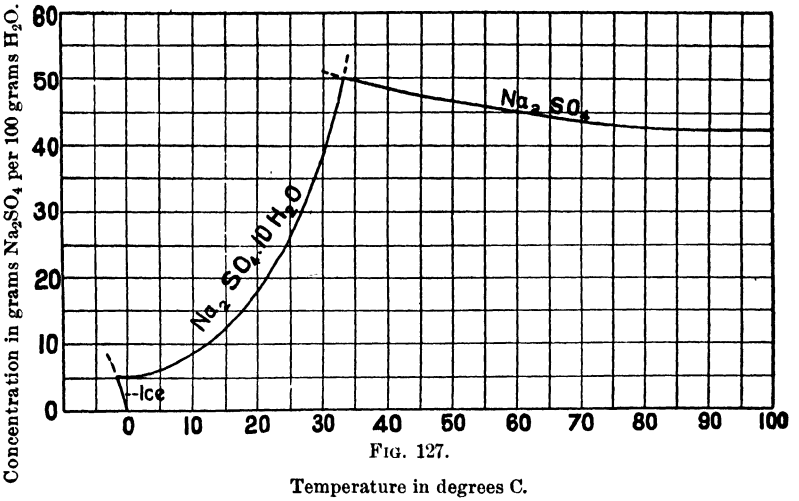


FIG. 127.

has an acid reaction in solutions. On heating, the salt loses water and forms **sodium metaphosphate** $NaPO_3$.

Sodium Sulphate $Na_2SO_4 \cdot 10\ H_2O$, also called **Glauber's salt,** crystallizes in large monoclinic crystals that effloresce on exposure to the air. It is manufactured as one of the products of the Le Blanc soda process, also by Hargreave's process, which consists of passing air, sulphur dioxide, and steam over sodium chloride at high temperatures, thus: —

$$2\,NaCl + H_2O + O + SO_2 = Na_2SO_4 + 2\,HCl.$$

At Stassfurt the salt is formed by the action of magnesium sulphate upon sodium chloride at low temperatures, when the sodium sulphate is deposited, while the magnesium chloride simultaneously formed remains in solution: —

$$MgSO_4 + 2\,NaCl = Na_2SO_4 + MgCl_2.$$

The salt was first prepared by Glauber, whence its name. The solubility of Glauber's salt $Na_2SO_4 \cdot 10\ H_2O$ increases with rise of temperature to 32.4°, beyond which it decreases, for at higher temperatures the salt loses water, becoming anhydrous Na_2SO_4, which is less soluble than the decahydrate. Figure 127 shows the solubility curve, which has a sharp point of inflection at 32.4°. This point is really the intersection of the solubility curve of the decahydrate and that of the anhydrous salt. Glauber's salt melts in its water of crystallization at 32.4°. When completely melted, the solution so obtained may be cooled to room temperature and even lower. This is a so-called **supersaturated solution**, for it contains more salt than would be taken up at the lower temperature *in presence of an excess of the solid salt.* Indeed, if a crystal of the solid $Na_2SO_4 \cdot 10\ H_2O$ is introduced into this supersaturated solution, the whole of it at once solidifies. Many other substances form similar supersaturated solutions. Glauber's salt simply furnishes an excellent illustration. Sodium sulphate occurs in many mineral waters. As Glauber's salt it is used as a purgative.

On treating sodium sulphate with an equivalent quantity of sulphuric acid, **acid sodium sulphate** or **sodium bisulphate** $NaHSO_4 \cdot H_2O$ is obtained. It becomes anhydrous above 50° and melts at about 300°. Its behavior is similar to that of potassium bisulphate.

Sodium Sulphite $Na_2SO_3 \cdot 7\ H_2O$ is formed by passing sulphur dioxide into a concentrated solution of sodium hydroxide or carbonate to neutrality. On saturating a strong solution of the sulphite with sulphur dioxide, **sodium bisulphite** $NaHSO_3$ is formed. This is frequently used as a source of sulphur dioxide in bleaching fabrics of silk, wool, etc.

Sodium Thiosulphate $Na_2S_2O_3 \cdot 5\ H_2O$ is made by boiling sulphur in a solution of sodium sulphite. It is also, though wrongly, called hyposulphite of soda or hypo. Its solution serves in photography as a "fixing bath," for it dissolves the excess of silver bromide on the photographic plate after the latter has been exposed to the light and developed. Sodium thiosulphate absorbs chlorine and is used as so-called "antichlorine," thus: —

$$2\ Na_2S_2O_3 + Cl_2 = 2\ NaCl + Na_2S_4O_6.$$

The salt is also used in chemical analysis.

The **sulphides of sodium** and **sodium hydrosulphide** are analogous to those of potassium and need no special description.

Sodium Silicate, or **sodium water glass**, is made by fusing silica with sodium hydroxide or carbonate, or with Glauber's salt and carbon. It is also prepared by boiling silica with concentrated solutions of sodium hydroxide under pressure. Sodium silicate may be obtained in form of monoclinic crystals of the composition $Na_2SiO_3 \cdot 8\ H_2O$. Water glass comes in the market as a thick sirupy solution containing various sodium silicates, the composition averaging about $Na_2Si_4O_9$. It is used in laundry soaps as a "filler," in making fabrics and wood fireproof, in the production of artificial stone, as a preservative for wood, and as a cement for glass, asbestus, mineral wool, etc.

Sodium Cyanide NaCN is very similar to potassium cyanide, and is used for the same purposes. It is made commercially by the action of ammonia gas upon a mixture of carbon and metallic sodium, and is extremely soluble in water.

Sodium Borate $Na_2B_4O_7 \cdot 10\ H_2O$, or **borax**, has been described under boron.

Lithium and its Compounds. — Lithium is found in the minerals, lepidolite or lithia mica, spodumene, triphylite, and a few others of rare occurrence. In very minute quantities lithium salts are also found widely distributed in soils, from which they pass into plants, a number, like tobacco and beets, being particularly prone to store up lithium. Many mineral waters contain lithium, though generally in rather small amounts. Lithium compounds are readily detected by means of the spectroscope; for they exhibit two characteristic red lines. To the Bunsen flame lithium salts impart a characteristic red color.

Metallic lithium may be obtained by electrolyzing the fused chloride or a concentrated solution of the latter in pyridine. It has a very low specific gravity, 0.59, and hence floats even on petroleum oils. In general, its chemical behavior is similar to that of sodium, only less vigorous. The atomic weight of lithium is 6.94, and its valence is 1.

Lithium chloride LiCl is deliquescent and extremely soluble in water. On the other hand, **lithium carbonate** Li_2CO_3 is very slightly soluble, for 100 parts of water dissolve but 0.77 part at 15°. **Lithium phosphate** Li_3PO_4 is also but slightly soluble, 1 part in 2500 of water. *This slight solubility of the*

carbonate and phosphate distinguishes lithium sharply from the other alkali metals and shows its similarity to the alkaline earth metals. The chloride of lithium dissolves in pyridine, whereas the chlorides of all the other alkali metals are insoluble in that liquid, which fact is used in separating lithium from the other members of the group.

Commercially, lithium carbonate is the most important of the lithium salts. With uric acid $C_5H_4N_4O_3$, lithium forms a moderately soluble salt, lithium urate $C_5H_2N_4O_3Li_2$, upon which fact is based the administration of lithium carbonate in medicine, in cases of gout, which is caused by deposits of uric acid in the joints and muscles.

The Alkali Metals as a Group. — The alkali metals form a natural group, the properties of whose members exhibit a regular variation with the atomic weights. The relations that obtain may be seen from the following table: —

Element	Atomic Weight	Melting Point	Specific Volume
Lithium, Li	6.94	180.0°	11.9
Sodium, Na	23.00	97.6°	23.7
Potassium, K	39.10	62.5°	45.2
Rubidium, Rb	85.45	38.5°	56.2
Cæsium, Cs	132.81	26.5°	70.7

The gradation of chemical properties has already been mentioned. It is evident that as the atomic weight increases the chemical activity of the members of the group also increases.

Spectrum Analysis. — A little of any sodium compound introduced into the Bunsen flame colors it a bright yellow. Similarly potassium compounds produce a violet and lithium compounds a characteristic red color. These colored flames may serve to detect the presence of small amounts of these metals. At the high temperature of the Bunsen flame, the salts of these and other metals are decomposed, and the incandescent vapors emit light of definite wave length, *i.e.* of definite color, in each individual case. When sodium and potassium are both present in the flame, the latter appears yellow, for that color completely masks the delicate violet of the potassium

flame. The latter, however, can be detected by viewing the yellow flame through a blue glass or through a layer of a solution of indigo, in which case the yellow light is absorbed and the violet color due to the potassium becomes apparent. Robert Bunsen sought to work out a system of detecting the presence of metals by noting the color which they impart to the flame. Later Bunsen and Kirchhoff (1859) passed the composite light through a glass prism, and thus the different colors could be

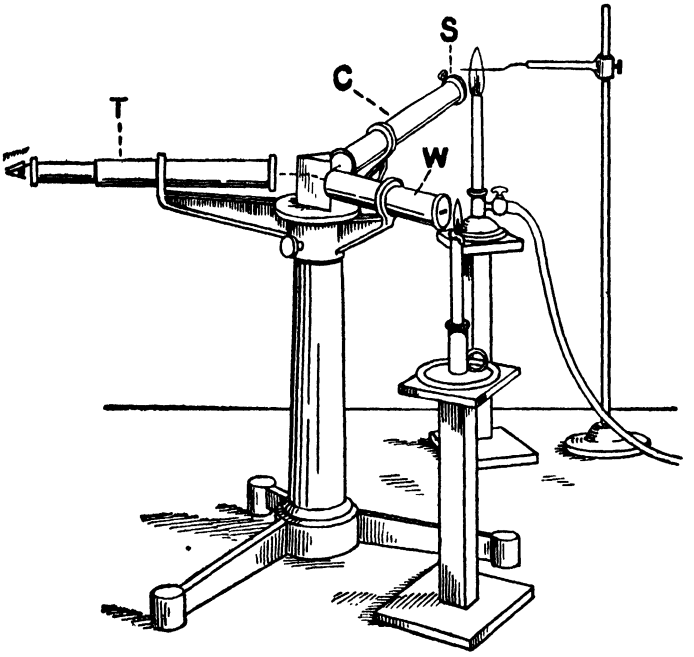


FIG. 128.

seen side by side instead of superimposed, for light of different color possesses different refrangibility. The instrument designed by Bunsen and Kirchhoff for producing and inspecting such spectra is called a **spectroscope**. Figure 128 shows a simple form of the instrument with the cover removed from the prism. The colored light from the flame enters a narrow adjustable slit at *S*, and a lens or set of lenses in *C* gathers the rays and transmits them to the prism. After passing the latter, they enter the telescope *T*, which can be moved so as to catch the rays. Thus, if the flame is colored by sodium alone, the observer sees

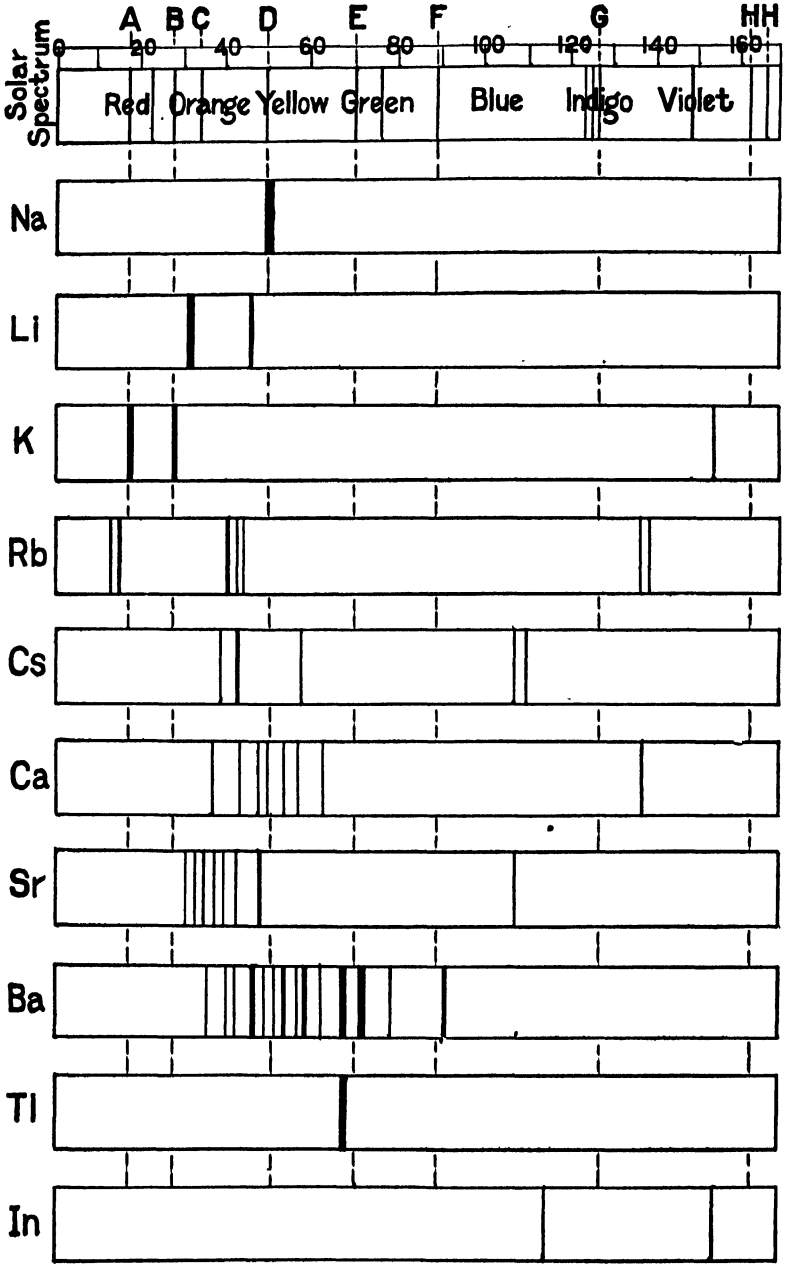

A
B
C
D
E
F
G
H
H
0
20
40
60
80
100
120
140
160
Solar Spectrum
Red
Orange
Yellow
Green
Blue
Indigo
Violet
Na
Li
K
Rb
Cs
Ca
Sr
Ba
Tl
In

FIG. 129.

simply one yellow line, the image of the slit magnified, of course, by the lenses of the telescope. If now potassium be added to the flame, the yellow line due to the sodium remains, but there appear in addition two characteristic red lines to the left of the sodium line, while to the extreme right of the latter a violet line is found. The two red lines and the violet line are due to potassium. They always appear when potassium is present and are located in the same relative position to the sodium line and to one another. In order to observe more accurately the relative positions of these lines a scale is required. In the tube *W* a photographic scale is placed which is illuminated by a candle or other luminous flame as shown. Light from this scale strikes the prism at such an angle as to be reflected through the telescope to the eye. Thus, the scale and the spectrum are seen together. *Every incandescent gas produces its own characteristic lines in the spectrum, and this fact constitutes the basis of spectrum analysis.* Figure 129 exhibits the spectra of a number of common elements, the color of the lines being evident from the solar spectrum given at the head of the figure. Very minute quantities of many substances can still be detected by means of the spectroscope; so one three-millionth of a milligram of sodium will still show its characteristic yellow line in the spectrum.

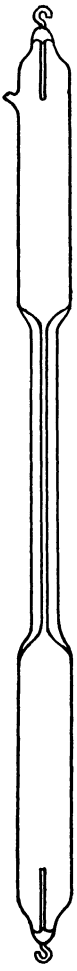


FIG. 130.

When a solid body is heated to incandescence in the flame, the spectrum observed is not a **band spectrum**, that is, it is not made up of a series of definite lines or bands, but consists of a **continuous spectrum** like that produced when sunlight passes through the slit. It is well known that sunlight passed through a prism is decomposed, yielding a continuous spectrum consisting of the colors of the rainbow.

The light of the sun thus yields a continuous spectrum; this is, however, crossed by numerous dark lines called the **Fraunhofer lines**. These dark lines are produced by light from the incandescent gases in the sun passing through the sun's atmosphere, which absorbs the light emitted by the gases, thus leaving black lines wherever colored lines would have been. The

Fraunhofer lines, then, are **absorption spectra.** When, for example, sodium light is passed through the slit of the spectroscope, we get its characteristic yellow line; but if the light is passed through an atmosphere of sodium vapor before entering the slit, we see a dark line just where the yellow line was before. This is because sodium vapor absorbs the light produced by

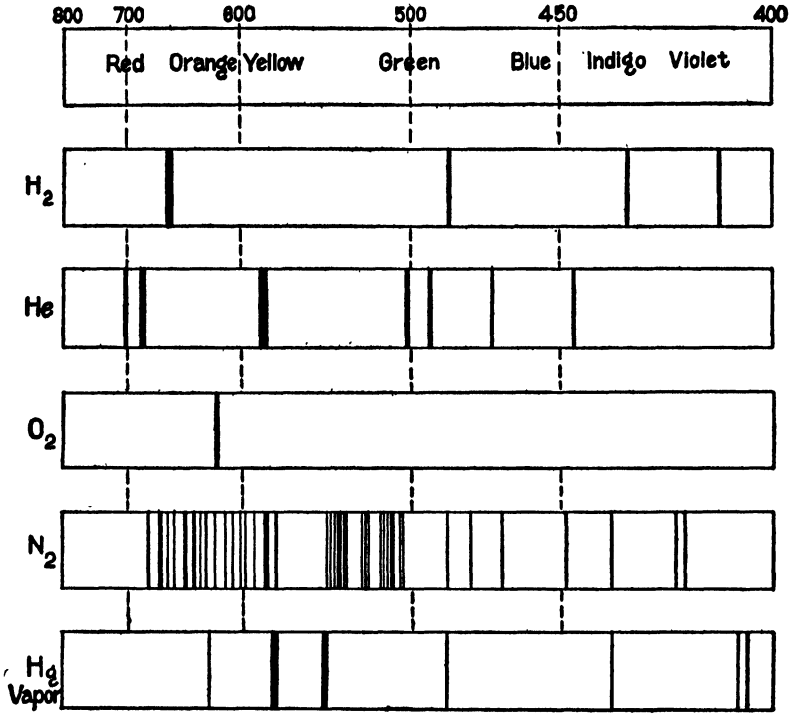


FIG. 131.

incandescent sodium vapor, and thus we have the dark line, the so-called **reversed spectrum.** Now the Fraunhofer lines are similar lines, for the sun's atmosphere contains the vapors of the very substances whose incandescent gases near the sun are sending out light. The principle established by Bunsen and Kirchhoff is that *the vapors of a substance absorb the same light which the incandescent gases of the substances emit.* Thus it has been possible to analyze the sun and other heavenly bodies that emit light of their own by means of the spectroscope. The result has been that it has been established that these bodies

contain practically the same elements that are found on the earth; though in some cases fewer and in other cases more lines have been found in the spectra of celestial bodies than correspond to known terrestrial elements.

By means of the spectroscope, a number of new elements have been discovered, among which are rubidium, cæsium, thallium, indium, gallium, helium, neon, crypton, and xenon.

Many metals whose salts cannot be vaporized in the Bunsen flame are heated in the electric arc. Spectra so obtained are called **spark spectra.** Again, gases are inspected spectroscopically by introducing them into a tube (Fig. 130), provided with platinum or aluminum electrodes, and then exhausting with a vacuum pump till the gas has a pressure of but a fraction of a millimeter. When such a tube is connected with an induction coil, the gas emits light and can thus be examined with the spectroscope in the usual way. Figure 131 gives the spectra of a few simple gases.

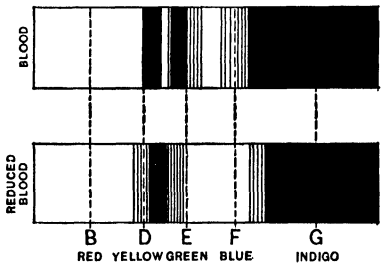


FIG. 132.

All colored solutions have their own characteristic absorption spectra. So if light from a Welsbach burner is passed through a colored solution and then through the slit of the spectroscope, it will appear that the continuous spectrum is crossed by black absorption bands characteristic of the solution. For example, blood yields the bands shown in Fig. 132, and thus it is clear that the spectroscope may be used to detect the presence of blood.

Ammonium Salts.—In their general behavior these are similar to the salts of sodium and potassium. All ammonium salts are volatile, however, when heated, decomposing into ammonia and the acid, or into other products of greater or less complexity. So when ammonium chloride NH_4Cl is heated, it dissociates into ammonia and hydrochloric acid; ammonium nitrite NH_4NO_2 similarly yields nitrogen and water; ammonium nitrate NH_4NO_3 yields nitrous oxide and water; and ammonium oxalate $(NH_4)_2C_2O_4$ decomposes into ammonia, water, carbon monoxide, and carbon dioxide. Ammonium salts may be ob-

tained by neutralizing solutions of the acids with ammonia dissolved in water and evaporating to dryness. They may frequently also be formed by direct union of ammonia with the acid in question. When treated with an hydroxide of an alkali metal, ammonium salts are decomposed, ammonia being liberated.

It has already been stated that ammonium chloride is obtained as a by-product in the manufacture of coal gas. **Ammonium chloride**, or sal ammoniac NH_4Cl, crystallizes in cubes and dissolves readily in water with absorption of heat. At 0°, 100 parts of water dissolve 28 parts of the salt, and at 100°, 73 parts. The salt has a very sharp, salty taste. Ammonium chloride is used in medicine, in making certain kinds of electric batteries, in the dyestuff industry, and, in general, as a source of ammonia. **Ammonium bromide** and **ammonium iodide** are deliquescent salts that also crystallize in cubes. They slowly decompose on exposure to the air.

Ammonium sulphate $(NH_4)_2SO_4$ is a very common ammonium salt, being generally manufactured by neutralizing the gas liquors with sulphuric acid. It crystallizes in the rhombic system, and is soluble in about 1.5 parts of cold water. The salt is used as a source of ammonia for making other compounds, and also as a fertilizer. Over 600,000 tons of this salt are manufactured annually.

On electrolysis of a concentrated solution of **ammonium bisulphate** NH_4HSO_4, **ammonium persulphate** $(NH_4)_2S_2O_8$ is produced. The latter forms monoclinic crystals that separate out from the solution. It serves as an oxidizing agent.

Ammonium sulphide $(NH_4)_2S$ is obtained by passing hydrogen sulphide into a solution of ammonia in water, till the latter is half saturated, thus: —

$$2\,NH_3 + H_2S = (NH_4)_2S.$$

On passing the hydrogen sulphide into the solution till it is completely saturated, **ammonium hydrosulphide** NH_4SH results: —

$$(NH_4)_2S + H_2S = 2\,NH_4SH.$$

The sulphide $(NH_4)_2S$ may be obtained in form of colorless needles which readily give off ammonia and thus pass over into the hydrosulphide NH_4SH, which also forms colorless crystals

that dissociate into ammonia and hydrogen sulphide even at room temperatures. At 50° this dissociation is nearly complete. Almost invariably aqueous solutions of ammonium sulphide or hydrosulphide are prepared for laboratory use as above stated. These are important in analytical chemistry. Ammonium sulphide solutions are colorless when freshly prepared. They have a disagreeable odor, due to the fact that by hydrolysis both ammonia and hydrogen sulphide are liberated. On standing in the air, the solutions turn yellow on account of oxidation. The sulphur thus liberated remains in solution, forming a yellow polysulphide. By dissolving sulphur in ammonium sulphide solutions, a series of **polysulphides** may be obtained which are analogous to the polysulphides of the alkali metals. The solutions of these polysulphides are commonly termed **yellow ammonium sulphide**. It serves in analytical chemistry for dissolving the sulphides of arsenic, antimony, tin, gold, and platinum, with which it forms ammonium sulpho-salts.

Ammonium nitrate NH_4NO_3 forms rhombic prisms that are isomorphous with potassium nitrate. It melts at about 160°, and on further heating, it decomposes into water and nitrous oxide. In water it dissolves readily with absorption of heat, and it is consequently sometimes used, mixed with ice, to produce low temperatures. The salt is also employed in explosives in place of potassium nitrate. **Ammonium nitrite** forms deliquescent crystals that readily decompose into water and nitrogen, even in aqueous solutions, on being heated to 70°.

Ammonium carbonate $(NH_4)_2CO_3 + H_2O$ is obtained in form of a crystalline precipitate by passing carbon dioxide into a concentrated solution of commercial ammonium carbonate. The latter consists of a mixture of **acid ammonium carbonate** NH_4HCO_3 and **ammonium carbamate** $NH_2 \cdot CO_2NH_4$, and is obtained by heating either ammonium sulphate or ammonium chloride with calcium carbonate. The sublimate formed is a hard white mass. The normal salt, $(NH_4)_2CO_3$, readily loses ammonia and passes over into the acid salt, NH_4HCO_3, which forms crystals that decompose into ammonia, carbon dioxide, and water at 60°. In aqueous solutions, the salt loses carbon dioxide, thus forming the normal carbonate.

Detection of Ammonium Salts. — These salts are characterized by their volatility and the fact that ammonia is evolved by

treating them with caustic alkalies. With ammonium chloride, platinic chloride forms **ammonium platinic chloride** $(NH_4)_2PtCl_6$, which, like the analogous potassium salt, is sparingly soluble. **Acid ammonium tartrate** $C_6H_5O_6 . NH_4$ is precipitated from concentrated solutions of ammonium salts by means of tartaric acid.

REVIEW QUESTIONS

1. Name the alkali metals. Why are they so called? Who discovered them? How?

2. Describe metallic potassium. Discuss the occurrence of potassium in: (*a*) sea water, (*b*) the earth's crust, (*c*) plants and animals.

3. Why is potassium hydroxide called caustic potash? Mention five other caustic alkalies, giving their formulas.

4. Explain what is meant by the term "fixed alkalies."

5. Make a list of the halides, nitrates, sulphates, sulphides, oxides, hydroxides, phosphates, and arsenates of sodium, potassium, and ammonium, giving the formula of each compound and arranging them so as to show their chemical relationships.

6. How demonstrate that a carrot contains potassium? How show that a seaweed contains sodium?

7. What is the maximum amount of potassium carbonate that could be prepared from 100 tons of carnallite? Give the chemical equations illustrating the steps in the process.

8. What use is made of each of the following compounds: potassium iodide, potassium carbonate, potassium cyanide, potassium chlorate, potassium nitrate, potassium bisulphate.

9. Characterize the compounds of rubidium and cæsium. How were these elements discovered, and by whom?

10. Where is sodium chloride found? By what processes may sodium chloride be changed into sodium carbonate? Write the appropriate equations showing the steps in these processes.

11. Discuss the uses of common salt.

12. How prepare caustic soda from common salt? Equations. How much pure caustic soda could be prepared from 250 kilograms of common salt?

13. What is saleratus? Write the equation, expressing what happens when it is used in making biscuits.

14. How may sodium silicate be made? Equation. What use is made of this compound?

15. Where does lithium occur in nature? Mention the chief characteristics of lithium compounds. What use is made of lithium carbonate and lithium citrate?

16. Why is the spectroscope of special value in detecting the alkali metals?

17. Explain fully what evidence we have that there is sodium in the sun.

18. In what respects are ammonium salts similar to those of the alkalies? In what respects are they different?

19. How detect the presence of an ammonium salt when it is mixed with salts of the alkalies?

20. In making a cream of tartar baking powder, how much baking soda is required to every five pounds of cream of tartar?

CHAPTER XXII

THE ALKALINE EARTH METALS

THE metals of the alkaline earths are calcium, strontium, and barium. They form another natural group of closely related elements. These metals never occur in the free state in nature. They are harder than the alkali metals, have higher atomic weights, and do not melt below red heat. They act on water, yielding hydroxides and hydrogen, though the action is less vigorous than in the case of the alkali metals. The hydroxides formed are alkaline and rather sparingly soluble in water, the solubility increasing as the atomic weight of the metal increases. On heating the hydroxides, they lose water, forming the oxides, which are white, earthy powders that give an alkaline reaction with moist litmus paper. This dehydration is accomplished most readily in the case of calcium hydroxide, and least readily in the case of barium hydroxide; that is, the stability of the hydroxides increases with the atomic weight of the metal.

In all their compounds calcium, strontium, and barium are bivalent. The chlorides, bromides, and iodides, $\overset{II}{M}X_2$, the nitrates, $\overset{II}{M}(NO_3)_2$, and the acetates, $\overset{II}{M}(C_2H_3O_2)_2$, are readily soluble in water; whereas the sulphates, $\overset{II}{M}SO_4$, phosphates, $\overset{II}{M}_3(PO_4)_2$, carbonates, $\overset{II}{M}CO_3$, silicates, $\overset{II}{M}SiO_3$, oxalates, $\overset{II}{M}C_2O_4$, and fluorides, $\overset{II}{M}F_2$, are sparingly soluble in water. It will be recalled that the carbonate and phosphate of lithium are also but slightly soluble, and thus lithium in a way represents a transition between the alkali metals and those of the alkaline earths. The chlorides of the alkaline earth metals are more soluble than the nitrates. The solubility of the sulphates decreases as the atomic weight increases. *The insoluble carbonates, sulphates, phosphates, and silicates are specially characteristic of this group.* They are of importance in nature, in the arts and industries, and in chemical analysis. The acid carbonates or bicarbonates are much more soluble than the carbonates.

Occurrence, Preparation, and Properties of Calcium. — This metal occurs very widely distributed and often in enormous masses as carbonate in form of marble, chalk, or limestone. It is further found as sulphate in form of gypsum and anhydrite, as phosphate, as fluoride or fluorspar, and as an essential constituent of many silicates. Nearly all natural waters contain calcium sulphate and bicarbonate. The bones and teeth of animals consist mainly of calcium phosphate together with some carbonate and small amounts of fluoride. In eggshells, coral, and the shells of molluscs and various crustaceans the carbonate of calcium predominates. Calcium salts are also found in plants. These are the sulphate, oxalate, phosphate, and carbonate, as well as salts of various complex organic acids. Similarly calcium compounds are distributed throughout the bodies of animals in small quantities.

Metallic calcium may be obtained by heating calcium iodide with sodium, or by heating an excess of calcium oxide with carbon or calcium carbide in the electric furnace. The best way to prepare the metal is by electrolysis of the molten chloride. The chloride is placed in a carbon container (Fig. 133), the walls of which serve as anode (see electrolysis). The cathode is of iron or copper. After the electrolysis has started, the heat developed by the current is sufficient to keep the salt in molten condition. The metal separates out at the cathode, and, being light, rises to the top of the molten chloride. By slowly raising the cathode as the electrolysis proceeds, a rough stick of calcium is obtained, for the metal adheres to the electrode. Metallic calcium may now be purchased at less than a dollar a pound.

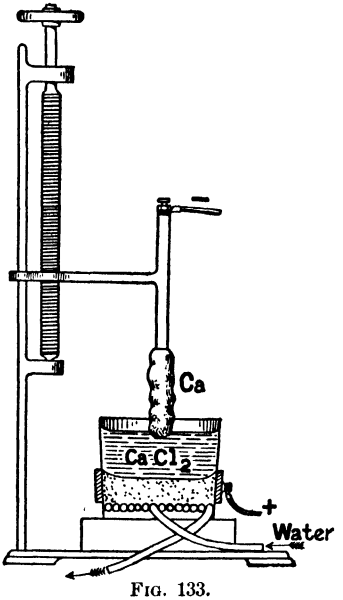


FIG. 133.

Calcium is a silver-white metal of specific gravity 1.85. It crystallizes in the hexagonal system and is fairly hard, tough, and malleable. It may readily be worked in a lathe.

It decomposes water, and consequently is kept under petroleum, or more frequently simply in air-tight containers of glass or tinned iron. Calcium melts at about 760°, and at that temperature catches fire in the air, burning to the oxide, CaO, and the **nitride**, Ca_3N_2. The latter is a yellow powder which is decomposed by water, yielding the hydroxide and ammonia. Calcium was formerly described as a yellow metal. The yellow color was due to the presence of calcium nitride as an impurity. With hydrogen, calcium readily forms **calcium hydride** CaH_2, a white powder that acts more vigorously on water than the metal itself. In general, calcium is very active chemically, for it unites with all the elements except those of the argon group.

Calcium Carbonate $CaCO_3$ is the most abundant of all the calcium compounds. In an impure form, as **limestone**, it forms mountains and strata of vast extent and great thickness. **Dolomite** is essentially a calcium, magnesium limestone of the composition $MgCO_3 \cdot CaCO_3$. It generally contains silica, iron, alumina, and other impurities. **Marl** consists of limestone mixed with clay. **Chalk** is fairly pure calcium carbonate. In a crystalline state calcium carbonate occurs as marble in many localities. In pure form it occurs as **calcite**, particularly as **Iceland spar** in Iceland. The stalactites and stalagmites found in many caves consist of calcium carbonate. Calcium carbonate crystallizes in the hexagonal system as calcite, commonly forming rhombohedra (Figs. 65 and 66) or scalenohedra (Figs. 64 and 67), and also in the orthorhombic system as **aragonite**. The hexagonal form is the stable one at ordinary temperatures; at higher temperatures the rhombic form is stabler. So from a cold solution calcium carbonate deposits in hexagonal, and from a hot solution in rhombic, crystals. Calcium carbonate is practically insoluble in water; but in water charged with carbon dioxide it dissolves fairly readily. The solution contains **calcium bicarbonate** $Ca(HCO_3)_2$, in all probability. On boiling such solutions, carbon dioxide is expelled and the normal carbonate is precipitated. Waters containing calcium salts in solution are said to be *hard*. The hardness that can be dispelled by boiling, as just mentioned, is termed temporary hardness, as compared with permanent hardness which is produced by the presence of calcium salts other than the bicarbonate, and consequently persists even on boiling.

Limestone and marble are used as building stones, in glass manufacture, in the reduction of iron ores, and in making lime, Portland cement, sodium carbonate, and many other products. Much calcium carbonate is also used as chalk and **whiting**. Mixed with linseed oil, calcium carbonate forms **putty**.

Calcium Oxide CaO, lime, is formed by heating calcium carbonate above 600°. To obtain the pure oxide, pure calcium carbonate is strongly ignited; whereas on a commercial scale, **lime** is prepared by heating limestone in limekilns (Fig. 134). **Lime** is a white, amorphous, porous solid. It may be melted in the electric furnace. Lime unites with water with evolution of heat, forming a powder, slaked lime or **calcium hydroxide** $Ca(OH)_2$. The unslaked oxide, CaO, is called **quicklime** or **caustic lime**. Calcium hydroxide is somewhat soluble in water. At 15°, 100 parts of water dissolve about 0.14 part of the hydroxide, while at 100° but half of that amount dissolves. The solution is alkaline and is known as **limewater**, when clear. When it contains excess of hydroxide in suspension, it is termed **milk of lime**. When exposed to the air, quicklime gradually absorbs moisture and carbon dioxide, and crumbles, being converted into calcium carbonate or air-slaked lime.

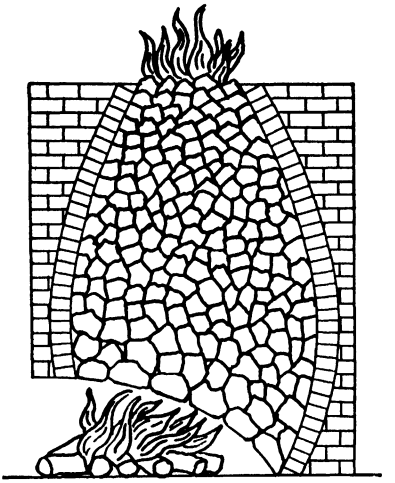


FIG. 134.

Besides being used in making mortar for building purposes, lime is generally employed in chemical industries when a cheap base is required. Large amounts are used in purifying coal gas and sugar, in removing hair from hides, in making bleaching powder, sodium and potassium hydroxides, glass, and oxalic, tartaric, and citric acids. Lime is also used as a disinfectant, and limewater is frequently employed in medicine.

Mortar consists of a pasty mass obtained by mixing sand, slaked lime, and water. After it has been applied, water dries out gradually and carbon dioxide is absorbed from the air, thus

forming hard calcium carbonate. This process is called the *setting of the mortar*. It will not take place while the mortar remains wet, and will commonly require a rather long time for its completion; for after the outer layer has become transformed to carbonate, the deeper layers are partially protected from the air and so are altered but slowly. When thoroughly hardened, the sand grains are firmly fixed in the matrix of crystalline calcium carbonate, which adheres well to the brick or stone used. Lime mortar is unfit for use in places that are always wet, for it hardens only when dry. After hundreds of years, some calcium silicate is formed by interaction of the lime with the sand grains. Lime mortar has been in common use for a very long time. It was quite generally employed by the Romans in their buildings.

Lime made from magnesian limestone, dolomite, consists of CaO and MgO. It slakes very slowly with cold water, owing to the presence of the magnesia. In cold weather, hot water is commonly employed in slaking this lime, which, however, makes very good mortar and hence is used in many localities.

Cement. — When limestone containing silicates of aluminum is heated in a kiln and the product ground to a powder, the latter forms a so-called **hydraulic cement**, for it will unite with water and form a hard, insoluble mass. The hardening process takes place uniformly, and relatively quickly throughout the mass even under water. The cement is very valuable, for it can be used in damp as well as in dry places. In some localities, as near Milwaukee and Louisville, limestone containing a suitable amount of aluminum silicates for producing cement is found and made into cement. Such cements are called **natural cements**. They generally contain notable quantities of magnesia and other ingredients. The following table gives the composition of Louisville cement in per cent: —

SiO_2	21.1	$CaSO_4$	6.8
Al_2O_3, Fe_2O_3	7.5	K_2O, Na_2O	0.8
CaO	44.4	CO_2	11.2
MgO	7.0	H_2O	1.2

Portland cement is made by artificially mixing materials containing silica, lime, and alumina in proper proportions and then

firing the mixture in a kiln. The hard mass or clinker thus obtained is ground to a fine powder and constitutes the so-called Portland cement. In practice, clay rich in silica, and calcium carbonate, are used in making this cement. Often marl or the slag from blast furnaces is employed. In all cases, it is necessary to determine the composition of the materials used by chemical analysis, so that they may be mixed in the proper proportions of silica, alumina, and lime. The following table gives the composition of Portland cement in per cent. The last column indicates the result of an analysis of a typical American Portland cement: —

COMPOSITION OF PORTLAND CEMENT IN PER CENT

SiO_2	20 to 25	22.5
CaO	58 to 65	62.9
Al_2O_3	5 to 10	6.4
MgO	traces to 5	3.1
Fe_2O_3	2 to 5	3.3
$K_2O + Na_2O$	traces to 3	——
$H_2O + CO_2$	traces to 2	0.7
SO_3	traces to 3	1.0
		99.9

No definite chemical formula can be ascribed to Portland cement, the composition of excellent cements varying within the limits indicated in the first column above. Experience has shown that the ratio of the amount of lime to that of silica plus alumina and ferric oxide should fall between 1.8 and 2.2, being about 2 on the average. That is,

$$\frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3}$$

should be greater than 1.8 and less than 2.2; for the cement whose analysis is given in the table above, the ratio is

$$\frac{62.9}{22.5 + 6.4 + 3.3} = 1.95.$$

The chemical changes involved in the making and hardening of cement have been the subject of much investigation and discussion. The clinker probably contains mainly **tricalcium**

silicate Ca_3SiO_5 and **calcium aluminate** $Ca_3Al_2O_6$. These when ground fine and then treated with water probably suffer decomposition thus: —

$$2\,Ca_3SiO_5 + 9\,H_2O = 4\,Ca(OH)_2 + (CaSiO_3)_2 \cdot 5\,H_2O, \text{ and}$$
$$Ca_3Al_2O_6 + Ca(OH)_2 + 11\,H_2O = Ca_4Al_2O_7 \cdot 12\,H_2O,$$

so that the hardened cement contains the hydrated calcium silicate $(CaSiO_3)_2 \cdot 5\,H_2O$ and the hydrated basic calcium aluminate $Ca_4Al_2O_7 \cdot 12\,H_2O$. The hardening of the cement is supposed to be due mainly to the formation of the former compound. Cement powder has a greenish gray color. Its specific gravity is 3.1 to 3.2. The hardened mass has a drab color, resembling the rock found at Portland, England, whence the name of the cement. Mixed with crushed stone and water in proper proportions, Portland cement hardens into a mass called **concrete**, which wears as well as excellent stone. Often concrete is strengthened by imbedding in it rods of iron or steel. The product is called **reënforced concrete**. Plain and reënforced concrete are much used in modern structures, and the production of cement has greatly increased in recent years. Over 90,000,000 barrels of Portland cement are made in the United States each year, and the demand for the product is still growing.

Calcium Sulphate $CaSO_4$ occurs in large quantities in nature as **gypsum** $CaSO_4 \cdot 2\,H_2O$, which forms monoclinic crystals (Fig. 73) called **selenite**, and also as **anhydrite** $CaSO_4$ in rhombic forms. **Alabaster** is a granular, crystalline form of gypsum. Calcium sulphate occurs in soils and natural waters. At 0°, 100 parts of water dissolve 0.19 part of calcium sulphate; at 35°, 0.21 part. In nitric or hydrochloric acids and in many salt solutions calcium sulphate dissolves much more copiously. At about 110°, gypsum loses water, forming $(CaSO_4)_2 \cdot H_2O$, which is a white powder known as **plaster of Paris**. When this is mixed with water, a paste may be obtained which soon hardens. This hardening or "setting" is due to the fact that water is again taken up, a crystalline, coherent mass of gypsum being formed, thus: —

$$(CaSO_4)_2 \cdot H_2O + 3\,H_2O = 2(CaSO_4 \cdot 2\,H_2O).$$

Plaster of Paris is much used for making casts, surgical bandages, and stucco.

At about 200°, gypsum loses all of its water, and is then said to be *dead burned*, for in this condition it unites with water but slowly and without hardening. Gypsum is often used as a fertilizer, **land plaster**. Its action probably depends on the fact that it reacts with the ammonium carbonate in soils, forming ammonium sulphate, which, being practically non-volatile, remains in the soil and is utilized by plants.

Calcium Sulphite $CaSO_3$ is formed by passing sulphur dioxide into calcium hydroxide. The salt crystallizes in prisms of the composition $CaSO_3 \cdot 2\,H_2O$, which are slightly soluble in water, 1 in 800. In aqueous solutions of sulphur dioxide, the salt dissolves more copiously, and such solutions are used in paper mills in preparing wood pulp.

Calcium Sulphide CaS is obtained by heating calcium sulphate with charcoal: —

$$CaSO_4 + 4\,C = CaS + 4\,CO.$$

With water the sulphide reacts thus: —

$$2\,CaS + 2\,H_2O = Ca(OH)_2 + Ca(SH)_2,$$

the latter compound being soluble in water. Calcium sulphide is used in making luminous match safes, clock faces, etc., for, after exposure to sunlight, it emits a faint light which is visible in the dark. **Barium sulphide** BaS and **strontium sulphide** SrS serve similarly for making so-called luminous paint.

Calcium Fluoride CaF_2 crystallizes in cubes, and is found in nature as fluorite. It is insoluble in water. It serves as a flux, and is used in making hydrofluoric acid and other fluorine compounds.

Calcium Chloride $CaCl_2$ occurs at Stassfurt in tachhydrite $CaCl_2 \cdot MgCl_2 \cdot 12\,H_2O$. It is obtained as a by-product in the Solvay soda process and in the production of ammonia by the action of lime on ammonium chloride. It is also made by the action of hydrochloric acid on calcium carbonate or hydroxide. From solutions it crystallizes in hexagonal prisms, $CaCl_2 \cdot 6\,H_2O$. These melt in their crystal water at 29°, and become a porous, anhydrous mass at 200°. The anhydrous salt melts at 719°. It is deliquescent, and is much used as a drying agent in chemical laboratories. With ice and the hydrate, $CaCl_2 \cdot 6\,H_2O$, temperatures as low as $-50°$ may be produced.

The anhydrous salt dissolves in water with liberation of heat. With alcohol, and also with ammonia, calcium chloride forms addition products, so that these substances must be dried with other agents like the oxide of calcium or barium. **Calcium bromide** $CaBr_2$ and **calcium iodide** CaI_2 are even more deliquescent than calcium chloride.

Bleaching Powder or **chloride of lime** is made in large quantities by passing chlorine into calcium hydroxide, *i.e.* slaked lime. The composition of the compound is expressed by the formula Ca(OCl)Cl, as explained under chlorine, where the reactions involved in its preparation and use are also described. Bleaching powder is slightly yellowish in color. It absorbs carbon dioxide and moisture from the air. Thus hypochlorous acid is formed, to which the odor of bleaching powder is due. Enormous quantities of bleach, as it is also called, are used in paper making and in the manufacture of cotton and linen goods.

Calcium Phosphate $Ca_3(PO_4)_2$ is found in nature as already stated, in apatite, and in the bones of animals. By treating a solution of calcium chloride with sodium ammonium phosphate, calcium phosphate is precipitated, thus : —

$$2\,Na_2NH_4PO_4 + 3\,CaCl_2 = 4\,NaCl + 2\,NH_4Cl + Ca_3(PO_4)_2.$$

Calcium phosphate is practically insoluble in water, but in acids it dissolves readily, also in many solutions of salts, like chlorides or nitrates of the alkalies. As the latter are present in soils, calcium phosphate is dissolved by their solutions and hence made available to plants. *Calcium phosphate is necessary to plant life, and also to the life of animals, into whose bones it enters as a prime constituent.* So-called **superphosphate of lime,** a fertilizer of great value, consists of calcium sulphate and primary calcium phosphate produced by the action of sulphuric acid on calcium phosphate, thus : —

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = CaH_4(PO_4)_2 + 2\,CaSO_4.$$

The primary calcium phosphate $CaH_4(PO_4)_2$ is soluble in water and hence is readily available to plants.

Each year the United States produces about 3,000,000 tons of **phosphate rock,** most of which is used as fertilizer. The most important beds of this rock are in South Carolina and Florida. As this material is of prime importance in maintaining the fer-

tility of the soil, its exportation has recently been forbidden by law.

Calcium Carbide CaC_2 is made by heating lime or calcium carbonate with carbon in the electric furnace, thus: —

$$CaO + 3\,C = CaC_2 + CO.$$

Pure calcium carbide is white, but the commercial article is dark in color, owing to the presence of impurities. The substance yields acetylene when treated with water, as already stated, and hence large quantities of it are manufactured annually.

Calcium Phosphide Ca_2P_2 is formed by heating lime and phosphorus together, thus: —

$$14\,CaO + 14\,P = 2\,Ca_2P_2O_7 + 5\,Ca_2P_2.$$

The product is a brown solid, which on treatment with water yields calcium hydroxide and phosphine.

Calcium Cyanamide $CaN \cdot CN$ is formed by passing nitrogen over calcium carbide heated to white heat in an electric furnace, thus: —

$$CaC_2 + N_2 = CaN \cdot CN + C.$$

Calcium cyanamide is used as a fertilizer, for in the soil its nitrogen gradually is converted into ammonia and nitrates, owing to the action of water and oxygen from the air.

Calcium Silicide $CaSi_2$ is produced by heating lime with silicon in the electric furnace. It forms hexagonal crystals that react but slowly with water. Dilute acids decompose the silicide readily.

Calcium Silicate $CaSiO_3$ is occasionally found in nature in monoclinic crystals as wollastonite. It occurs very frequently in complex silicates like mica, feldspar, garnet, hornblende, and many others. Calcium silicate may be formed by heating together silica and lime or calcium carbonate, also by adding sodium silicate to a solution of a calcium salt, thus: —

$$CaCl_2 + Na_2SiO_3 = CaSiO_3 + 2\,NaCl.$$

Calcium silicate is practically insoluble in water; but in hydrochloric acid it dissolves, being decomposed into calcium chloride and silicic acid.

Glass is a mixture of the silicates of sodium and calcium. Sodium silicate is transparent and soluble in water, while

calcium silicate is neither transparent nor soluble in water. When sodium silicate is fused together with calcium silicate in proper proportion, a liquid results which on cooling forms ordinary glass. This is practically insoluble in both water and acids, except hydrofluoric acid. **Ordinary glass** varies somewhat in composition. It is a mixture of silicates of sodium and calcium which approximates the composition $Na_2O \cdot 3\,SiO_2 + CaO \cdot 3\,SiO_2$. This **soda-lime glass,** as it is also called, is used for windows and various ordinary vessels. It melts readily and is consequently relatively easy to work into desired forms. In making glass, finely ground and intimately mixed quartz sand SiO_2, calcium carbonate $CaCO_3$, and soda Na_2CO_3 are melted together in large pots of special fire clay. These pots are about 4 feet high and 4 feet in diameter; Fig. 135 shows an open and a closed form. During this process carbon dioxide escapes. The temperature is raised after the mass has melted, to expel all gases. The scum and various impurities that have gathered on top of the molten material are removed mechanically. In making **plate glass,** the molten, viscous material is poured upon large iron or bronze plates and rolled to the desired thickness with hot iron rollers. The plates are afterwards ground and polished. For ordinary **window glass,** the glass is first blown into cylindrical forms which are cut open lengthwise and then flattened out. Heavy glass dishes and many other similar articles are made by pressing the plastic glass into suitable molds. Bottles are made by taking glass on the end of an iron pipe and blowing it into molds. All flasks, retorts, beakers, and many other thin glass dishes are blown into suitable molds. Glass tubing is made by blowing a small bulb on the end of an iron blowpipe, and then attaching the bulb at its lower end and drawing the plastic mass out into the form of a tube. *All glass articles must be annealed.* This

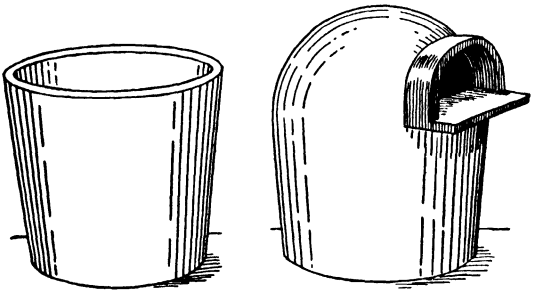


FIG. 135.

process consists of cooling the glass gradually in suitable furnaces. Glass suddenly cooled is under internal strain, and a slight scratch will cause it to break; thus the "Prince Rupert's drop" of suddenly chilled glass is shattered by nipping off its tail. The strength and transparency of glass depends upon its amorphous nature, for when glass crystallizes it becomes opaque and brittle. Since the composition of glass may be varied to a considerable extent at will, it is of the nature of a solution; and indeed it is sometimes called a solid solution, resulting from the supercooling of the liquid mass. Since sodium silicate is soluble in water, and calcium silicate is readily decomposed by hydrochloric acid, and on the other hand glass is practically not attacked by water or hydrochloric acid, it is clear that in glass the silicates of sodium and calcium are chemically combined with each other, in spite of the fact that their relative proportions may gradually be varied to some extent.

Soda-lime glass is unsuitable for laboratory utensils, for it is too easily attacked by chemical reagents, especially by alkalies. For this reason **potash-lime glass**, in the manufacture of which potassium carbonate is used instead of sodium carbonate, is commonly employed in making finer glassware, for it is much harder and less readily acted upon by reagents. This potash glass is also called **Bohemian glass** or **hard glass**; it has a much higher melting point than ordinary soda glass, which is frequently called **soft glass**. **Crown glass** is a potash-lime glass. **Flint glass** is produced by melting together silica, potash, and lead oxide. It has a high specific gravity and also a high index of refraction, hence it is used in making lenses, prisms, and other optical instruments as well as ornaments. **Cut glass** is made by grinding and polishing flint glass. **Jena glass**, which is now much used for utensils, contains boric anhydride. **Colored glass** is made by adding small quantities of various metallic oxides to molten glass. In this way colored silicates are formed. Thus cobalt oxide colors glass blue; chromic oxide produces a bright green shade; manganese dioxide yields a violet color; cuprous oxide or gold produces a red shade owing to the very finely suspended particles of these substances in the glass. The ordinary green bottle glass is colored by ferrous oxide, while the brown or brownish yellow glass is colored by ferric oxide. Window glass also contains small amounts of

iron, which produces the green color observed when viewing the glass on edge. Black or very dark glass is produced by large amounts of cobalt, iron, and other oxides. **Bottle glass** is commonly made from impure, cheap materials that contain relatively large amounts of iron and other oxides that color the glass. **Enamel glass** is a lead glass to which oxide of tin has been added, while **milk glass** contains calcium phosphate in suspension, which produces the characteristic white, opaque appearance.

The following table gives the approximate percentage composition of a few typical kinds of glass.

	SiO_2	Na_2O	K_2O	CaO	PbO
Quartz glass	100	—	—	—	—
Common glass . . .	75.5	12.9	—	11.6	—
Bohemian or crown glass	70.8	—	18.3	10.9	—
Crystal or flint glass .	53.5	—	13.8	—	32.7

The art of making glass is very old. It is supposed to have originated with the Phœnicians. The Egyptians practiced it long before the Christian era. From the thirteenth to the seventeenth century Venice was noted for its glass manufactures. The general introduction of the use of window glass dates from about the sixteenth century. Bohemian glass was placed in the market as early as the fifteenth century, though glass was manufactured in Germany and Bohemia even in the tenth century.

Occurrence, Preparation, and Properties of Strontium. — Strontium occurs in nature as **celestite** $SrSO_4$ and **strontianite** $SrCO_3$. It is of much rarer occurrence than either calcium or barium. The metal, which has properties similar to those of calcium, may be obtained by electrolysis of the molten chloride, $SrCl_2$. Metallic strontium acts on water, liberating hydrogen and forming strontium hydroxide. In the air, strontium is slowly oxidized. The metal is silver white and plastic like lead. It melts at about 800° and volatilizes readily at 950°.

Strontium Compounds. — These are in general very similar to the compounds of calcium. They are prepared by treating the carbonate with acids. The native sulphate serves as the

chief source of strontium salts. It is first reduced to sulphide by heating with charcoal and then treated with acids. Strontium salts impart a brilliant red color to the Bunsen flame. The spectrum contains a blue line, an orange line, and six bright lines in the red. **Strontium carbonate** is not as readily decomposed into **strontium oxide** SrO and carbon dioxide as calcium carbonate. With water, the oxide readily forms **strontium hydroxide** $Sr(OH)_2$, which is more soluble than calcium hydroxide. With sugar, strontium hydroxide forms insoluble compounds, hence it is used in extracting sugar from molasses that will no longer yield crystals of sugar. **Strontium dioxide** SrO_2 is also known.

Strontium chloride $SrCl_2$ is hygroscopic, but it does not possess this property to as marked a degree as calcium chloride. The salt is isomorphous with calcium chloride, forming hexagonal prisms of the composition $SrCl_2 + 6\,H_2O$.

Strontium sulphate $SrSO_4$ is precipitated from solutions of strontium salts by adding a solution of a soluble sulphate. It dissolves in about 7000 parts of water. In alcoholic solutions it is much less soluble. On boiling strontium sulphate with sodium or potassium carbonate, the salt is transformed into the carbonate: —

$$SrSO_4 + Na_2CO_3 = Na_2SO_4 + SrCO_3.$$

Under like treatment, barium carbonate remains practically unchanged.

Strontium nitrate $Sr(NO_3)_2$ forms octahedra or cubes when crystallized from concentrated solutions. At low temperatures the hydrate, $Sr(NO_3)_2 \cdot 4\,H_2O$, separates from solutions in monoclinic crystals. These effloresce on exposure to the air. Though readily soluble in water, strontium nitrate is insoluble in alcohol. When heated, the nitrate is decomposed, yielding the oxide. *Strontium nitrate is much used in fireworks and red Bengal lights.* The latter usually consist of a mixture of about 50 parts strontium nitrate, 30 parts shellac, and 20 parts potassium chlorate.

Besides being used in the sugar industry, strontium salts are sometimes prescribed in medicine.

Occurrence, Preparation, and Properties of Barium. — Barium occurs as **witherite**, the native carbonate, $BaCO_3$, and as barite, or **heavy spar**, the native sulphate, $BaSO_4$. These serve as sources for the preparation of barium compounds. Metallic

barium may be obtained as a silver-white metal by electrolysis of the molten chloride. In general, its properties are like those of strontium and calcium. Barium has a specific gravity of 3.78. It melts at about 850° and boils at 1150°.

Compounds of Barium. — These are analogous to those of calcium and strontium. *They are, however, poisonous in character.* **Barium oxide** BaO is best prepared by heating the nitrate, for the carbonate requires even a higher temperature to decompose it than strontium carbonate. On treating the oxide with water, **barium hydroxide** $Ba(OH)_2$ is formed, which is more soluble than calcium hydroxide. The solutions of barium hydroxide are alkaline and yield a precipitate of barium carbonate $BaCO_3$ on treatment with carbon dioxide. Barium hydroxide is frequently used in place of limewater in testing for carbon dioxide.

On heating barium oxide in the air or in oxygen, **barium dioxide** BaO_2 is formed. This interesting substance, discovered by Thénard and Gay-Lussac, is a grayish white powder which is insoluble in water. When barium dioxide is heated to high temperatures, it is converted into barium oxide and oxygen. This affords a method of preparing oxygen from the air, as already mentioned. Barium dioxide is used in preparing hydrogen peroxide. By treating a solution of barium hydroxide with hydrogen peroxide a precipitate of the composition $BaO_2 \cdot 8\ H_2O$ is obtained which loses water at 130°, and yields barium dioxide.

Barium chloride $BaCl_2 \cdot 2\ H_2O$, prepared by treating either the carbonate or the sulphide with hydrochloric acid, forms rhombic prisms soluble in about 3 parts of water. The salt is not deliquescent. It is practically insoluble in alcohol. This salt is then less soluble than the chloride of strontium, and the latter is less soluble than calcium chloride. Barium chloride has a bitter taste, and is a fairly strong *poison.*

Barium fluoride BaF_2 is practically insoluble in water, but readily soluble in acids. **Barium bromide** $BaBr_2$ and **barium iodide** BaI_2 are soluble in water, and also in alcohol.

Barium nitrate $Ba(NO_3)_2$ forms anhydrous crystals of the regular system. It is soluble in about 12 parts of water, and hence is precipitated by adding sodium nitrate to a concentrated solution of barium chloride. It may also be obtained by the

action of nitric acid on the carbonate, hydroxide, or sulphide. On heating, it decomposes, yielding the oxide, oxygen, and oxides of nitrogen. Barium nitrate is used in making green Bengal lights.

Barium carbonate $BaCO_3$ occurs in rhombic crystals as witherite, and is prepared commercially by heating the natural sulphate or barium sulphide with sodium carbonate. The product consequently is contaminated with sodium carbonate, which it is practically impossible to remove by washing. Pure barium carbonate may be obtained by adding ammonium carbonate to a solution of barium chloride. It requires white heat (1500° C.) to decompose barium carbonate, but by heating it with carbon it may readily be reduced to barium oxide.

Barium sulphate $BaSO_4$ is the chief source of barium. In nature it is found in compact masses or rhombic crystals of specific gravity 4.48. Barium sulphate is almost completely insoluble in water and dilute acids. Though alkaline carbonates in aqueous solution affect barium sulphate but slightly, the latter may readily be transformed to carbonate by fusion with sodium carbonate, thus: —

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$

Barium sulphate is easily prepared by treating a solution of a barium salt with any soluble sulphate. The precipitate is usually composed of very small crystals. These grow larger on standing and can then be filtered off readily. In analytical operations, *the fact that barium sulphate is insoluble and readily prepared is much used in testing for barium and also for sulphates.* Barium sulphate is often used as a white pigment, known as **permanent white.**

On heating barium sulphate with carbon, **barium sulphide** BaS is produced, which, like the sulphides of calcium and strontium, phosphoresces in the dark. This fact was discovered in 1603 by Casciorolo, a shoemaker of Bologna, who, in an attempt to make silver, had heated native barium sulphate with carbon, thus forming the sulphide of barium. In 1774 Scheele investigated barium sulphate and showed that it contains an earth quite different from lime. Barium carbonate was then soon prepared artificially, and its probable occurrence in nature was foretold, when indeed in 1783 native barium carbonate was

discovered in Scotland by Withering, after whom the mineral is called witherite. Barium receives its name from the Greek word meaning heavy. It was reported that native barium carbonate also occurred at Strontium in Scotland. Investigations by Crawford in 1790 showed, however, that this mineral was still another carbonate. Thus strontium was discovered. It derives its name from the locality where the native carbonate, strontianite, was found.

Detection of the Alkaline Earth Metals. — These may readily be detected by means of the spectroscope, as already stated. In addition the following facts are frequently used in detecting calcium, strontium, and barium.

By adding a calcium sulphate solution to a solution of a barium or strontium salt an insoluble sulphate is precipitated; but by similar treatment solutions of calcium salts remain clear. Strontium sulphate solution precipitates barium sulphate from solutions of barium salts. Ammonium oxalate precipitates the oxalates of barium, strontium, and calcium from solutions of their salts. The oxalates of barium and strontium are soluble in dilute acetic acid, while the oxalate of calcium is not. Calcium nitrate is soluble in alcohol, while strontium and barium nitrates are not. Barium chromate $BaCrO_4$ is insoluble in water, while calcium chromate is soluble. The sulphates of calcium and strontium are converted into carbonates by boiling with sodium carbonate solution, while barium sulphate is not changed by this treatment.

Radium and Radio-activity. — In 1896 Becquerel discovered that photographic plates, carefully protected from light by means of dark coverings, are nevertheless affected as though they had actually been exposed to light, when kept near uranium or its compounds. Furthermore, it was found that a well-insulated, charged electroscope would soon become discharged in the neighborhood of uranium or its compounds, showing that by the latter the air had been rendered a conductor of electricity. It was consequently concluded that these phenomena are due to peculiar rays emitted from uranium. These rays were called **uranium rays** or **Becquerel rays**, and the substances from which they issued were called **radio-active**. The mineral pitchblende, uraninite, consisting essentially of a black oxide of uranium U_3O_8, together with various impurities in minor quan-

tities, shows this radio-activity in a high degree; and M. and Mme. Curie found that the residues of this mineral after removal of the uranium were still very radio-active. This led them to further investigations, and in 1898 they announced that they had discovered in these residues a new element, **radium**, to which the radio-active phenomena are due. In pitchblende radium is found together with relatively very much larger quantities of barium, so that a ton of residues yielded about thirty pounds of barium chloride, from which by very many repeated fractional crystallizations a few tenths of a gram of radium chloride were finally obtained. This compound was over a million times as radio-active as pitchblende.

Radium chloride or bromide is less soluble than the corresponding barium salt, hence the possibility of effecting a tolerable separation from the latter by fractional crystallization. Radium compounds exhibit a spectrum similar to that of the alkaline earths. The metal radium itself has not yet been isolated.

The analysis of the chloride has shown that 35.46 grams of chlorine are combined with 113.2 grams of radium, hence, regarding radium as bivalent like the alkaline earth metals, to which it appears to be analogous, the atomic weight is 226.4. The symbol of radium is Ra. On account of the scarcity of the element, but few of its compounds have been studied. The **chloride** $RaCl_2$, the **bromide** $RaBr_2$, the **nitrate** $Ra(NO_3)_2$, the **carbonate** $RaCO_3$, and the **hydroxide** $Ra(OH)_2$ have been prepared. All of the compounds show radio-activity. *In the dark they are luminous.* They also emit heat continually. It has been estimated that a gram of radium in its compounds gives off heat at the rate of approximately 100 calories per hour. As the rays from radium compounds impinge upon a screen of barium platinocyanide or zinc sulphide, they cause these to phosphoresce; furthermore, radio-activity may be communicated from radium compounds to substances placed near them. So the walls of containers of radio-active substances acquire this property, and solids kept in contact with radium salts also become active. The rays emitted from radio-active substances are able to kill germs, destroy the germinating power of seeds, and act destructively on living tissues, so that experimentation with the purer and consequently more powerful radium compounds must be conducted with great care. Glass con-

tainers of radium salts slowly turn violet in color, while cloth is gradually disintegrated by the action of the rays.

The rays emitted from compounds of radium are complex in character. This is shown by the fact that a portion of them (the α rays) is readily absorbed by metals, the air, etc., and is deflected with great difficulty by a magnetic field. Another portion (the β rays) is readily deflected by a magnet, and is particularly active on photographic plates; while a third portion (the γ rays) is not deflected by a magnet and has great penetrating power, passing even through a thickness of 30 cm. of iron. The study of these rays has largely been conducted by testing their ability to affect photographic plates and to discharge an electroscope.

Radium compounds emit an **emanation** which may be condensed at about $-150°$, by the aid of liquid air. This emanation is therefore of the nature of a gas. Indeed, it may be passed from one tube to another like air. When examined in a vacuum tube by means of the spectroscope, *the emanation from radium compounds after a time shows the spectrum of helium.* For this reason it has been concluded that radium is slowly changing to helium. Furthermore, since radium compounds gradually lose their activity, and since uranium compounds gradually again acquire the ability of giving off emanations after having been deprived of the same, the assumption has been made that uranium is gradually changing into radium and that the latter is "decaying" into emanations, which in turn are transformed into helium. Thus, the study of radio-active phenomena has opened up the question of the possibility of the transmutation of the chemical elements.

Thorium compounds also exhibit radio-activity and give off emanations. A particularly active constituent, known as **thorium** *X*, has been separated by chemical means from thorium, while a similar product, **uranium** *X*, has been obtained from uranium, and another, **actinium** *X*, from actinium. **Actinium** is a radio-active substance found in uranite by Debierne. It acts like thorium, but more intensely. The elementary character of actinium and of **polonium**, which has also been found in pitchblende by Mme. Curie, still awaits confirmation.

REVIEW QUESTIONS

1. Why are calcium, strontium, and barium called the alkaline earth metals? Make a list of the formulas of their oxides, hydroxides, carbonates, sulphates, nitrates, phosphates, silicates, borates, oxalates. Indicate which of these compounds are soluble in water, and which are not soluble.

2. Compare the alkali metals with the alkaline earth metals in their physical properties and their chemical action on water.

3. Make a list of the forms in which calcium carbonate is found in nature, and state the use of each.

4. How is lime made from limestone? Equation. Write an equation expressing what happens when mortar sets. What is the function of hair or wood fiber in mortar used for plastering walls?

5. Besides its use for building purposes, what other uses are made of lime?

6. What are the chief ingredients in Portland cement? In what proportions should these be present?

7. In what respects does the setting of Portland cement differ from the setting of mortar? From the setting of plaster of Paris? How is plaster of Paris made?

8. How prepare calcium sulphite? What use is made of it?

9. How much calcium chloride could be made from 12 pounds of pure chalk? Describe the properties of calcium chloride and compare it with the chlorides of strontium and barium.

10. What is superphosphate of lime fertilizer? Write the equation showing how it is formed from phosphate rock.

11. How is calcium carbide made? Write the reaction showing how acetylene is made from calcium carbide. How many liters of acetylene measured under standard conditions could be produced from one kilogram of calcium carbide?

12. Name four different kinds of glass, stating their similarities and differences in chemical composition.

13. How do strontium and barium occur in nature, and what use is made of their compounds?

14. Given a solution which contains the chlorides of calcium, barium, and strontium, describe two distinctly different methods of demonstrating the presence of each of these three metals in the solution. Write equations.

15. Write chemical equations expressing the action of a barium chloride solution upon the solution of (a) copper sulphate, (b) ammonium oxalate, (c) sodium phosphate.

16. How much pure gypsum would be required to produce one thousand pounds of plaster of Paris?

17. How is the element radium related to the alkaline earth metals? Where does radium occur? What are some of its striking properties? What is meant by the term "radium emanation"?

*

CHAPTER XXIII

THE METALS OF THE MAGNESIUM GROUP

THE metals of this group are glucinum, magnesium, zinc, cadmium, and mercury. Of these, magnesium closely resembles the alkaline earth metals. Zinc, cadmium, and mercury, on the other hand, have a much higher specific gravity, and are much less readily oxidized; their affinity for oxygen diminishes in the order named. Glucinum, unlike the other members of this group, has a high melting and boiling point. It really is a transition element between the magnesium group and the metals of the earths.

Glucinum, or Beryllium, Gl, or Be, At. Wt. 9.1, is found in nature as a constituent of the rather rare minerals **beryl** $Gl_3Al_2Si_6O_{18}$, phenacite Gl_2SiO_4, and chrysoberyl $Gl(AlO_2)_2$. When colored green by traces of chromium silicate, beryl is called **emerald**, which is used as a gem. Glucinum is a white, malleable metal having a specific gravity 1.8. It does not liberate hydrogen from water even on boiling. It dissolves in hydrochloric or sulphuric acid, while nitric acid attacks it but slightly. In caustic potash, glucinum dissolves readily, liberating hydrogen. The metal is obtained by electrolysis of molten chrysoberyl, or by heating the oxide with magnesium powder. In its compounds, glucinum is always bivalent. The compounds have a sweetish taste, whence the name glucinum (sweet); the element is also called beryllium from beryl, in which it occurs.

Glucinum oxide GlO was discovered in 1797 by Vauquelin. It is basic, but also possesses very weak acidic properties, forming soluble salts with caustic alkalies. From solutions of glucinum salts, ammonium hydroxide precipitates **glucinum hydroxide** $Gl(OH)_2$.

Among the well-known salts are **glucinum sulphate** $GlSO_4$, **glucinum chloride** $GlCl_2$, and **glucinum carbonate** $GlCO_3$. Basic salts, notably basic nitrates and sulphates, are also known.

Occurrence, Preparation, and Properties of Magnesium. — Magnesium is very widely distributed. It occurs in large quanti-

ties in dolomite $MgCO_3 \cdot CaCO_3$, which often forms mountains. It is also found in carnallite $MgCl_2 \cdot KCl \cdot 6\,H_2O$, in kieserite $MgSO_4 \cdot H_2O$, in schönite $MgSO_4 \cdot K_2SO_4 \cdot 6\,H_2O$, in kainite $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6\,H_2O$, in magnesite $MgCO_3$, in soapstone or talc $Mg_3H_2Si_4O_{12}$, in meerschaum $Mg_2Si_3O_8 \cdot 4\,H_2O$, in serpentine $Mg_3Si_2O_7 \cdot 2\,H_2O$, in hornblende $Mg_2CaFeSi_4O_{12}$, in asbestus $Mg_3Si_2O_7 \cdot 2\,H_2O$, and in many other complex silicates. Sea water contains magnesium chloride and sulphate. These salts also occur in many spring waters, which are called bitter waters. Magnesium salts are found in soils, being decomposition products of rocks. Plants and animals contain magnesium, which appears in their ash as carbonate and phosphate. Guano contains magnesium ammonium phosphate.

Metallic magnesium is prepared by electrolyzing molten carnallite in an iron pot, which also serves as cathode, a carbon anode being employed. The metal is silver-white, and when hot it may be drawn into ribbon or wire. At ordinary temperatures magnesium is but slightly malleable. Exposed to air, it gradually becomes covered with a thin, white layer of oxide. It melts at 633° and boils at 1100.° Its specific gravity is 1.75. It may be sublimed in a vacuum, yielding hexagonal, prismatic crystals. In an atmosphere of hydrogen the metal may be distilled. It acts but very slightly on pure water even at 100°; but when heated in a current of steam, it takes fire. Dilute acids act vigorously on magnesium. In the air, the metal burns with a brilliant white light, yielding the oxide MgO, together with some **nitride** Mg_3N_2. Magnesium light has a powerful effect upon photographic plates and is consequently used in flash lights. **Flash light powder** consists of about 5 parts of powdered magnesium to 9 parts of potassium chlorate. Magnesium is also used in fireworks, for signal lights, and as a reducing agent in chemical operations.

The metal was first obtained in pure form by Liebig and Bussy in 1830. Bunsen prepared it by electrolysis twenty-two years later. The atomic weight of magnesium is 24.32, and its valence is two.

Magnesium Oxide MgO is a white powder, usually prepared by heating the carbonate. It is also called **magnesia, magnesia usta,** or **calcined magnesia.** In contact with water it does not dissolve, but it forms **magnesium hydroxide** $Mg(OH)_2$, which is

very sparingly soluble. Magnesium oxide is used in medicine. It is even more difficult to melt magnesia than lime, consequently magnesia is used in making fire brick and in the construction of the electric furnace. Magnesium oxide does not have acidic properties.

Magnesium Carbonate $MgCO_3$ occurs in nature as **magnesite** in hexagonal crystals that are isomorphous with calcite. On adding a solution of an alkaline carbonate to a solution of a magnesium salt, **basic magnesium carbonate** is precipitated, the composition of which varies according to the temperature and concentration of the solutions used. The ordinary magnesium carbonate of commerce, called **magnesia alba**, is prepared by precipitation. Its composition is approximately $(MgCO_3)_3 \cdot Mg(OH)_2 \cdot 3\,H_2O$. Though insoluble in water, magnesium carbonate, like calcium carbonate, dissolves in water charged with carbon dioxide. From such solutions crystals of the composition $MgCO_3 \cdot 3\,H_2O$ (and at low temperatures $MgCO_3 \cdot 5\,H_2O$) have been obtained. Magnesium carbonate is used in medicine, also as a cosmetic.

Magnesium Chloride $MgCl_2 \cdot 6\,H_2O$ forms highly hygroscopic, monoclinic crystals. On heating these they completely decompose, thus: —

$$MgCl_2 \cdot 6\,H_2O = MgO + 2\,HCl + 5\,H_2O.$$

The anhydrous salt $MgCl_2$ may be obtained by heating **magnesium ammonium chloride** $MgCl_2 \cdot NH_4Cl \cdot 6\,H_2O$. Figure 136

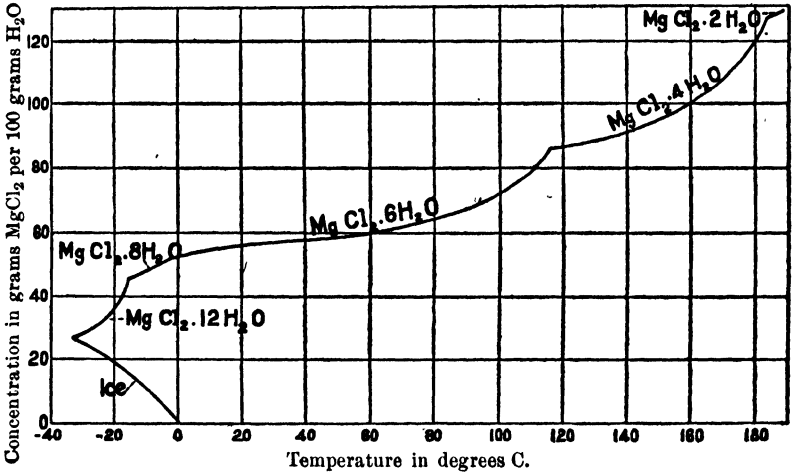


FIG. 136.

presents the solubility curve of magnesium chloride. It will be seen from the figure that five different hydrates are known.

Magnesium Sulphate $MgSO_4 \cdot 7\,H_2O$, also known as **Epsom salt** and **bitter salt**, forms large rhombic prisms that dissolve in about four parts of water. The solution has a disagreeable bitter taste. The salt is found in the waters of Epsom springs and many other mineral springs. It is used as a purgative, and is also employed in "loading" cotton goods and in making the sulphates of potassium and sodium. Occasionally it serves as a fertilizer.

Magnesium Phosphates are in general similar to those of calcium. **Magnesium ammonium phosphate** $MgNH_4PO_4$ is important in analytical chemistry. The salt forms rhombic crystals that are insoluble in ammonia water. On ignition they yield **magnesium pyrophosphate** $Mg_2P_2O_7$.

Magnesium Ammonium Arsenate $MgNH_4AsO_4$ is analogous to magnesium ammonium phosphate. On ignition it yields **magnesium pyroarsenate** $Mg_2As_2O_7$.

Tests for Magnesium. — In testing for magnesium compounds, the following facts are of importance: —

Basic carbonate of magnesium is precipitated by carbonates of the alkalies. Hydroxides of the alkalies precipitate magnesium hydroxide; but ammonium hydroxide does not precipitate magnesium hydroxide in presence of ammonium chloride, for the solutions of the latter dissolve magnesium hydroxide. In presence of ammonium chloride, clear ammoniacal solutions of magnesium salts are precipitated by sodium phosphate, magnesium ammonium phosphate being formed.

Occurrence, Preparation, and Properties of Zinc. — Zinc occurs in nature mainly as the carbonate, $ZnCO_3$, in the mineral called smithsonite, calamine or zinc spar, and as the sulphide, ZnS, in zinc blende or black-jack. Other ores of zinc are franklinite $Zn(FeO_2)_2$, gahnite $Zn(AlO_2)_2$, also called zinc spinel, and red zinc ore ZnO. Most of the ores of zinc also contain some cadmium.

In making metallic zinc, the ores are first roasted. Thus carbonates and sulphides are finally all transformed to zinc oxide. The latter is then reduced by heating it with carbon. The reactions involved are: —

$$ZnCO_3 = ZnO + CO_2.$$
$$ZnS + 3\,O = ZnO + SO_2.$$
$$ZnO + C = Zn + CO.$$

The operation of reducing the zinc oxide is conducted in earthenware retorts. At the bright red heat developed, 1200° to 1300°, zinc is converted into vapor, which is condensed in iron receivers connected with the retorts. **Zinc dust**, consisting of finely divided zinc plus 5 to 10 per cent of zinc oxide, is at first obtained on the sides of the condenser; later, the metal condenses to a liquid and is run into molds. This crude zinc, called **spelter**, is contaminated with carbon, iron, arsenic, lead, and cadmium. It is purified by redistillation. Chemically pure zinc is made by heating pure, precipitated zinc carbonate with pure carbon, or still better by the electrolysis of pure zinc salts.

Zinc crystallizes in the hexagonal system. It is bluish white, and has a bright metallic luster. Cast zinc has a specific gravity of 6.9; but hammered zinc, or zinc wire, is denser, having a specific gravity of 7.2. Zinc is rather brittle, but at 120° it becomes malleable and ductile. When heated to 200°, it becomes so brittle that it may be pulverized. Zinc melts at 420° and boils at 918°. Its atomic weight is 65.37 and its molecular weight is the same, for the vapor is 33.93 times as heavy as hydrogen. Zinc is always bivalent. On exposure to moist air, the luster of zinc is dimmed by the formation of a thin coating of white basic carbonate. At high temperatures, zinc burns in the air with a brilliant, bluish white flame. On water zinc does not act, but when steam is passed over heated zinc, the oxide and hydrogen are formed. Nearly all dilute acids act on zinc; the purer the zinc, the less rapid is the action. In general, hydrogen is liberated when zinc acts on acids, though in some cases, like that of nitric acid for instance, the hydrogen is not set free, for it at once reduces some of the acid present. On heating zinc with concentrated sulphuric acid, sulphur dioxide and zinc sulphate are formed: —

$$Zn + 2\,H_2SO_4 = ZnSO_4 + SO_2 + 2\,H_2O.$$

In hot caustic alkalies, zinc dissolves, as already stated, forming a zincate and hydrogen: —

$$Zn + 2\,NaOH = Na_2ZnO_2 + H_2.$$

When introduced into solutions of many of the salts of either lead, tin, copper, mercury, silver, platinum, or gold, zinc precipitates these metals, usually as finely divided powders, thus: —

$$CuSO_4 + Zn = ZnSO_4 + Cu.$$

Zinc is used in sheet form for many purposes, such as making roofs, gutters, and architectural ornaments. **Galvanized iron,** so-called, consists of sheet iron which has been coated with zinc by dipping the thoroughly clean sheets of iron into highly heated molten zinc. The zinc coating prevents the iron from rusting. Much zinc is also used in making electrical batteries (which see), and in preparing many alloys, especially brass.

Brass, which is an alloy of zinc and copper, was known long before zinc, for it was obtained by melting native copper ores that contained zinc. On the European continent zinc production on a commercial scale began about one hundred years ago; though in England zinc was manufactured some fifty years earlier. Every year the United States produces about 360,000 tons of zinc, which is approximately one third of the world's annual output.

Zinc Oxide ZnO, also called **flores zinci** or **lana philosophica,** is a white, bulky powder obtained by burning zinc in the air or by heating the basic carbonate of zinc. When hot, it is yellow, but on cooling, it turns white. It is much used in white paints under the name **zinc white.** The oxide is also used in pharmacy for making ointments. Zinc hydroxide is obtained as an amorphous precipitate by adding caustic alkalies to solutions of zinc salts. The hydroxide is soluble in an excess of the precipitant, forming a zincate. On heating the hydroxide, it loses water, forming the oxide. Native oxide of zinc is frequently colored red because of the presence of oxides of manganese.

Zinc Carbonate $ZnCO_3$ occurs in nature, as already stated. It forms rhombohedral crystals that are isomorphous with calcite. On treating solutions of zinc salts with alkali carbonates, **basic zinc carbonates** are precipitated, whose composition varies according to the temperature and concentration of the solutions. These carbonates are approximately $ZnCO_3 \cdot 2\,Zn(OH)_2$ or $(ZnCO_3)_2 \cdot 3\,Zn(OH)_2$. They are soluble in an excess of ammonium carbonate, but not in sodium or potassium carbonate.

Zinc Chloride $ZnCl_2$ is made by burning zinc in chlorine, or by the action of hydrochloric acid on the carbonate, oxide, hy-

droxide, or the metal itself. It is a white, deliquescent mass, having caustic properties. It is soluble in alcohol as well as in water. On attempting to dehydrate the salt by heating it, hydrochloric acid is given off, as in the case of magnesium chloride. On mixing concentrated zinc chloride solutions with zinc oxide, **oxychlorides** like Zn(OH)Cl are formed, the mass hardening in a manner not unlike the setting of plaster of Paris. Such zinc chloride and zinc oxide mixtures are used as cements in filling teeth. Zinc chloride is further employed in preserving railroad ties, which, after being soaked in its solutions, do not rot readily. It is also used to cleanse the surface of metals in the process of soldering. In medicine zinc chloride is used as a caustic agent and as a disinfectant. In the laboratory it is used in connection with certain syntheses of organic compounds. **Zinc bromide** $ZnBr_2$ is analogous to the chloride. The **iodide** ZnI_2 is also very soluble; it readily splits off iodine. The **fluoride** ZnF_2 is but sparingly soluble.

Zinc Sulphate $ZnSO_4$, **white vitriol**, is formed by the oxidation of zinc sulphide or by the action of sulphuric acid on the metal, oxide, or carbonate. It crystallizes in the rhombic system in colorless prisms of the composition $ZnSO_4 \cdot 7\,H_2O$, which effloresce on exposure to the air. The crystals are ismorphous with $MgSO_4 \cdot 7\,H_2O$. They are readily soluble in water. With sulphates of the alkalies, zinc sulphate forms double salts, like $K_2SO_4 \cdot ZnSO_4 \cdot 6\,H_2O$, which is analogous to schönite, $K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O$. Like other zinc compounds, zinc sulphate is *moderately poisonous*, upon which its use as an antiseptic depends.

Zinc Sulphide ZnS is white when pure. Native sulphide of zinc, **black-jack**, is colored dark brown by ferric oxide and other impurities. It crystallizes in the regular system. On adding sulphides of the alkalies or of ammonium to a solution of a zinc salt, a white precipitate of zinc sulphide is formed. This is soluble in dilute mineral acids but not in acetic acid.

Analytical Tests for Zinc Salts. — The reactions that are used in testing for zinc salts are: —

Ammonium sulphide precipitates white zinc sulphide from solutions of zinc salts. The sulphide is insoluble in acetic acid but soluble in mineral acids.

Alkaline hydroxides precipitate zinc hydroxide from solutions

of zinc salts. The precipitate dissolves in an excess of the reagent.

Alkaline carbonates precipitate basic zinc carbonate, which is soluble in ammonium carbonate but not in sodium or potassium carbonate.

Zinc oxide is white when cold and yellow when hot. When moistened with cobalt nitrate solution and then strongly heated on charcoal, zinc oxide yields a green mass called **Rinmann's green.**

Occurrence, Preparation, and Properties of Cadmium.—Cadmium is a rather rare element. It frequently occurs in small quantities in ores of zinc. It is also found, though rarely, as the native sulphide, CdS, known as greenockite, which is hexagonal and isomorphous with a rare, native zinc sulphide, würzite. Cadmium is commonly obtained in connection with the reduction of zinc from its ores. The metal boils at 775° and hence passes over into the condensers before the zinc, which boils at 918°. Cadmium is silver-white, malleable and ductile even at ordinary temperatures. It resembles tin in appearance, melts at 320°, and has a specific gravity of 8.6. Its atomic weight is 112.4, and its molecular weight is the same, for its vapor is 55.65 times as heavy as hydrogen. In the air, cadmium is quite stable, though its luster becomes somewhat tarnished, due to the formation of a thin layer of oxide. When strongly heated in the air or in oxygen, it burns, forming a brown oxide. Cadmium is always bivalent. Dilute acids act on cadmium, liberating hydrogen. The element was discovered in 1817 by Stromeyer, who investigated a yellowish zinc oxide which contained no iron. Almost simultaneously, cadmium was discovered by Hermann. The metal is used in preparing standard cells for measuring electromotive forces. It is also used in certain alloys of low melting point, like Wood's metal, which has already been described.

Cadmium Compounds. — The **oxide**, CdO, is a brown powder which is readily reduced at higher temperatures by means of carbon or hydrogen. The **hydroxide**, $Cd(OH)_2$, is white. It is formed by leaving the oxide in contact with water or by precipitation from solutions. It is soluble in ammonium hydroxide. The **chloride**, $CdCl_2$, may be obtained from solutions in the form of crystals of the composition $CdCl_2 \cdot 2\,H_2O$, which effloresce.

The anhydrous salt melts at 540°, and may be distilled at about 900°. The **bromide**, $CdBr_2 \cdot 4\,H_2O$, is soluble in alcohol as well as in water. The **iodide**, CdI_2, is obtained by the direct union of iodine and cadmium in presence of water. This salt is soluble in alcohol, and is used in photography. The **nitrate**, $Cd(NO_3)_2 \cdot 4\,H_2O$, is a deliquescent salt obtained by the action of nitric acid upon either the metal, the hydroxide, or the carbonate. The **sulphate**, $3\,CdSO_4 \cdot 8\,H_2O$, forms monoclinic crystals that readily dissolve in water. The salt effloresces on exposure to the air. It will be observed that the sulphate is not analogous to zinc sulphate $ZnSO_4 \cdot 7\,H_2O$ and magnesium sulphate $MgSO_4 \cdot 7\,H_2O$. Cadmium sulphate is used in treating diseases of the eye. The **sulphide**, CdS, is obtained as a bright yellow precipitate by conducting hydrogen sulphide into a solution of a cadmium salt. Dilute acids do not affect it. It is used as a pigment in paints.

The behavior of the hydroxide, carbonate, and sulphide, as above described, is used in testing for cadmium salts.

Occurrence, Preparation, and Properties of Mercury. — Mercury, or hydrargyrum, meaning silver water, is the only metal that is liquid at ordinary temperatures. It was known at least three hundred years before the Christian era. In nature it is sometimes found uncombined in small drops in the interstices of rocks. Its principal ore is **cinnabar**, the sulphide, HgS, which forms dark red, hexagonal, prismatic crystals. Mercury ores occur at Almaden in Spain, Idria in Austria, New Almaden in California, in Prussia, Peru, Japan, and China. The metal is obtained by simply roasting the sulphide: —

$$HgS + O_2 = Hg + SO_2.$$

The mercury vapors are condensed and collected. Sometimes the ore is heated with lime in iron retorts, when calcium sulphide remains behind and mercury passes over in form of vapor and is condensed. Mercury is purified by redistillation after treatment with dilute nitric acid, ferric chloride solution, or dilute sulphuric acid plus potassium bichromate. Mechanical impurities are removed from mercury by filtration through cloth or chamois skin. Perfectly pure mercury is made by liberating the metal from pure mercury salts, and finally distilling the product, preferably in vacuo.

Mercury is silver-white, and has a brilliant metallic luster. It melts at $-39.4°$ and boils at 357°. Its specific gravity is 13.59. Its atomic weight is 200.6, which is also its molecular weight, for mercury vapor is about 100 times as heavy as hydrogen. Mercury vapor has a very characteristic spectrum, exhibiting a bright yellow and a green line, besides a red, a blue, and three violet lines. The vapor conducts electricity and emits a bright, pale, greenish light rich in rays that affect photographic plates. The **mercury lamp** depends on the principle that mercury vapors emit light when they are conducting high tension electricity.

The vapors of mercury are very poisonous, which is also true of compounds of mercury. Mercury crystallizes in the regular system. Solid mercury is malleable. It may be cut with tools, and beaten into sheets with a hammer. In the air mercury remains practically unchanged. By sulphuric or hydrochloric acids it is attacked but slightly. Nitric acid or hot, concentrated sulphuric acid readily dissolves it. With sulphur or the halogens it combines at slightly elevated temperatures.

Mercury is used in making thermometers, barometers, mirrors, various amalgams in dentistry, and many compounds that find application in medicine. Large amounts of mercury are also employed in extracting gold and silver from their ores. The United States produces about 750 tons of mercury per year, which is about one fourth of the annual amount produced in the world. Mercury is shipped in iron flasks containing about 75 pounds each (Fig. 137).

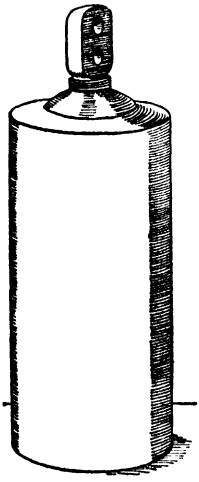


FIG. 137.

Amalgams. — The alloys or combinations of mercury with other metals are called amalgams. These are usually made by simply bringing the metals in contact with mercury, though they may also be obtained by electrolyzing a salt, using a mercury cathode; or frequently by introducing a metal into a solution of a mercury salt, like the nitrate. *In general, amalgams are of the nature of solutions of the metals in mercury.* They are liquid when the mercury preponderates, and solid when relatively less mercury is used.

Sodium combines with mercury with evolution of light and heat. **Sodium amalgam** containing less than 1 per cent sodium is liquid; a 1 per cent sodium amalgam is viscous, while amalgams containing 2 per cent or more of sodium are solid. Crystalline sodium amalgams corresponding to the formulæ Na_3Hg and $NaHg_6$ have been isolated. Sodium amalgam is used as a reducing agent, as already mentioned under sodium. With the exception of iron and platinum, practically all the metals form amalgams with mercury. Even platinum may be amalgamated by electrolyzing a mercury salt with a platinum cathode. However, the readiness with which the various metals unite with mercury varies very greatly. So gold and silver dissolve with ease in mercury, which fact is used in extracting these metals from pulverized rocks with which they are mixed. Copper, cadmium, and tin also readily unite with mercury. The amalgam used in filling teeth usually consists of mercury mixed with an alloy containing essentially silver and tin, together with smaller amounts of other metals, among which are copper, cadmium, and gold. The amalgam is made into a stiff paste and introduced into the cavity in the tooth, where it soon hardens or sets without material change of volume. **Tin amalgam** is used in making **mirrors.** **Amalgamated zinc** is hardly acted upon by dilute acids; on the other hand, **magnesium amalgam**, which forms only on heating mercury and magnesium together, is a black incoherent mass which violently decomposes water with liberation of hydrogen.

When sodium amalgam is treated with a concentrated solution of ammonium chloride or other ammonium salt, a bulky mass called **ammonium amalgam** is obtained. It is supposed to contain ammonium NH_4, dissolved in mercury. The large bulk is produced by hydrogen and ammonia gases that are set free. This so-called ammonium amalgam is also formed by electrolyzing a solution of an ammonium salt, using mercury as a cathode. By some it is considered practically certain that the material contains NH_4, dissolved in mercury; by others this has been denied. At any rate, if ammonium amalgam exists at all, it is very unstable.

Compounds of Mercury. — Mercury forms two distinct series of compounds: the mercurous compounds, in which the metal

is univalent; and the mercuric compounds, in which it is bivalent.

Oxides of Mercury.—**Mercurous oxide** Hg_2O is a dark brown, slightly greenish, unstable powder obtained as a precipitate by adding sodium or potassium hydroxide solution to a mercurous salt. It decomposes into mercuric oxide and mercury on exposure to light or when slightly heated. Mercuric oxide HgO may be obtained by prolonged heating of mercury in the air at about 360°. It is made on a large scale by heating a mixture of mercuric nitrate and mercury. It is a bright red, crystalline powder also known as **red precipitate.** On heating mercuric oxide, it turns dark and gives off oxygen. Above 500° the decomposition into mercury and oxygen progresses rapidly. Red oxide of mercury is used in medicine in red precipitate ointment. The yellow variety is also used for similar purposes; being finely divided, it is more active than the red. By adding caustic soda to a solution of a mercuric salt, mercuric oxide is obtained in form of a finely divided, amorphous, yellow powder. On heating, it behaves like the red oxide. Hydroxides of mercury are not known, probably because they are so unstable, decomposing at once into oxide and water.

Halides of Mercury.—**Mercurous chloride** HgCl, also called **calomel,** is obtained as a slightly yellowish, crystalline mass by heating mercury with mercuric chloride: —

$$Hg + HgCl_2 = 2\,HgCl.$$

It may also be formed by passing sulphur dioxide into a hot solution of mercuric chloride: —

$$2\,HgCl_2 + 2\,H_2O + SO_2 = 2\,HCl + H_2SO_4 + 2\,HgCl.$$

Other reducing agents may be employed instead of sulphur dioxide; thus, with stannous chloride the reaction is,

$$2\,HgCl_2 + SnCl_2 = SnCl_4 + 2\,HgCl.$$

By adding a soluble chloride to a solution of a mercurous salt, mercurous chloride is precipitated, thus: —

$$HgNO_3 + NaCl = NaNO_3 + HgCl.$$

Mercurous chloride is not soluble in water. It may be sublimed, and thus obtained in crystalline form. The precipitated variety is an amorphous powder. This salt is much used in medicine as a purgative and as a stimulant for the secretory organs.

It should be kept in the dark, for on exposure to light it gradually decomposes somewhat, yielding mercury and mercuric chloride, which is a strong poison, thus:—

$$2\,HgCl = Hg + HgCl_2.$$

Mercurous bromide HgBr is obtained as a white, insoluble powder by adding a soluble bromide to a mercurous salt. It may be obtained in crystalline form by sublimation, or by treating mercury with bromine water.

Mercurous iodide HgI is formed by triturating mercury and iodine together in presence of a little alcohol, or by precipitating a solution of a mercurous salt with sodium or potassium iodide. It is a dark, yellowish green powder which readily decomposes into mercury and mercuric iodide, especially in the light, thus:—

$$2\,HgI = Hg + HgI_2.$$

The salt is used in medicine.

Mercuric chloride $HgCl_2$, also called **corrosive sublimate**, or **sublimate**, is made on a large scale by heating mercuric sulphate with common salt, thus:—

$$HgSO_4 + 2\,NaCl = Na_2SO_4 + HgCl_2.$$

In this process the mercuric chloride vapors formed are condensed, thus yielding beautiful, rhombic, prismatic crystals that readily dissolve in water (1 in 15) and also in alcohol and in ether. The salt melts at 265° and boils at 307°. Mercuric chloride may also be made by the action of hydrochloric acid on mercuric oxide, or by dissolving mercury in aqua regia. Mercuric chloride is reduced to mercurous chloride by reducing agents as already stated above. An excess of stannous chloride reduces mercuric chloride to metallic mercury:—

$$HgCl_2 + SnCl_2 = SnCl_4 + Hg.$$

Mercuric chloride is a powerful poison. It is used as a disinfectant in surgery, for cleansing wounds and washing the hands and surgical instruments. It is employed only in dilute solutions. The solutions have corrosive properties and a sharp, very disagreeable, "metallic" taste. Mercuric chloride is also employed in preserving anatomical specimens, herbaria, stuffed animals, wood, etc. With albumen it unites, forming insoluble compounds, hence the use of white of egg and milk in case of

poisoning with corrosive sublimate. With chlorides of the alkalies, mercuric chloride forms double salts, like $HgCl_2 \cdot KCl \cdot H_2O$.

Mercuric bromide $HgBr_2$ is similar to mercuric chloride. It is isomorphous with the latter and melts at 325°.

Mercuric iodide HgI_2 may be prepared by the direct union of iodine and mercury, or by adding potassium iodide to a solution of mercuric chloride, when a yellowish precipitate forms which soon becomes bright red. Though insoluble in water, it readily dissolves in alcohol, from which solutions it crystallizes in bright red, tetragonal pyramids. In aqueous potassium iodide solutions, mercuric chloride is readily soluble, forming a yellow solution containing the double salt $HgI_2 \cdot 2\,KI$. This solution may be concentrated till it has a specific gravity of over 3. It is known as **Thoulét's solution** and is used by mineralogists in determining the specific gravity of small pieces of minerals. Potassium mercuric iodide solution to which caustic potash has been added is **Nessler's reagent**, which is used in determining ammonia in the analysis of potable waters. With ammonia such solutions give a brown precipitate having the composition $O\begin{smallmatrix}Hg\\ \diagup\diagdown\\ Hg\end{smallmatrix}NH_2 \cdot I$. If the ammonia solutions are very dilute, only a yellowish brown coloration is observed.

Mercuric Cyanide $Hg(CN)_2$, the only cyanide of a heavy metal that is soluble in water, is obtained by the action of hydrocyanic acid on mercuric oxide. It forms tetragonal prisms, which when heated yield mercury and cyanogen.

Nitrates of Mercury.—**Mercurous nitrate** $HgNO_3 \cdot H_2O$ forms monoclinic crystals, obtained by action of nitric acid upon an excess of mercury in the cold. On diluting its solutions with water, yellow basic salts separate out, like $Hg(OH)HgNO_3$. This hydrolysis is counteracted by keeping a slight excess of nitric acid in the solutions.

Mercuric nitrate $Hg(NO_3)_2$ is formed by dissolving mercuric oxide in nitric acid, also by the action of an excess of hot, concentrated nitric acid on mercury. From the solutions, deliquescent crystals $2\,Hg(NO_3)_2 + H_2O$ may be obtained. On dilution with water, these suffer hydrolysis, forming a series of basic salts whose composition varies according to the relative amount of water present; so we have, for instance,

$Hg(NO_3)_2 \cdot 2\,HgO + H_2O$. On boiling with much water, these basic salts are decomposed, yielding nitric acid and mercuric oxide. Addition of nitric acid, of course, reverses the reaction. Under the name **Millon's reagent**, mercuric nitrate solution is used in testing for albumins, which are coagulated by it.

Mercuric Fulminate $HgC_2O_2N_2$, also called **fulminating mercury**, is made by the action of nitric acid on mercury in presence of alcohol. It is a white powder, which is *very explosive when dry*. It is used in making **percussion caps**. The explosion of a small amount of the substance will cause gun cotton or nitroglycerine to explode.

Sulphates of Mercury. — **Mercurous sulphate** Hg_2SO_4 is formed by treating an excess of mercury with sulphuric acid, or by precipitating a mercurous nitrate solution with sulphuric acid. The colorless crystals so obtained are sparingly soluble in water. The salt is used in making standard cells for comparison of electromotive forces.

Mercuric sulphate $HgSO_4$ is made by digesting mercury or mercuric oxide with an excess of sulphuric acid. The salt so obtained is a white, crystalline mass. On treatment with water, it is hydrolyzed, forming sulphuric acid and a yellow basic salt $HgO \cdot HgSO_4$, known as **Turpeth mineral**, which is insoluble. With sulphates of the alkalies, mercuric sulphate forms double salts like $K_2SO_4 \cdot HgSO_4\ 6\,H_2O$. These are isomorphous with the analogous magnesium double salts.

Mercuric Sulphide HgS is very stable. It is readily obtained by triturating mercury and moist sulphur together, by heating mercury with sulphur, or by conducting hydrogen sulphide into a solution of a mercury salt. Mercurous sulphide is not known with certainty; the black precipitate produced when a mercurous salt is treated with hydrogen sulphide or an alkaline sulphide is mercuric sulphide mixed with mercury. When made by precipitation, mercuric sulphide is a black, amorphous powder, which is insoluble even in concentrated acids on boiling. It is soluble in aqua regia, however. **Black mercuric sulphide** may be sublimed, and thus converted into dark red rhombohedral crystals that are identical with **cinnabar**, which occurs in nature. Towards acids the red and black varieties act alike. **Red sulphide of mercury** serves as a pigment in

paints under the name of **vermilion**. It has been used thus since ancient times.

Compounds of Mercury Salts with Ammonia. — When mercury salts are treated with ammonia, compounds are formed which may be regarded as ammonium salts in which one or more of the hydrogen atoms are replaced by mercury. So when mercurous chloride is treated with ammonia water, a black insoluble powder, **mercurous ammonium chloride**, is formed: —

$$2\,HgCl + 2\,NH_3 = (NH_2\overset{I}{H}g_2)\,Cl + NH_4Cl.$$

Similarly, mercurous nitrate yields black **mercurous ammonium nitrate** $(NH_2\overset{I}{H}g_2)NO_3$ plus mercury.

Mercuric ammonium chloride $(NH_2\overset{II}{H}g)Cl$, known as *infusible white precipitate*, is formed by adding ammonia to mercuric chloride solution: —

$$HgCl_2 + 2\,NH_3 = (NH_2\overset{II}{H}g)Cl + NH_4Cl.$$

The so-called *fusible white precipitate*, **mercuric diammonium chloride** $(NH_3Cl)_2\overset{II}{H}g$, is obtained by treating a boiling hot ammoniacal solution of ammonium chloride with mercuric chloride.

Physiological Properties of Mercury Compounds. — It has already been stated that mercury compounds are poisonous. When mercury is introduced into the system, it produces a peculiar taste in the mouth commonly described as metallic. Salivation follows, and the gums, teeth, liver, kidneys, and other organs frequently also become involved. In small doses mercury compounds stimulate the action of various glands; this furnishes the basis for the internal use of calomel. The introduction of mercury compounds into medicine dates back to Paracelsus, who lived in the first half of the sixteenth century.

Tests for Mercury. — Mercury is very readily detected in its compounds. By mixing any mercury compound with soda and heating, mercury is driven off, which condenses in drops in the cooler parts of the ignition tube. With iodine these drops form red iodide of mercury.

In solutions of mercurous salts, chlorides produce a white precipitate of calomel which turns black on treatment with ammonia, as already stated.

The fact that stannous chloride reduces mercuric chloride to

mercurous chloride, and that the latter is further reduced to mercury by adding more stannous chloride, is frequently used in testing for mercury. Further, bright copper when introduced into a solution of a mercury salt becomes coated with mercury. The sulphide of mercury is also very characteristic, as already mentioned.

General Remarks. — It will be observed that the compounds of magnesium and zinc bear close resemblances to each other, and also a fair resemblance to the compounds of cadmium. On the other hand, the mercury compounds do not resemble those of zinc, magnesium, and cadmium. To be sure, in the mercuric compounds, mercury is bivalent, and between this series and the compounds of the other metals mentioned, some analogies are apparent. It will be seen later that the compounds of mercury bear a closer resemblance to those of copper. Glucinum stands rather isolated, being, as has already been mentioned, a transition element between this group and that of the earth metals. Thus it is evident that the metals of the magnesium group do not form as closely related a family as some of the others that have already been studied.

REVIEW QUESTIONS

1. Why are beryllium, zinc, cadmium, and mercury grouped with magnesium?

2. What is beryl? What characterizes the solutions of beryllium compounds?

3. Mention ten compounds in which magnesium occurs in nature, writing the appropriate formulas.

4. How is metallic magnesium obtained, and what use is made of it? Equations.

5. Write the formulas of magnesium carbonate, sulphate, chloride, nitrate, phosphate, and oxalate, and compare the solubilities of these salts in water with those of the corresponding compounds of: (*a*) the alkalies, (*b*) the alkaline earths, (*c*) zinc, cadmium, mercury.

6. How much magnesium oxide may be prepared from 30 grams of pure magnesium carbonate? How may this be done? Equation.

7. If a solution contains salts of barium, strontium, and magnesium, how demonstrate that the latter is present?

8. What are the principal ores of zinc? By means of equations, show how the metal may be extracted from these ores.

9. What is zinc dust, spelter, brass, galvanized iron?

10. State what use is made of each of the following: zinc oxide, zinc chloride, zinc sulphate.

11. If a solution contains a mixture of zinc and magnesium salts, how demonstrate the presence of these two metals in the solution? Equations.

12. How was cadmium discovered? Describe the properties of this metal and mention its uses.

13. Given a solution of cadmium nitrate and one of zinc nitrate, how distinguish between the two by means of a single reagent. Equations.

14. What property have all mercury compounds in common?

15. What two series of salts does mercury form? Give the formulas of five salts in each series.

16. In what form does mercury occur in nature? Where does it occur?

17. Describe mercury.

18. What is an amalgam? Mention ten different amalgams. How may each be formed? What use is made of each of these amalgams?

19. Mention three compounds of mercury that are used in medicine, stating the purpose for which they are employed.

20. How much corrosive sublimate may be prepared from 5 lb. of mercury? How may this be done? Write equations.

21. What is the action on corrosive sublimate of: (*a*) stannous chloride, (*b*) hydrogen sulphide? Equations.

22. What antidote is used in case of poisoning with mercury compounds? Explain.

23. State the chemical nature and the use of each of the following: Thoulet's solution, Nessler's reagent, Millon's reagent, fulminating mercury, cinnabar, calomel.

24. Given a solution of mercuric chloride, describe five different ways of showing that mercury is present in the solution. Write the appropriate reactions.

25. Explain why mercury, which is so different outwardly from magnesium, zinc and cadmium, is nevertheless classified with these metals.

26. How much zinc sulphate can be prepared from 250 grams of pure zinc oxide?

27. Given 2000 grams of corrosive sublimate, how much calomel could be prepared from it?

28. How much mercury would 40 grams of copper precipitate from a solution of corrosive sublimate?

29. How much cadmium sulphide may be formed from 60 grams of cadmium chloride?

30. How much cadmium would 24 grams of magnesium displace from a solution of cadmium sulphate?

CHAPTER XXIV

SOLUTIONS, ELECTROLYSIS, AND ELECTRO-CHEMICAL THEORIES

Nature and Kinds of Solutions. — As stated in Chapter I, solutions were formerly regarded as chemical compounds according to variable proportions. This designation expresses the fact that the process of solution is accompanied by all the phenomena that are observed when chemical change takes place, and that the composition of the final homogeneous product obtained may gradually be varied at will within certain limits, as has already been explained. The term *solution* has of recent years received a somewhat broader meaning than it formerly had. So mixtures of gases are sometimes spoken of as solutions. Glass, various alloys, isomorphous mixtures of crystalline substances, gases absorbed by solids, etc., are frequently termed **solid solutions.** A solution is commonly defined as a homogeneous mixture, the constituent parts of which cannot be separated by mechanical means. The term *mixture* as here used is, however, not to be confused with a mere mechanical mixture like that of sulphur and iron filings ground together, as already remarked in Chapter I. The word *mixture*, as used in connection with a solution, indicates solely that the proportions of the ingredients may be varied arbitrarily, at least to some extent.

Any gas will mix with any other gas or mixture of gases in all proportions, as would naturally be expected, for in a gas the molecules are relatively remote from one another. But *gases will not be absorbed by liquids or solids in all proportions.* Here *the specific nature of the gas and that of the liquid or solid under consideration is of prime importance. The specific nature of liquids and solids is also the determining factor in fixing the solubility of liquids or solids in other liquids or solids.* Moreover, *in all cases of solution, the temperature is very important, being second only to the effect of the nature of the substances.* Pressure is also a factor, which is particularly important when gases

come into play, for these are highly compressible. On the other hand, the pressure factor is of less importance when liquids and solids only are used. Indeed, *the factors mentioned are of the same relative importance in the process of solution as in chemical action.*

Absorption of Gases by Liquids. — The amount of a gas absorbed by a liquid increases as the temperature is lowered and as the pressure is increased. *At constant temperature, the amount of gas absorbed by a liquid is directly proportional to the pressure.* This law was discovered in 1803 by Henry, whose name it bears. **Henry's law** holds only in case the gas is not very soluble in the liquid, like oxygen or hydrogen in water, or nitrogen in alcohol. When gases are copiously soluble, like hydrochloric acid or ammonia in water, the law does not hold. Gases that follow Henry's law have a very low heat of solution, showing that but little affinity exists between the gas and the liquid. Gases that do not follow the law have a high heat of solution, indicating the prominence of the affinity factor; for the heat developed is frequently greater than that produced when the dry gas is liquefied by pressure. Thus we have: —

$$NH_3 + (aq) = (NH_3\,aq) + 8.8 \text{ Cal.},$$

whereas the heat of liquefaction of 17 grams of ammonia is only 4.4 Cal.

Solutions of Liquids in Liquids. — Many liquids mix perfectly with one another in all proportions, forming solutions. Thus water will mix with glycerine, alcohol, or acetone; ether with kerosene or fatty oils; olive oil with linseed oil; carbon disulphide with ether, hydrocarbon oils, or fats. In general, liquids like hydrocarbon oils and their halogen substitution products, ethers, esters, carbon disulphide, and the various fatty and oily products of plant or animal origin, are readily soluble in one another in all proportions. *Liquids that are miscible in all proportions are called* **consolute liquids.**

Now, hydrocarbon oils and animal and vegetable oils, carbon disulphide, and carbon tetrachloride are practically insoluble in water. When such substances are added to water, the liquids separate in two distinct layers. When the specific gravities of the two non-miscible liquids are nearly alike and the liquids are shaken together, a mixture of milky appearance is obtained, which on closer inspection is found to consist of small globules

of one liquid suspended in the other. This is an **emulsion** The greater the difference in specific gravity between the two liquids, the sooner will they again separate into two layers. The specific nature of the liquids also has to do with the length of time the globules remain in suspension, for the greater the adhesion between the liquids, the longer the emulsion lasts. In milk, the butter fat is present in the form of minute globules in suspension, that is, in emulsified condition. On standing, the fat gradually comes to the top, forming a layer of cream. *By centrifugal force, the constituents of an emulsion can be rapidly separated*, which fact is used in separating butter fat from milk by means of the cream separators in use in creameries.

A few liquids like alcohol and acetone are consolute either with hydrocarbons and fats or with water. It is to be observed that, when alcohol or acetone is added to water, the resulting solution will then take up much more hydrocarbon or fatty oil than will pure water. A knowledge of this fact is often of practical value.

Ether is soluble in water to a limited extent. When an excess of ether is added to water, two layers form, the upper one finally becoming a saturated solution of water in ether and the lower one a saturated solution of ether in water. The solubility in this case, as in all others, is a function of the temperature. Phenol C_6H_5OH and water are also only partially miscible at ordinary temperatures; however, at and above 68.4° the two liquids become perfectly consolute. Again, above 20° triethylamine $N(C_2H_5)_3$ and water act like ether and water, that is, they are not consolute. But below 20° triethylamine and water are miscible in all proportions. In this case the miscibility increases as the temperature is lowered, though more frequently the opposite is true — as in the pair, phenol and water.

Solutions of Solids in Liquids. — *Whether a given solid will dissolve in a given liquid and to what extent, depends primarily upon the specific nature of the two substances, and also upon the temperature.* The pressure is also a factor, strictly speaking, but ordinarily it is of little practical importance. A liquid that dissolves a solid adheres to or wets the latter. Nevertheless, in many cases a liquid will wet a solid without dissolving it appreciably. We may look upon adhesion as an unsuccessful attempt to form a solution, for here the attraction between solid and liquid is

insufficient to overcome their cohesions and thus form a solution.

Many solids have definite solubility in a given liquid, which varies with the temperature. Thus the ordinary salts and other

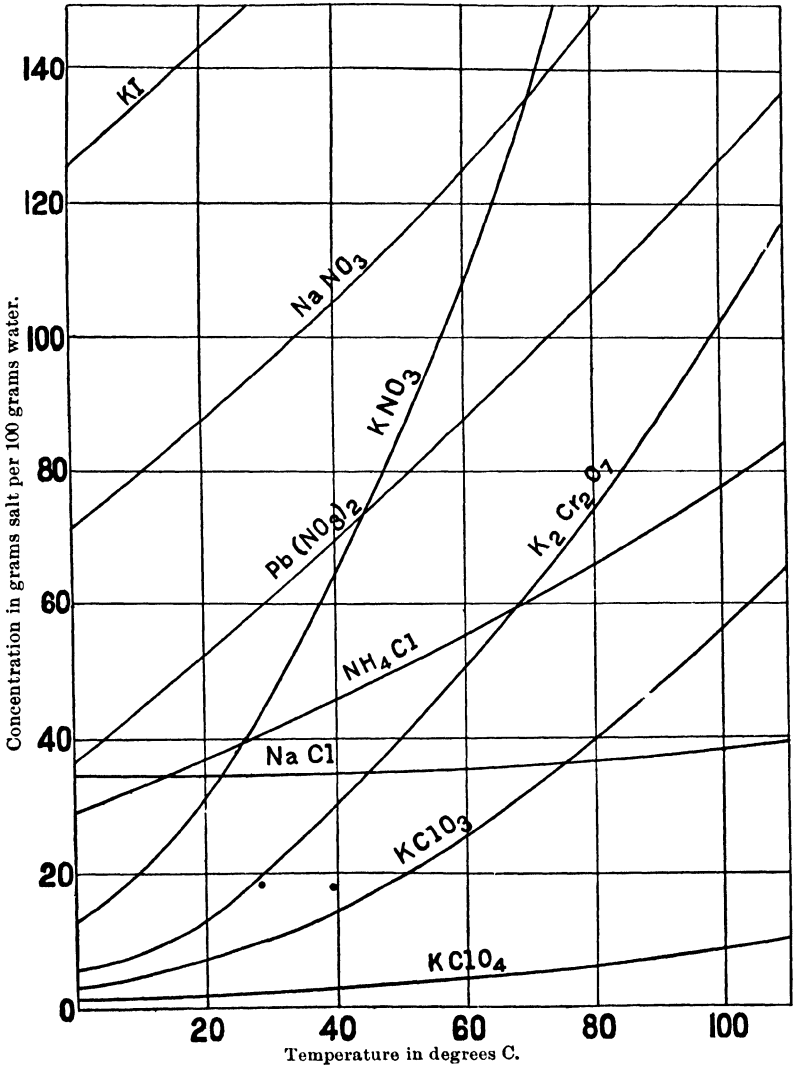


FIG. 138.

crystalline solids, like sugar or urea, have a definite solubility in water. On the other hand, substances like gelatine, gum arabic,

and many others of similar non-crystalline character do not have a definite solubility; they are practically consolute with water. So when water is dropped on glue, the latter swells up, and as more and more water is gradually added all stages of plasticity are obtained, till a thick sirup, and finally a limpid liquid, results. In general, crystalline substances have sharply defined melting points as well as definite solubilities, whereas non-crystalline substances frequently lack definite melting points and solubilities, though this rule is not without its exceptions.

The solubilities of solids in liquids vary very greatly with the nature of the substances brought together, as well as with the temperature. Some substances, like common salt in water, are about as soluble at lower as at higher temperatures.

More frequently, the solubility increases with rise of temperature, as in the case of saltpeter in water.

The number of grams of a substance dissolved by 100 grams of a given liquid at a certain temperature is called the **solubility** of that substance at the given temperature. **Solubility curves** are commonly constructed by charting temperatures as abscissas and solubilities as ordinates. Figure 138 shows a number of solubility curves of well-known salts. It will be observed that these by no means have the same trend. Even much greater varieties than these are met frequently.

Degrees of Saturation. — In determining the solubility of a solid, the usual practice is to shake the liquid with an excess of the solid till no more is dissolved. This process is conducted at the temperature at which the solubility is sought. The liquid finally obtained is said to be a **saturated solution** at that temperature. The strength of the saturated solution is found by analyzing a given weight of it. This frequently consists simply of evaporating the solution to dryness and weighing the residue. If the saturated solution thus obtained at a given temperature, say 30°, is carefully decanted from the excess of solid substance so that none of the latter is present, and then this liquid is heated above 30°, the solution is said to be **unsaturated**; for at this higher temperature it would take up more of the solid if some of the latter were introduced. On the other hand, if the saturated solution is cooled slightly below its temperature of saturation *out of contact with the solid*

it contains, the liquid usually remains clear. The solution is now said to be **supersaturated**, for when brought into contact with some of the solid (even traces will suffice), more of the latter will drop out and the solution will then become **saturated** at this lower temperature. This is another method of making a saturated solution. The **degree of supersaturation** that may be obtained by cooling saturated solutions as described varies in the case of different solutions. *The phenomena of supersaturated solutions are analogous to those of the supercooling of liquids.* So, out of contact with ice, water may be cooled several degrees below zero and still be a liquid. On touching this supercooled water with a piece of ice, however, the whole congeals.

Unsaturated, saturated, and supersaturated solutions are similarly obtained in case of solutions of gases in liquids and of liquids in liquids.

Solid Solutions. — These have already been mentioned. They are commonly prepared by melting two solids together and allowing the liquid to congeal. Sometimes by crystallizing certain substances from solution, crystals of variable composition, solid solutions, result. Again, gases are absorbed by solids to form so-called solid solutions. In these cases we may also have either restricted solubility, or miscibility in all proportions.

Precipitation. — *The process of precipitation is the opposite to that of solution.* Thus when a salt has been dissolved in water, the latter may be evaporated from the solution till the salt separates out. Again, common salt is soluble in water, but not in alcohol; hence by adding alcohol to salt brine, some of the salt is precipitated. Similarly, camphor is soluble in alcohol but not in water; consequently camphor is precipitated by adding water to a solution of camphor in alcohol. Sodium chloride is insoluble in liquid hydrochloric acid, hence it is readily comprehended why the salt is precipitated when hydrochloric gas or even a concentrated solution of it is added to salt brine. Calcium phosphate is soluble in nitric or hydrochloric acids but not in water; hence by neutralizing such an acid solution of calcium phosphate with ammonia or caustic soda, calcium phosphate is precipitated. These are all simple, typical illustrations.

Precipitation may, however, also be caused by double decomposition in solutions. So silver chloride is precipitated thus: —

$$AgNO_3 + NaCl = NaNO_3 + AgCl.$$

This reaction occurs because under the conditions that obtain silver chloride and the solution of sodium nitrate are the stabler products. The precipitation does not take place simply because there is an opportunity for the insoluble silver chloride to form, it proceeds also because there is the chance to form the stable and soluble sodium nitrate. In other words, reactions of this kind must be considered as a whole. When silver nitrate solution is shaken with carbon tetrachloride, silver chloride does not form. Clearly there is plenty of silver and chlorine to form silver chloride, but the other product would have to be a nitrate of carbon, which is unknown, probably because of its great instability. *This lack of action between silver nitrate and carbon tetrachloride is not to be ascribed to the fact that the latter compound is a non-electrolyte, as is often done, for similar changes do occur in the best of insulators*, as will be shown below. By heating carbon tetrachloride with silver nitrate and nitric acid to high temperatures in a sealed tube (method of Carius) silver chloride is indeed obtained, for here there are conditions under which carbon is oxidized. Thus carbon tetrachloride is destroyed, carbon dioxide, oxides of nitrogen, and silver chloride resulting as the stable products under the conditions to which the mixture was subjected. *The method of precipitation by double decomposition in solutions is very commonly employed in chemistry. In all cases the explanation is similar to that of the precipitation of silver chloride.*

Liquids also may be thrown out of solution. So, many oils are insoluble in water but soluble in alcohol. By adding water to such alcoholic solutions, the oil separates out in the form of a layer.

Gases also may be liberated from their solutions in liquids. In many cases this can be done by simply heating the solution. But it may also be accomplished by adding some other appropriate liquid, solid, or gas to the solution. So, for instance, by adding concentrated sulphuric acid to a strong solution of hydrochloric acid, hydrochloric acid gas is liberated; similarly, ammonia is set free when concentrated caustic potash solution is added to a strong aqueous solution of ammonia.

Colloidal Solutions. — These may be made by dialysis, as already explained. When an electric arc is formed between two rods of silver dipping into water (Fig. 139) a dark-colored liquid

results which is an extremely finely divided suspension of silver. This is sometimes called a colloidal solution of silver. Similar colloidal solutions of other metals, like platinum or gold, can be formed.

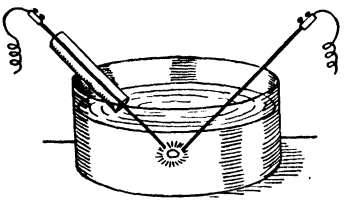


FIG. 139.

In general, *colloidal solutions boil at the same temperature as the pure solvent.* They vary from mere suspensions to true solutions. In living beings, colloidal solutions play an important rôle. Many colloidal solutions are precipitated by slight additions of various salts, sugar, alcohol, etc. The statement sometimes made that only electrolytes precipitate colloidal solutions is erroneous. For instance, sugar added to colloidal solutions of ferric hydroxide causes precipitation.

Boiling Points of Solutions. — *The boiling point of a liquid is the temperature at which its vapor tension just overcomes atmospheric pressure.* It consequently varies with the pressure. At constant pressure, the boiling point of a liquid is changed by dissolving substances in it. Thus solutions are obtained which may have a higher or lower boiling point than the solvent, depending on the nature of the substances brought together. So water boiling at 100° and alcohol boiling at 78° yield solutions that boil between these temperatures. Formic acid boiling at 101° may yield an aqueous solution that boils at 107°. Pyridine boiling at 115° and water may yield a solution boiling at 93°.

Use of Boiling Points of Solutions in Molecular Weight Determinations. — When a substance that is practically non-volatile, as compared with the solvent liquid, is dissolved in the latter, the solution so obtained boils higher than the pure solvent. So, when sugar is added to water, the solution obtained boils above 100°. The rise of the boiling point is proportional to the amount of solute added. Furthermore, *the elevations of the boiling point are approximately the same for equimolecular quantities of solute each dissolved in an equal quantity of solvent.* This offers a simple method of determining the molecular weights of substances in solution. So 342 grams of sugar $C_{12}H_{22}O_{11}$, 60 grams of urea $CO(NH_2)_2$, 94 grams of glycerine $C_3H_5(OH)_3$, 120

grams of magnesium sulphate, 159 grams of copper sulphate $CuSO_4$, each dissolved in 5000 grams of water, will yield solutions that boil at 100.104°. This rise of 0.104° in 5000 grams of water would be proportional to a rise of 50 × 0.804° or 5.20° in 100 grams of water. The value 5.20° is termed the *molecular rise of the boiling point* when water is used as the solvent. For other solvents this value is quite different. For instance, for ether it is 21.6°, for alcohol 11.7°, for carbon tetrachloride 41.0°, for benzene 26.7°. It is possible to compute these values from the absolute boiling point T and the latent heat of evaporation L of the solvent by means of the formula,

$$\text{Molecular rise of boiling point} = \frac{2\,T^2}{100\,L}.$$

The theoretical considerations upon which this formula is based will not be entered into here.

To ascertain the molecular weight of any substance soluble in water, dissolve so much of the substance in 5000 grams of water till the solution boils at 100.104°. The amount of solute added is its molecular weight in grams. In practice one would, of course, take a much smaller, convenient amount of water and solute to determine the boiling point of the solution, and compute the quantity of solute required to elevate the boiling point 5.2° per every 100 grams of water. Instead of the rise of the boiling point of a solution, the lowering of the vapor tension caused by the introduction of the solute may be used to determine the molecular weight of the solute.

The Freezing Point of Solutions. — The freezing point of a solution is lower than that of the pure solvent. *The lowering of the freezing point is also about the same for equimolecular quantities of solutes each dissolved in an equal amount of solvent.* Thus, in aqueous solutions, the molecular lowering of the freezing point is about 18.9° per 100 grams of water. The value varies for different solvents, but may be computed approximately from the absolute freezing point and the latent heat of fusion of the solvent according to theoretical considerations of van't Hoff, which will not be reproduced here, the formula being —

$$\text{Molecular lowering of the freezing point} = \frac{2\,T_1^2}{100\,L_1}.$$

The method of determining molecular weights in solution from

the lowering of the freezing point is analogous to that of making such estimations from the rise of the boiling point.

Discussion of Molecular Weights Determined in Solutions. — The freezing and boiling point methods yield only approximate results at best, and can be used with success only in dilute solutions. Special care must be exercised in interpreting the results obtained, for they are often anomalous. So, many substances like gelatine, dialyzed silicic acid, or soap when dissolved in water hardly cause any rise of the boiling point. These substances consequently have enormous molecular weights as found by these methods. Such substances are consequently frequently regarded as highly **associated** or **polymerized.** Again, many substances, among them a large number of the ordinary acids, salts, and bases, when dissolved in water and tested by the freezing or boiling point method, yield much lower molecular weights than the formulæ usually ascribed to them indicate. These substances are by some chemists regarded as **dissociated in solution**; they seek to connect the abnormally low molecular weights observed with the fact that such solutions are frequently electrolytic conductors. So, for instance, common salt, saltpeter, caustic potash, nitric acid, etc., yield molecular weights that are usually somewhat over half of those represented by the formulæ of these compounds (see the theory of Arrhenius).

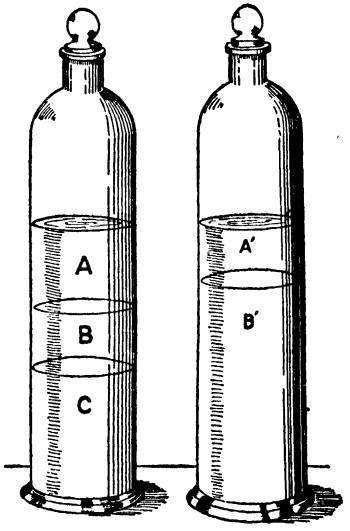


FIG. 140. FIG. 141.

Osmosis and Osmotic Pressure. — If carbon disulphide C (Fig. 140) be placed in a tube and a layer of water B be poured upon it, and again a layer of ether A be carefully poured upon the water, there will, after long standing, eventually be but two layers A' and B' (Fig. 141). The lower layer B' consists of carbon disulphide and ether saturated with water, whereas the upper layer A' consists of water saturated with carbon disulphide and ether. The change which has

occurred is easily explained. Ether dissolves very readily in carbon disulphide, but much less readily in water. Again, carbon disulphide and water hardly dissolve each other at all. In Fig. 140 the water layer *B* dissolves ether and in turn the ethereal layer *A* also takes up some water. When the ether has gone into *B* till it touches the carbon disulphide *C*, the latter extracts ether from the aqueous layer *B*. Thus the carbon disulphide layer *C* becomes enriched with ether, whereas the aqueous layer becomes depleted in ether. The depletion is made good by a continuous supply of ether from *A* till the latter is exhausted and equilibrium is produced. Water charged with ether dissolves carbon disulphide to a greater extent than pure water does, and so the aqueous layer *B* always contains some carbon disulphide. Moreover, before equilibrium is reached, some of this carbon disulphide is extracted from the layer *B* by the ethereal layer *A*. Thus, in the attempt to reach equilibrium, ether is passing from *A* through *B* into *C*, and on the other hand carbon disulphide is traveling from *C* through *B* into *A*. The former current is much the stronger, and so the layer *A* gradually disappears.

The example just cited is a typical case of osmosis. The layer *B* is the septum which separates the liquids *A* and *C*. Whether the latter substances will pass through *B* or not is determined by the specific nature of *B* and also that of *C* and of *A*. Furthermore, the specific nature of the septum *B* and that of the liquids *A* and *C* which bathe it also determines the direction which the major current will take. *In all osmotic processes there is a major and a minor current, but in some cases the latter is so slight as to be almost negligible. Under these conditions the osmotic process appears to be one-sided and the septum used is said to be* **semipermeable.**

It is clear that if the layer *B* in Fig. 140 could be held rigidly in place, pressure would result on the walls of the compartment *C* because of the influx of ether. Figure 142 shows an apparatus of glass containing mercury, carbon disulphide in *C*, and ether in *A*, while *B* is a slice of cork which is saturated with water, and tightly jammed into the tube. As the apparatus stands, the mercury rises in the limb at the right because the major current consists of the passage of ether from *A* through *B* into *C*, as already explained. The pressure so produced is

called the **osmotic pressure.** *It is clear that this pressure is the result of differences in solubility.* The apparatus shown in Figure 142 serves only to demonstrate the existence of osmotic pressure, not to measure its value, for the water-soaked cork will give way long before the maximum pressure is reached.

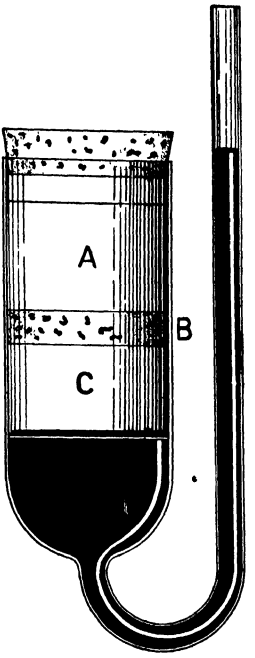


FIG. 142.

Osmosis has been studied for over a hundred years. The water, ether, carbon disulphide experiment was performed by L'Hermite in 1854. The importance of osmotic investigations in physiological processes was recognized very early, and physiologists have contributed largely to our knowledge of osmosis. When septa, like parchment paper, or pieces of animal bladder, are used to separate an aqueous sugar solution *S* from pure water *W* (Fig. 143), the main osmotic current is from the water through the membrane to the solution, for the latter extracts water from the water-soaked septum. At the same time much sugar passes through the septum into the water *W*. If, however, a precipitate of copper ferrocyanide $Cu_2Fe(CN)_6 \cdot x\,H_2O$ is formed in the pores of the septum, almost no sugar passes from the cell into the outer liquid *W*; that is to say, copper ferrocyanide is a semipermeable membrane, for it allows water to pass through it, whereas it is nearly impervious to sugar. The precipitate of copper ferrocyanide is formed in the membrane by first placing about a three per cent potassium ferrocyanide solution in the cell and then immersing the latter for a time in a solution of copper

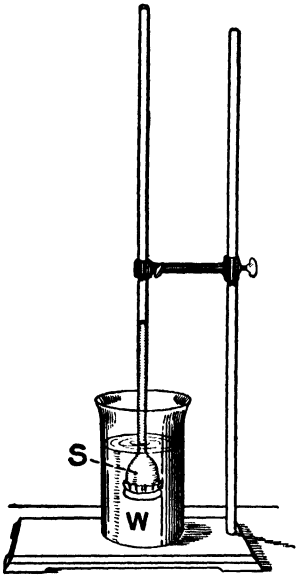


FIG. 143.

sulphate of about equal strength. Thus the precipitate forms in the pores of the septum: —

$$K_4Fe(CN)_6 + 2\,CuSO_4 = 2\,K_2SO_4 + Cu_2Fe(CN)_6.$$

By forming this precipitate in the pores of a small unglazed porcelain cup C (Fig. 144), the plant physiologist, Pfeffer, in 1877, measured the maximum osmotic pressure of dilute cane sugar solutions of several concentrations at a number of different temperatures. Figure 144 shows the cell, with manometer M attached, immersed in the large glass dish filled with water. T and T' are thermometers. In 1887 van't Hoff showed that Pfeffer's results indicate that the osmotic pressure is proportional to the absolute temperature, and that the osmotic pressure of the sugar solution is the same as the gas pressure that would be produced if the sugar were in the gaseous state and confined in the same volume that the solution occupies. In other words, van't Hoff showed that *when dilute aqueous cane sugar solutions are separated from water by means of copper ferrocyanide membranes, the osmotic pressures developed may be represented by the gas equation* $PV = RT$, where P is the osmotic pressure measured, V the volume of the solution, T the absolute temperature, and R the usual gas constant. More recently, Morse, also using copper ferrocyanide membranes, showed by similar, though far more elaborate, experiments that aqueous cane sugar solutions do develop osmotic pressures that approxi-

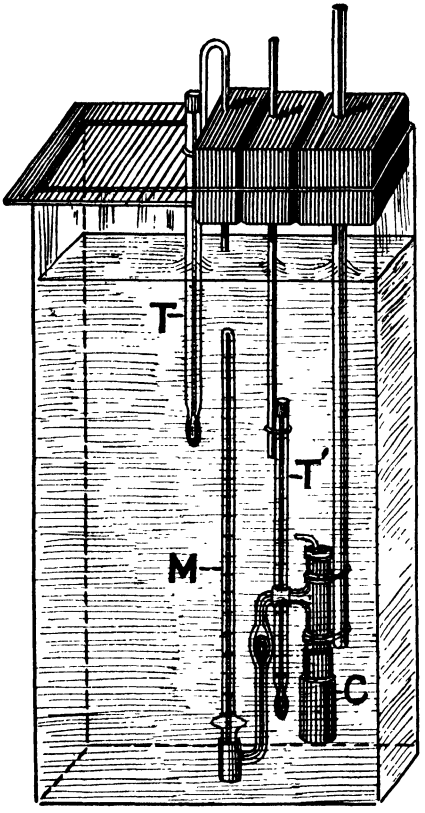


FIG. 144.

mately follow the gas laws. On the other hand, in 1906, Kahlenberg found that vulcanized caoutchouc, so-called sheet rubber, acts as a semipermeable membrane when used to separate cane sugar solutions in pyridine from pure pyridine. Moreover, the osmotic pressures measured in pyridine solutions thus far indicate that here the gas laws do not hold at all. Experimental osmotic investigations are still being pursued at the present time, and it is to be hoped that they will cast more light upon the laws that regulate osmotic pressure in the various cases. The subject is by no means as simple as it was formerly regarded by physical chemists, for specific selective action on the part of the so-called semipermeable membrane comes strongly into play.

Solutions having the same freezing or boiling point are frequently termed **isosmotic** *or* **isotonic**, for they are said to have the same osmotic pressure. The latter is sometimes computed on the basis of the assumption that the gas laws hold universally for osmotic pressures of all solutions, provided that the membrane is semipermeable. This assumption is, however, not justified by known experimental facts. Indeed, in speaking of the osmotic pressure of a solution it is always necessary to specify what membrane separates that solution from the pure solvent. A more detailed consideration of osmotic processes belongs to the subject of physical chemistry.

Electrolysis. — *There are two kinds of conductors of electricity:* (1) *those that show no chemical change as electricity passes through them, and* (2) *those that conduct with concomitant chemical decomposition.* To the **conductors of the first class** belong all metals, alloys, and graphite. A few other solids, like lead peroxide, manganese peroxide, pyrite, and other native sulphides and arsenides also conduct slightly and probably without decomposition. Those conductors that are decomposed chemically by the electric current are said to conduct electrolytically. They are called **electrolytes** or **conductors of the second class.** To this class belong many metallic oxides, hydroxides, sulphides, chlorides, nitrates, sulphates, carbonates, and silicates, as well as other salts of metallic bases, when these compounds are in molten condition. Some of these substances even conduct electrolytically to an appreciable degree before they are actually molten. So, for instance, at room temperatures a

block of rock salt is a non-conductor; but on heating it strongly, it begins to conduct quite noticeably before it is actually melted. Again, the oxides of the earths are non-conductors at room temperatures, whereas at higher temperatures they conduct, as is well known in the case of the glower of the Nernst lamp. Water, alcohols, ethers, acids, esters, aldehydes, ketones, mercaptans, sulphur ethers, hydrocarbons and their halogen substitution products, fats, oils, waxes, pitch, resin, caoutchouc, and the chlorides, bromides, iodides, sulphides, oxides, and hydrides of non-metallic elements, *when pure* are practically all either exceedingly poor conductors or insulators, whether they are liquefied or not. On the other hand, *solutions* of many acids, bases, and salts in water, liquid ammonia, amines, liquid hydrocyanic acid, alcohols, esters, ketones, sulphur dioxide, etc., are very good electrolytes. *This is particularly the case with the ordinary acids, salts, and bases in aqueous solutions; but it would be quite wrong to think that electrolytic conduction is confined to aqueous solutions, for some non-aqueous solutions conduct quite as well and even better than those in which water is the solvent.* Furthermore, many salts when in the liquid condition or in solution are insulators. So the oleates, palmitates, and stearates of the heavy metals are insulators whether solid, molten, or dissolved, though, to be sure, they do not happen to dissolve in water. Pure tetrachloride of tin $SnCl_4$ is an insulator at all temperatures from its freezing point to its critical temperature. The analogous chlorides, $SiCl_4$, $TiCl_4$, and CCl_4, are also insulators. Since the days of Michael Faraday (1791–1867), who first investigated the subject, a large amount of data on electrolytic conductors has been gathered, and yet *no way has been found to foretell with certainty whether a new compound will prove to be a conductor or not. The only way is to actually test the compound with the electric current itself.*

All highly rarefied gases conduct electricity; and in some gases, like hydrochloric acid, for instance, this conductivity has been found to be accompanied with chemical decomposition. Electrolysis was discovered in 1800 by Nicholson and Carlisle, who decomposed water by means of the electric current. This new means of effecting chemical decomposition was studied by Berzelius and Hisinger, Sir Humphry Davy, and especially by

Faraday. The latter called substances that can be decomposed by the electric current *electrolytes;* while the process of such decomposition he named *electrolysis.* In electrolysis two plates, usually consisting of metal or conducting carbon, dip into the electrolyte. These plates Faraday termed the *electrodes.* The plate from which the positive current passes into the electrolyte he called the *anode,* and the other electrode, by which the current leaves the electrolyte, he called the *cathode.* It is a remarkable fact that the products of decomposition first appear right on the surface of the electrodes. As these products are eliminated or produced at the electrodes, the corresponding material in the electrolyte is continually moving towards the electrodes. The particles which thus move towards the electrodes during electrolysis Faraday termed the *ions.* Those particles that move towards the anode he termed *anions,* and those that move towards the cathode the *cations.* To Faraday, the simplest conceivable case of electrolysis consisted of two silver electrodes dipping into molten silver chloride. As a current passes through this electrolyte, silver is deposited on the cathode, and chlorine is simultaneously produced at the anode, which is thus at once attacked, forming silver chloride. Thus, while the cathode is increasing in thickness, the anode is wearing away. This process is, of course, accompanied by a continuous movement of the cations, silver, toward the cathode, and of the anions, chlorine, toward the anode. If the anode consisted of carbon, the chlorine would appear as a gas. Now, why should molten silver chloride thus conduct electrolytically and molten tetrachloride of tin not? This is a question which we cannot yet answer, any more than we can tell why a piece of silver conducts electricity and a piece of sulphur is an insulator. In solutions, electrolysis is precisely the same as in molten electrolytes, though, to be sure, the products eliminated at the electrodes in solutions react with the electrolyte more frequently because of the more complex nature of the latter. So, on electrolysis of an aqueous sodium sulphate solution, hydrogen appears at the cathode and oxygen at the anode. This is because the sodium eliminated at the cathode at once reacts with the water, forming caustic soda and hydrogen, which is consequently a secondary product. If a mercury cathode is used, the sodium liberated dissolves in the latter and no hydro-

gen appears. At the anode SO_4 is liberated, which, however, at once reacts with water, yielding sulphuric acid and oxygen, which is consequently of secondary origin, like the hydrogen at the cathode.

In 1833 Faraday demonstrated that *the passage of the electric current through an electrolyte is always accompanied by the appearance of decomposition products at the electrodes, and that the amount of such decomposition is proportional to the current.* Furthermore, he found that *chemically equivalent amounts of substances are separated out from different electrolytes by the same amount of current.* These facts are commonly known as **Faraday's law.** *They are fundamental in all electrolytic work.* Faraday tested his law on molten electrolytes as well as on aqueous solutions, and its validity has since been confirmed by many careful investigations. In 1900 Kahlenberg showed that the law holds also in non-aqueous solutions. A current of 1 ampere will effect the deposition of a gram-equivalent of a substance in 96,540 seconds; that is to say, whenever 96,540 coulombs of electricity pass through an electrolyte, a gram-equivalent of decomposition product is deposited at each electrode. The quantity 96,540 coulombs is known as the **constant of Faraday's law**; it is now generally called a faraday.

Electrolytic Theories. The Grotthus Theory. — The first explanation of the process of electrolysis was made by Grotthus, in 1805. He assumed that each molecule of an electrolyte possesses electrical polarity similar to that of a magnet, and that these molecules are irregularly distributed throughout the electrolyte. On closing the electric circuit, the + poles of the molecules would be attracted by the − electrode, and the − poles of the molecules by the + electrode. Thus the molecules in the electrolyte would all arrange themselves with their + poles directed toward the − electrode, and their − poles toward the + electrode. The molecules in actual contact with the electrodes were then conceived as decomposed by the attraction of the + electrode for the − part of the molecule, and of the − electrode for the + part of the molecule. So with molten silver chloride as electrolyte between two platinum electrodes (Fig. 145), after closing the circuit, the arrangement would be as shown in line (1). A moment later silver would be deposited at *C* and chlorine at *A*, and line (2) would represent the

condition of the remaining molecules. A general decomposition all along the line would then take place, so that the arrangement in line (3) would result. Then these molecules would turn on an axis, their − poles heading toward the + electrode,

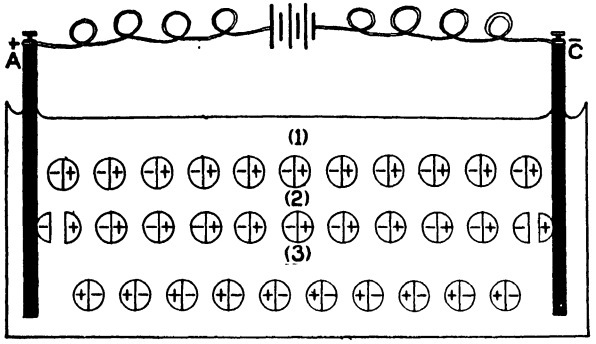


FIG. 145.

and the + poles toward the − electrode, as in line (1), after which the whole process would repeat itself.

Faraday's View. — This mechanical explanation of Grotthus held its own for over half a century, though Faraday protested that any explanation that the molecules were rent asunder by an attraction of the electrodes for the molecules was untenable. According to Faraday, all that can be maintained is that the electric current acts as an axis of force, ejecting the decomposition products at the electrodes, which simply serve as doors for the exit of the products.

Clausius's Theory. — In 1856 Robert Clausius called special attention to the fact that the theory of Grotthus does not explain why a small electro-motive force suffices to send an appreciable current through an electrolyte, though, to be sure, such current might pass for but a short time. It was at the time when the kinetic theory of gases and the mechanical theory of heat were taking form. In these theories Clausius was interested. He consequently naturally assumed the molecules of an electrolyte to be in motion due to heat, just as the molecules of a gas are supposed to be in motion. He further stated that sometimes some of the molecules would collide in such a way that the basic and acid radicals of two different molecules would unite to form a new molecule, thus leaving a basic and an acid radical in an uncombined or free state for

a moment. At any instant, then, there would be a certain number of free positive basic radicals and free negative radicals, and these would be separated at the electrodes by electrical attraction, as Grotthus explained. However, Clausius did not assume that the molecules ever arranged themselves definitely in the electrolyte. He thought that the electric current merely directed the general trend of the decomposition within the electrolyte. Moreover, Clausius held that the free, or undecomposed, parts of an electrolyte would at any moment not amount to more than a small fraction of 1 per cent. This distinguishes Clausius's theory from that of Arrhenius.

Arrhenius's Theory. — The theory of Arrhenius, also known as the **theory of electrolytic dissociation**, and frequently nowadays designated as the **ionic theory**, is founded upon a supposed connection between the vapor tensions, boiling points, or freezing points of dilute solutions of electrolytes, on the one hand, and their electrolytic conductivity on the other hand. In 1887 Arrhenius published a series of data intended to show that dilute solutions of electrolytes lower the freezing point to a much greater extent than similar solutions of non-electrolytes containing equimolecular quantities, and that consequently the solutions that conduct the current must contain relatively more dissolved molecules; that is, the latter must be dissociated. Because this dissociation is supposed to occur in electrolytes, it has been named **electrolytic dissociation**. Arrhenius assumes that when an acid, base, or salt is dissolved, yielding a solution that conducts the current, the molecules of the dissolved substance are by the very act of solution decomposed into part molecules, which are charged with electricity, thus: —

$$HCl \rightleftarrows \overset{+}{H} + \overset{-}{Cl}.$$

$$NaOH \rightleftarrows \overset{+}{Na} + \overset{-}{OH}.$$

$$NaCl \rightleftarrows \overset{+}{Na} + \overset{-}{Cl}.$$

$$H_2SO_4 \rightleftarrows \overset{+}{H} + H\overset{-}{SO_4} \text{ or } \overset{+}{H} + \overset{+}{H} + \overset{-}{\overset{-}{SO_4}}.$$

$$CuSO_4 \rightleftarrows \overset{+}{\overset{+}{Cu}} + \overset{-}{\overset{-}{SO_4}}.$$

$$AgNO_3 \rightleftarrows \overset{+}{Ag} + \overset{-}{NO_3}, \text{ etc.}$$

In each case the dissociation from left to right is supposed to be complete in *infinitely dilute solutions*. At any *finite* concen-

tration the solution contains a certain percentage of undissociated molecules and a certain percentage of charged part molecules. The latter according to Arrhenius are the only particles in the solution that are active in conducting the current. He calls these part molecules the ions, and conceives each gram-equivalent of cations charged with 96,540 coulombs of positive electricity and each gram-equivalent of anions charged with the same amount of negative electricity, postulating further that any conducting solution contains equivalent amounts of cations and anions. It will be observed that in the Arrhenius theory the word *ion* is used in a different sense from that proposed by Faraday, who regarded the ions as the substances that migrate toward the electrodes during actual electrolysis, not as part molecules charged with electricity which are at all times present in an electrolyte. The explanation of the passage of the electric current through an electrolyte on the basis of Arrhenius's theory is simple, consisting merely of the movement of the free charged cations and anions toward the cathode and anode respectively, under the influence of the impressed electro-motive force (Fig. 146). This explanation is then essentially the same

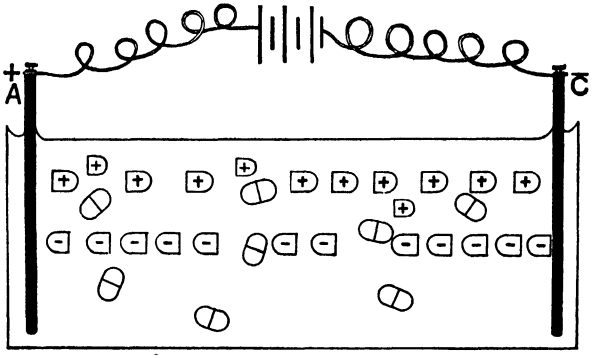


FIG. 146.

as that given by Clausius. Indeed, the main difference between the Clausius and Arrhenius theories is that the latter assumes the presence of a very much larger percentage of dissociation, and claims this may be computed from either conductivity or freezing point or boiling point measurements of dilute solutions.

According to Arrhenius's theory all the physical, chemical, and physiological properties of solutions that are electrolytes are

determined by the properties of the undissociated molecules of solute and those of the ions. The latter are the chief factor in dilute solutions where dissociation has often progressed to the extent of 80 per cent or more. Thus, the adherents of this theory hold that copper ions are blue, cobalt ions are red, MnO_4 ions are purple, sodium ions are colorless, etc., since aqueous solutions of copper salts are blue, those of cobalt are red, those of permanganates purple, and those of sodium chloride, etc., colorless. Again, the sour taste and other acid properties of electrolytic solutions of acids would be due to hydrogen ions, and the alkalinity of caustic alkali solutions to hydroxyl ions. Indeed, *in terms of the theory of electrolytic dissociation an acid would be defined as a substance capable of yielding hydrogen ions, while a base would be a substance capable of yielding hydroxyl ions.* Moreover, the act of neutralization in dilute solutions would consist essentially of the union of hydrogen and hydroxyl ions to form undissociated water, thus: —

$$\overset{+}{K}, \overset{-}{O}H + \overset{+}{H}, \overset{-}{Cl} = \overset{+}{K}, \overset{-}{Cl} + H_2O.$$

Since $\overset{+}{K}$ and $\overset{-}{Cl}$ appear on both sides of the equation, the latter might even be written: —

$$\overset{-}{O}H + \overset{+}{H} = H_2O.$$

In the chapter on thermochemistry it has been stated that the heat of neutralization of strong acids by strong bases is approximately the same for all. This fact clearly would readily be explained by the above assumption that the neutralization in all cases consists essentially of a union of $\overset{+}{H}$ and $\overset{-}{O}H$. On the other hand, it is to be noted that the heats of neutralization of some of the weaker acids, like oxalic and acetic acids, are nearly the same as that of hydrochloric acid; though according to the theory, the latter is far more highly dissociated.

Again, the fact that two solutions of neutral salts which form no precipitate when mixed also exhibit no change of temperature on being poured together (so-called **law of thermoneutrality of Hess**) is readily explained by Arrhenius's hypothesis, for there would be no action to occasion a thermal effect. However, when similar salt solutions that are non-electrolytes are mixed, there is also no thermal effect.

Precipitation in electrolytic solutions by double decomposi-

tion is explained on the basis of the Arrhenius theory by saying that certain ions meet to form insoluble compounds. The precipitation of silver chloride when silver nitrate and common salt solutions are brought together would be expressed as follows: —

$$\overset{+}{Ag}, \overset{-}{NO_3} + \overset{+}{Na}, \overset{-}{Cl} = \overset{+}{Na}, \overset{-}{NO_3} + AgCl.$$

In other words, the chlorine ions and silver ions meet to form neutral silver chloride, which is difficultly soluble. Since all conducting chloride solutions are supposed to contain free chlorine ions, it is clear that these would all precipitate silver chloride from solutions of silver salts that contain silver ions. Similarly, the fact that barium sulphate is precipitated when a solution of a barium salt and one of a soluble sulphate are brought together finds a ready explanation, etc. At one time the view was even advocated that all chemical reactions, or at least those that take place instantaneously, occur only between free ions, that is to say, they occur only in electrolytes.

Now the fact is that *all chemical reactions known to occur in solutions that are electrolytes can be reproduced, as to type, in solutions that are the best of insulators.* So, for instance, from copper oleate solutions in hydrocarbon oils, brown cupric chloride is instantly precipitated by adding any of the following chlorides, also dissolved in the same hydrocarbon: HCl, PCl_3, $SnCl_4$, $SiCl_4$, $SbCl_3$, etc., though these solutions are all non-electrolytes. Lead will precipitate copper from insulating copper oleate solutions just as zinc precipitates copper from aqueous copper sulphate solutions. Furthermore, the colors exhibited, for example, by solutions of copper oleate, cobalt oleate, nickel oleate, etc., each dissolved in a hydrocarbon like benzene, toluene, etc., are entirely similar to the colors of aqueous electrolytic solutions of copper and cobalt salts respectively. In fact *all the physical and chemical properties exhibited by salt solutions that are electrolytes can be duplicated in salt solutions that are insulators, except the phenomena of electrolysis themselves.*

But the distinguishing feature of Arrhenius's theory is the claim that there is a quantitative relation between lowering of the freezing point or elevation of the boiling point and the electrical conductivity of solutions. It must be stated that the numerous cases thus far adduced to support this claim are not

at all conclusive, for they show variations that are far beyond the limits of experimental errors. Furthermore, solutions of magnesium sulphate as well as those of all the other vitriols are good electrolytes, whereas according to the freezing points of their solutions they ought to be non-electrolytes. Again, soap solutions boil at practically the same temperature as water, yet they conduct electricity well. And so numerous other cases might be cited, the field of non-aqueous solutions being especially replete with such. It should be stated that the behavior of electrolytes is in general not in harmony with the law of mass action, as ought to be the case if Arrhenius's theory were tenable.

A more detailed account of this interesting theory cannot be given here, for it belongs to the subject of physical chemistry. Suffice it to say that, taking all known facts into consideration, the theory of Arrhenius is in the author's opinion untenable. This view was also clearly voiced by Mendeléeff in the last edition of his great work on the "Principles of Chemistry," when, referring to the theory of electrolytic dissociation, he said, "I do not consider the hypothesis in question to be in accordance with fact, and therefore refrain from giving a detailed exposition of it in this work." The reader will have no difficulty in comprehending books that still use the nomenclature of the theory of electrolytic dissociation by remembering that the term *ion* as used in expressing chemical changes means the same as atom or radical, the atoms or radicals being simply thought of as charged with electricity, as already explained.

The **electron theory** considers electricity itself to be material in character and to consist of corpuscles or electrons that weigh about 0.0005 as much as a hydrogen atom. This theory has developed from a study of radium rays and the discharge of electricity through rarefied gases. The electrons are considered to be negative electricity itself. Positive electrons appear to be much more difficult to isolate. J. J. Thomson has advanced a theory that the atoms of the various elements are composed entirely of electrons, and has shown that, on the basis of such an assumption, the properties of the elements would exhibit periodicity as indicated by the periodic system. The electron theory has thus far not proved to be of special value in chemistry.

Electric Batteries are contrivances for converting chemical energy into electrical energy. So when a zinc plate and a

graphite plate are dipped into dilute sulphuric acid, as shown in Fig. 147, zinc dissolves and hydrogen is liberated on the graphite; while at the same time an electric current passes through the solution from the zinc to the graphite and from the latter through the wire to the zinc. Some hydrogen also appears at the zinc, though in very small amounts if the zinc is pure or if it is amalgamated. The chemical action that takes place is:—

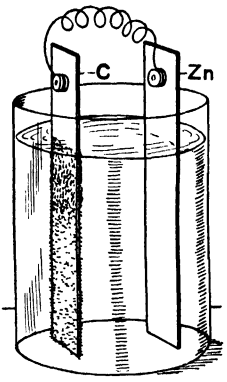


FIG. 147.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

But the zinc dissolves at one plate and the hydrogen appears at the other, while in the middle of the electrolyte there is no visible change for some time. The explanation of the passage of the current through the electrolyte is the same as in the case of electrolysis. In a battery, however, no external electro-motive force is used to force the current through the electrolyte. Batteries develop electro-motive force of their own because of the chemical affinity that comes into play; and *the electrical energy developed by batteries comes from the energy of the chemical changes that take place while the battery is in action.* The cell above mentioned will exhibit an E. M. F. of about 1.3 volts, which on closed circuit soon drops rapidly because of the accumulation of hydrogen on the graphite, for this hydrogen-laden plate produces a counter E. M. F. Any two different conductors of the first class dipping into an electrolyte will show an E. M. F. when connected with a voltmeter as shown in Fig. 148. A complete consideration of electric batteries belongs to the subject of electro-chemistry and cannot be entered into here.

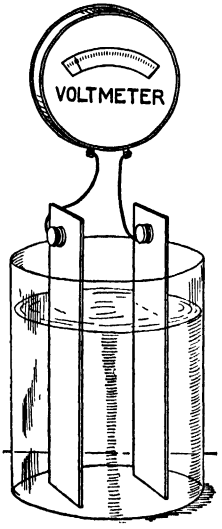


FIG. 148.

The ordinary batteries used for ringing doorbells consist of zinc and carbon dipping into a concentrated solution of ammonium chloride. As the battery acts, zinc is

dissolved, forming zinc chloride, while hydrogen is liberated on the carbon, thus: —

$$Zn + 2\,NH_4Cl + 2\,H_2O = ZnCl_2 + 2\,NH_4OH + H_2.$$

The ammonium hydroxide forms at the carbon. As these batteries are used only occasionally, and then only for a short time, this hydrogen ordinarily escapes while the battery is at rest, thus prolonging its life and usefulness. The **dry batteries** in use commonly consist of zinc, ammonium chloride solution, and carbon, the latter being surrounded with coarsely powdered manganese dioxide which serves to oxidize the hydrogen liberated. These batteries are not perfectly dry, as their name would indicate, but they contain enough plaster of Paris to solidify their contents.

Another battery, which frequently is used in telegraphic work, consists of zinc dipping into dilute sulphuric acid, and copper surrounded by a saturated solution of copper sulphate. The two solutions, being of different density, are kept separate by gravity (Fig. 149). The battery must be kept in use all the time, however, or the solutions will diffuse into each other, and the copper sulphate solution will reach the zinc and react with it, forming zinc sulphate and copper, which by coating the zinc would spoil the battery. The E. M. F. of this battery, known as the **blue cup battery**, is about 1.1 volts.

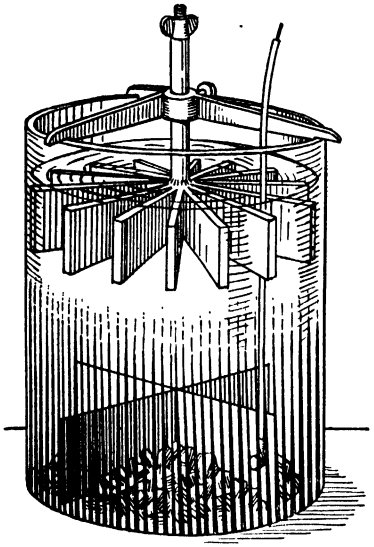


FIG. 149.

The ordinary **storage battery** consists of two lead plates, one of which is coated with lead peroxide, dipping into a solution of sulphuric acid of 1.2 specific gravity. As the battery acts, lead sulphate is formed. The complete change may be represented thus: —

$$Pb + H_2SO_4 = PbSO_4 + 2\,H, \text{ and}$$

$$PbO_2 + 2\,H + H_2SO_4 = PbSO_4 + 2\,H_2O; \text{ or}$$

$$Pb + 2\,H_2SO_4 + PbO_2 = 2\,PbSO_4 + 2\,H_2O.$$

At the cathode lead dissolves, while at the anode the hydrogen liberated reduces the lead peroxide, which is then acted upon by sulphuric acid, forming lead sulphate. The E. M. F. of the storage cell is about 2 volts. When in use its voltage decreases. When the E. M. F. has run down to 1.8 volts, the battery should be recharged. This is done by passing a current from a dynamo through the cell in the opposite direction from that produced by the battery when in action. In the charging process the reactions just given are reversed; that is, lead is deposited at the cathode and lead peroxide is formed at the anode.

Electro-chemical Series of the Metals. — If in the battery zinc, dilute sulphuric acid, carbon (Fig. 147), the zinc be replaced successively by iron, copper, silver, and gold, the voltage will diminish. The order in which the metals are mentioned is the same as that in which they will replace one another in solutions of their salts. All of the metals may thus be arranged in a series, beginning with the most basic, and ending with the least basic; or, as it is sometimes stated, beginning with the most electro-positive metal and ending with the least electro-positive. Such a series is called the electro-chemical series of the metals. The series varies somewhat for different solutions, but the usual order for the common metals is about as follows: K, Na, Ba, Sr, Ca, Mg, Al, Mn, Zn, Cd, Fe, Co, Ni, Pb, Bi, Sb, Sn, Cu, Hg, Ag, Pt, Au. This is also called arranging the metals in the order of their *electrolytic solution tensions* by those who think of the metals as having a tension or tendency to form ions in the sense of the theory of Arrhenius.

The ease with which the metals are separated from electrolytes by electrolysis is in the reverse order of that given above.

REVIEW QUESTIONS

1. What is the difference between a solution and a mechanical mixture? Illustrate by giving five examples of each.

2. In what respects does a solution differ from a chemical compound? Give three examples of each by way of illustration.

3. What are the factors that determine the amount of a gas that will be absorbed by a given liquid? Give a concrete example. State Henry's law and discuss its exceptions.

4. Why is a solution of hydrochloric acid gas in water heavier than water and a solution of ammonia gas in water lighter than water?

5. What is meant by the term "solid solution"? Give three examples of solid solutions.

6. What are consolute liquids? Give six examples.

7. What determines the solubility of one liquid in another? Of a solid in a given liquid?

8. What is the difference between a solution and an emulsion?

9. What is a solubility curve? What fact does it show?

10. Compare supercooled liquids with supersaturated solutions. Examples.

11. Given a 20 per cent solution of cane sugar in water; describe two essentially different methods of obtaining solid sugar from the solution.

12. Give three different methods by means of which solid salt may be obtained from a 15 per cent solution of common salt. Explain each case.

13. How does a solution of barium chloride react with one of sodium sulphate? Write the equation. Compare this case of precipitation with those you have described in answer to questions 11 and 12.

14. Mention two distinctly different methods of obtaining hydrochloric acid gas from a concentrated aqueous solution of that substance.

15. How form a solution of colloidal gold? Mention four other colloidal solutions. How do they differ from ordinary solutions?

16. Mention three methods of determining the molecular weight of grape sugar in solution. What results would be obtained if these methods were applied to: (*a*) a solution of common salt, (*b*) a solution of Epsom salt, (*c*) a soap solution? Explain these peculiar results from the standpoint of the theory of Arrhenius. What other explanation may be given?

17. Define osmosis and osmotic pressure, giving an illustration of each.

18. What are isotonic solutions?

19. Distinguish between conductors of the first class and conductors of the second class and give ten illustrations of each.

20. Define the following terms: electrolyte, electrolysis, electrode, cathode, anode, ion, cation, anion. Give an example in each case.

21. What is Faraday's law?

22. Explain the electrolysis of a copper chloride solution by: (*a*) the Grotthus theory, (*b*) the Clausius theory, (*c*) the Arrhenius theory.

23. State the essential features of the theory of electrolytic dissociation. By what other name is this theory also known? Using this theory, write the equations expressing the following reactions: (*a*) the neutralization of nitric acid by sodium hydroxide, (*b*) the precipitation of lead sulphate by pouring together solutions of lead nitrate and potassium sulphate, (*c*) the precipitation of silver iodide, by mixing solutions of potassium iodide and silver nitrate.

24. Upon what facts is the theory of Arrhenius based? What objections are there to this theory?

25. What is the so-called electron theory?

26. What is an electric battery? Give four concrete illustrations.

27. What is the essential difference between a primary battery and a storage battery? What happens when a lead storage battery is charged?

28. What is meant by the term electrochemical series of the metals?

29. How much copper would a current of one ampere precipitate from a copper sulphate solution in ten hours? How much silver would be precipitated by this current?

30. How much zinc is required to precipitate ten grams of silver from a silver nitrate solution?

CHAPTER XXV

COPPER, SILVER, AND GOLD

COPPER, silver, and gold occur in nature in the uncombined state, and consequently have been known to man since earliest times. These metals have a high specific gravity, are very malleable and ductile, and most excellent conductors of heat and electricity. The atomic weights of the elements of this group are relatively high: Cu, 63.57; Ag, 107.88; Au, 197.2. Chemically these metals are rather inert, and their chemical activity decreases as the atomic weight increases. Like mercury, copper forms two series of compounds, the *cuprous*, in which copper is univalent, and the *cupric*, in which it is bivalent. Silver is practically always univalent in its compounds. Gold, on the other hand, forms *aurous* compounds, in which the metal is univalent, and *auric* compounds, in which it is trivalent. The compounds of copper, silver, and gold in which these metals are univalent are analogous to those of the alkali metals, which are also univalent. On the other hand, copper in cupric compounds, in which it is bivalent, is analogous to mercury in mercuric compounds. Copper and gold are the only colored metals known. Copper, silver, and gold are used in all civilized countries in making coins.

Occurrence, Metallurgy, and Properties of Copper. — In the uncombined condition copper is found in large quantities near Lake Superior. It also occurs in the Urals, in Sweden, Japan, and China. Large amounts of chalcocite or copper glance Cu_2S, chalcopyrite or copper pyrites $Cu_2S \cdot Fe_2S_3$, and bornite $(Cu_2S)_3Fe_2S_3$ occur in Montana, where they are mined and smelted for copper. Other important copper ores are ruby copper Cu_2O, malachite $CuCO_3 \cdot Cu(OH)_2$, and azurite $Cu(OH)_2 \cdot 2\,CuCO_3$. Malachite occurs especially in Siberia. In extremely small amounts copper compounds are also sometimes found in plants and animals. Thus, in plants growing in copper-bearing regions, copper is frequently met; similarly

in oysters; also in the feathers of some birds, like those of the genus *turacus*.

In extracting copper from its ores, the process is simple when the ores are oxides or carbonates, for then all that is necessary is to heat the ore with coke or coal in a blast furnace; the reaction involved is: —

$$Cu_2O + C = 2\,Cu + CO.$$

But if the ores contain sulphides, which is commonly the case, the process is much more difficult, for iron and other impurities, like lead, arsenic, and antimony, besides sulphur, must be eliminated. For ores rich in copper a dry process is used, whereas for ores that have a low copper content the wet process is commonly adopted.

In the **dry process**, the ores are roasted to convert most of the sulphides into oxides. In this way, sulphur burns to sulphur dioxide, and iron to iron oxides to a large extent. The mass is then mixed with carbon and silicates rich in silica, and heated in a blast furnace. Thus iron enters the slag as a silicate, which floats on top and is tapped off. In the process, copper oxides are reduced, the copper formed uniting with any sulphides still present, forming a heavy liquid which accumulates at the bottom of the furnace. This liquid is run off, frequently into water so as to granulate the product, which is called **copper matte**, and consists mainly of copper and iron sulphides containing about 33 per cent copper. This copper matte is then roasted, and again melted with silicates and carbon. Thus more iron is removed as silicate, and copper and other oxides are reduced to metal containing 90 to 95 per cent copper. This product is then melted on the hearth of a furnace in a current of air, whereby metals like iron, arsenic, lead, and antimony are oxidized before copper, and these oxides either pass off as vapors or float on the surface and are removed. The copper is also slightly oxidized, and this oxide reacts with any cuprous sulphide left over, forming copper and sulphur dioxide, thus: —

$$Cu_2S + 2\,CuO = 4\,Cu + SO_2.$$

Finally, by adding carbon, any further copper oxide is reduced to metal. Bessemer converters (which see) are sometimes used in effecting the oxidation of the ores or the copper matte.

Air containing sand or other finely divided silicates is blown into these converters containing the molten matte. Thus the process above described is conducted in practically one operation.

In the **wet process**, ores low in copper, like oxidized pyrites residues from sulphuric acid factories, are roasted with common salt, thus forming cupric chloride, which is leached out with water. From the clear solution, copper is precipitated by scrap iron, thus: —

$$CuCl_2 + Fe = FeCl_2 + Cu.$$

Or the ores are moistened with water and exposed to the air; thus ferric sulphate gradually forms, in a solution of which copper is soluble. This solution is then treated with scrap iron to precipitate the copper. The supernatant solution, consisting essentially of ferrous sulphate, is again poured upon fresh ore, and so on.

Electrolysis is used in **copper refining**. The impure copper from the above processes is melted and cast into thick plates. These serve as anodes, a copper sulphate solution is used as the electrolyte, and thin copper plates serve as cathodes. The copper is easily eroded from the anode and deposited on the cathode. As the process virtually consists of simply transferring copper from anode to cathode, an E. M. F. below one volt is sufficient to keep the current flowing. The deposited copper is stripped off from the cathodes when they have become sufficiently thick. As the impure copper anodes are dissolving, the impurities, like copper sulphide, silver, gold, bismuth, and lead, fall to the bottom of the vats, forming a thick mud or slime, from which the two precious metals mentioned are separated. Electrolytically refined copper is in a high state of purity. Its malleability, ductility, and electrical conductance are much greater than that of impure copper.

The United States produces about 620,000 tons of copper each year, which is nearly two thirds of the world's annual output.

Copper is a rather hard, tough, very ductile and malleable metal of reddish brown color and high metallic luster. It may be crystallized in regular octahedra or cubes. In dry air it remains unchanged. In moist air it gradually becomes coated with a greenish basic copper carbonate known as **verdigris**. The specific gravity of copper is 8.94. Its melting point is 1084°,

and its boiling-point 1500°. Just below its melting point copper becomes so brittle that it may be pulverized. At red heat it may be welded. Molten copper absorbs gases like carbon monoxide, hydrogen, and sulphur dioxide, which are given off with some violence on cooling. Copper is readily oxidized by heating it in the air. It imparts a green color to the Bunsen flame. In dilute sulphuric acid, copper is insoluble, but the hot concentrated acid attacks it, forming copper sulphate, sulphur dioxide, and water. In dilute nitric acid copper is readily soluble: —

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO.$$

Cold hydrochloric acid is practically without action on copper, but the hot concentrated acid attacks the metal somewhat, hydrogen and cuprous chloride being formed. Ammonia water slowly dissolves copper in contact with air. The deep blue solution thus obtained, known as **Schweitzer's reagent,** *is a good solvent for cellulose.* Many dilute acids also gradually act on copper, in presence of oxygen or air, which fact is important, since copper compounds are poisonous and copper is often used in making cooking pots, kettles, and other utensils. Large quantities of copper are used for electric wires and cables, for covering the bottoms of ships, for coins, for roofing and architectural ornamentation, for electroplating, and for a number of important alloys. *Copper salts are important as germicides in agriculture.* From solutions of its salts, copper is precipitated by magnesium, zinc, iron, phosphorus, and various other reducing agents.

Alloys of Copper. — Most of the copper produced is used in the form of alloys. Pure copper does not make good castings, for on cooling it contracts and does not fill the molds. Many alloys of copper, however, are excellent for making castings, and they are constantly of very great importance. The alloys are made by melting the metals together in the proportions required. Copper readily forms alloys with most of the metals. Among the most important of these alloys are the following:—

Brass is a golden yellow alloy consisting of 2 parts copper and 1 part zinc. Other proportions may be used, however; thus 5 parts copper and 1 part zinc yield a reddish brass known as **tombac, Dutch brass,** or **Dutch metal. Muntz metal** contains

3 parts copper and 1 part zinc. The larger the content of zinc, the paler the color of the brass obtained; the varieties of brass on the market commonly contain from 18 to 50 per cent zinc. Brass is harder than copper. It is nevertheless malleable and ductile and makes good castings. It can also readily be worked in a lathe. **German silver** consists of about 80 to 95 per cent brass plus 5 to 10 per cent nickel.

Bronzes are alloys of tin and copper. **Gun metal** consists of about 9 parts copper and 1 part tin; bell metal of 3 parts copper and 1 part tin. Many bronzes also contain some zinc and lead. This is particularly the case with bronze used for statuary, which consists of from 80 to 90 parts copper, 3 to 8 parts tin, 1 to 3 parts lead, and 1 to 10 parts zinc. Bronze used in machinery commonly contains rather more lead than this, and correspondingly less copper. **Phosphor bronze** is bronze to which from 0.5 to 3 per cent phosphorus has been added. It is particularly hard, and is often used in making machinery. **Aluminum bronze** consists of from 5 to 10 per cent aluminum and 90 to 95 per cent copper. It has a golden yellow color and is quite hard.

Oxides of Copper. — Cuprous oxide Cu_2O is obtained as one of the products of the incomplete oxidation of copper when the latter is slightly heated in the air. By reducing hot, alkaline solutions of cupric salts with glucose, cuprous oxide is readily obtained; also by heating cuprous chloride with sodium carbonate, thus: —

$$2\,CuCl + Na_2CO_3 = Cu_2O + CO_2 + 2\,NaCl.$$

Cuprous oxide is a bright red, crystalline powder which remains unchanged in the air. Dilute acids convert it into cupric salts and copper, thus: —

$$Cu_2O + 2\,HNO_3 = Cu(NO_3)_2 + H_2O + Cu.$$
$$Cu_2O + H_2SO_4 = CuSO_4 + H_2O + Cu.$$

Cuprous oxide is fused with glass to give the latter a red color.

Cupric oxide CuO is a black powder formed by heating copper in oxygen or in the air. It is also obtained by ignition of the nitrate or carbonate. *It readily gives up its oxygen when heated with carbon or carbon compounds; hence the use of cupric oxide in the analysis of organic compounds.*

Cuprous hydroxide is not known with certainty. **Cupric**

hydroxide $Cu(OH)_2$ is an amorphous, blue precipitate formed when caustic alkali is added to a solution of a cupric salt. The precipitate readily loses water on boiling it in the solution from which it has separated, thus forming a black hydrated oxide of approximately the composition $Cu(OH)_2 \cdot 2\,CuO$. In ammonia water cupric hydroxide is soluble, yielding the deep blue solution called Schweitzer's reagent. When treated with acids, cupric hydroxide yields cupric salts.

Halides of Copper. — **Cuprous chloride** CuCl is formed by boiling cupric chloride $CuCl_2$, with metallic copper and hydrochloric acid: —

$$CuCl_2 + Cu = 2\,CuCl.$$

The cuprous chloride separates out in the form of a white, finely crystalline powder, on dilution with cold water. Cuprous chloride is insoluble in water and also in alcohol; but it dissolves in hydrochloric acid or ammonia. *The hydrochloric acid solution absorbs carbon monoxide*, forming a product which separates from the concentrated solutions in unstable, shining scales that probably have the composition $CO \cdot Cu_2Cl_2 \cdot 2\,H_2O$. With ammonia, cuprous chloride forms the compound $Cu_2Cl_2 \cdot 2\,NH_3$. This ammoniacal solution also has the property of absorbing gases. In many ways, *cuprous chloride is analogous to mercurous chloride* HgCl, *silver chloride* AgCl, *and thallous chloride* TlCl.

Cupric chloride $CuCl_2$ is made by burning copper in chlorine, also by dissolving the metal in nitro-hydrochloric acid, or by treating cupric oxide, hydroxide, or carbonate, with hydrochloric acid. The anhydrous salt is brown. The aqueous solutions are bluish green, and from them green, rhombic, prismatic crystals, $CuCl_2 \cdot 2\,H_2O$, may be obtained. These readily dissolve in water or in alcohol. At 500° anhydrous cupric chloride melts, and on further ignition it may be converted into cuprous chloride. With ammonia, cupric chloride forms $CuCl_2 \cdot 6\,NH_3$, a dark blue, unstable powder. From aqueous ammoniacal solutions of cupric chloride, dark blue crystals of the composition $CuCl_2 \cdot 4\,NH_3 \cdot H_2O$ may be obtained. At about 150° these compounds are converted into $CuCl_2 \cdot 2\,NH_3$, which is a green powder.

Cuprous bromide CuBr, like cuprous chloride, is a white, insoluble powder. It may be melted without decomposition. **Cuprous iodide** CuI *is the only iodide of copper known.* It is

formed by heating copper and iodine together, also by adding potassium iodide to solutions of cupric salts: —

$$CuSO_4 + 2\ KI = K_2SO_4 + CuI + I.$$

The cuprous iodide so formed is thus precipitated together with free iodine. Cuprous iodide is a white, insoluble, crystalline powder. It may be melted at red heat. **Cuprous fluoride** CuF is also known. It is a bright red, insoluble powder.

Cupric bromide $CuBr_2$, like cupric chloride, is readily soluble in water, yielding green solutions. **Cupric fluoride** CuF_2 is also known, but cupric iodide CuI_2 is not known.

Cyanides of Copper. — When a solution of a cupric salt is treated with potassium cyanide, **cupric cyanide** $Cu(CN)_2$ is formed as a yellow unstable compound which at once decomposes into cuprous cupric cyanide and cyanogen, thus: —

$$CuSO_4 + 2\,KCN = Cu(CN)_2 + K_2SO_4, \text{ and}$$
$$3\,Cu(CN)_2 = Cu(CN)_2 \cdot Cu_2(CN)_2 + (CN)_2.$$

This reaction is frequently used in making cyanogen. **Cuprous cyanide** CuCN may be obtained as a white precipitate by adding potassium cyanide to a solution of copper sulphate saturated with sulphur dioxide. Potassium cyanide forms a soluble double cyanide with cuprous cyanide $CuCN \cdot KCN$. When potassium ferrocyanide is added to a solution of a cupric salt, **copper ferrocyanide** forms as a dark brownish red, hydrous, amorphous precipitate: —

$$2\,CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 2\,K_2SO_4.$$

Copper Salts of Oxy-acids. — *No cuprous salts of oxy-acids are known; in its salts with such acids, copper is always bivalent.* The following are the most important of these salts: —

Copper sulphate $CuSO_4$ is obtained by heating copper with concentrated sulphuric acid. On a commercial scale it is formed by heating copper pyrites, or copper plus sulphur, in a current of air, and lixiviating the mass with water and evaporating the clear solution, from which large, blue, triclinic crystals $CuSO_4 \cdot 5\,H_2O$, known as **blue vitriol**, are obtained (Fig. 75). *This is a very common copper salt.* On exposure to the air the crystals effloresce. At 100° they lose about four fifths of their water, but it requires about 200° to dehydrate them completely. The anhydrous salt is a gray-

ish white powder, insoluble in alcohol. It is hygroscopic, and is consequently sometimes used in the laboratory as a drying agent. Blue vitriol is soluble in about 3 parts of water. It is used in large quantities in copperplating, as a mordant in dyeing fabrics, as a source for the preparation of other copper compounds, and as a germicide, particularly in spraying plants to protect them from insect pests. Mixed with calcium hydroxide solution, copper sulphate forms the so-called **Bordeaux mixture**, which is often used in spraying fruit trees and other plants.

With alkali sulphates, copper sulphate forms double salts, like $K_2SO_4 \cdot CuSO_4 \cdot 6\,H_2O$. These are monoclinic and isomorphous with the analogous magnesium salts. *With ammonia, copper sulphate yields deep blue solutions* from which dark blue, orthorhombic crystals of the composition $CuSO_4 \cdot 4\,NH_3 \cdot H_2O$ are precipitated by adding alcohol. On heating this compound carefully, it may be converted into $CuSO_4 \cdot 2\,NH_3$, a green powder which is called **cuprammonium sulphate.** It is regarded as ammonium sulphate in which two hydrogen atoms are replaced by a bivalent copper atom, thus: —

$$SO_4 \begin{matrix} \diagup NH_3 \diagdown \\ \diagdown NH_3 \diagup \end{matrix} Cu.$$

Basic copper sulphates, of the formulæ $CuSO_4 \cdot Cu(OH)_2$, $CuSO_4 \cdot 2\,Cu(OH)_2$, and $CuSO_4 \cdot 3\,Cu(OH)_2$, have also been prepared.

Copper nitrate $Cu(NO_3)_2$ is formed by dissolving copper, cupric oxide, hydroxide, or carbonate in nitric acid. From the solutions the salt may be obtained in deliquescent crystals, $Cu(NO_3)_2 \cdot 6\,H_2O$. On heating the nitrate, it yields cupric oxide.

Copper Carbonates. — *Only basic carbonates of copper are known.* On adding an alkaline carbonate to a solution of a copper salt, a green **basic copper carbonate** $CuCO_3 \cdot Cu(OH)_2$ is formed, thus: —

$$2\,CuSO_4 + 2\,Na_2CO_3 + H_2O = 2\,Na_2SO_4 + CuCO_3 \cdot Cu(OH)_2 + CO_2.$$

This behavior is then analogous to that of zinc and magnesium salts when they are similarly treated with alkaline carbonates. **Malachite**, which, as already stated, occurs in nature,

is $CuCO_3 \cdot Cu(OH)_2$, and **verdigris**, which forms in the air on copper roofs, etc., is also basic copper carbonate. The mineral **azurite** forms monoclinic crystals of the formula, $Cu(OH)_2 \cdot 2\,CuCO_3$.

Copper Arsenite. — $Cu_3(AsO_3)_2 \cdot 2\,H_2O$ is a beautiful, green precipitate formed by adding potassium arsenite to a solution of copper sulphate. It is known as **Scheele's green** and is used as a pigment.

Sulphides of Copper. — **Cuprous sulphide** Cu_2S is formed by heating cupric sulphide or a mixture of copper and sulphur in a current of hydrogen, also by burning copper in sulphur vapors. It forms black crystals of the regular system. **Cupric sulphide** is obtained as a black precipitate by passing hydrogen sulphide into a solution of a copper salt. It is practically insoluble in water and also in dilute acids.

Analytical Tests for Copper. — In testing copper, the following characteristic reactions are generally used: —

An excess of ammonia yields deep blue solutions with copper salts. Potassium or sodium hydroxide precipitates blue cupric hydroxide, which turns black on boiling. Hydrogen sulphide produces a black precipitate, insoluble in dilute acids. Potassium ferrocyanide produces a reddish brown precipitate of copper ferrocyanide. Alkaline carbonates precipitate basic copper carbonate. Hydrogen sulphide does not precipitate copper sulphide from solutions of potassium cuprous cyanide; whereas, in a similar solution of potassium cadmium cyanide, yellow cadmium sulphide is precipitated, and thus copper may be separated from cadmium.

Occurrence, Metallurgy, and Properties of Silver. — In nature, silver frequently occurs in the uncombined condition, usually scattered in quartz and other rocks, in small amounts, though at times it is found in masses of a hundred pounds or more. Native silver generally is contaminated with other metals, like gold, copper, iron, and lead. It is frequently found in fairly well-developed crystals of the regular system. The most important ores of silver are argentite or silver glance Ag_2S, pyrargyrite or ruby silver ore $Sb_2S_3 \cdot 3\,Ag_2S$, proustite or light red silver ore $As_2S_3 \cdot 3\,Ag_2S$, and other complex sulphides of silver, copper, arsenic, and antimony. Horn silver AgCl and other halides of silver are occasionally found. Nearly all

galenite PbS contains some silver, and a considerable amount of silver is obtained from this source. The world's supply of silver comes mainly from the United States, Mexico, western South America, Australia, Germany, and Austria.

The extraction of silver from its ores is carried on by several processes; these vary according to the nature of the ore and the locality. The method of obtaining silver from ores rich in lead consists of roasting the ores to get rid of the sulphur, and then heating the residues with carbon and suitable fluxes in a blast furnace. Thus the lead containing the silver in solution settles to the bottom of the furnace and is drawn off. To this molten lead, zinc is added, and the mixture is thoroughly stirred. Zinc is but slightly soluble in lead, but silver is much more greedily taken up by zinc than by lead. Therefore the silver enters the molten zinc, and this solution of silver in zinc floats on top, where it solidifies in the form of a foam, which is skimmed off and then treated with superheated steam at red heat. This oxidizes the zinc and leaves the silver in metallic form. The process of thus using zinc in separating silver from its solutions in molten lead is known as **Parke's process.** The **amalgamation process** consists of extracting silver from its ores by dissolving the metal in mercury and then distilling off the latter. In order to accomplish this, the silver in the ores must first be converted into the metallic form. This is done by roasting the ores with sodium chloride, thus forming silver chloride, which is then moistened with water and treated with iron. In this way ferrous chloride is formed, which remains dissolved, and metallic silver is precipitated. The latter is then extracted from the mass by means of mercury. Where fuel is expensive, as in some of the South American countries, the roasting process is not used, the ores first being finely ground and then mixed with sodium chloride, copper sulphate, water, and mercury. This thick pasty mass is mixed by driving mules through it, and shoveling it over occasionally. The sodium chloride and copper sulphate react, forming cupric chloride, which in turn converts the silver in the ores to silver chloride. The latter is then decomposed by mercury, forming mercurous chloride and silver, which is dissolved in the excess of mercury present. This process usually requires a week or more. The silver amalgam formed is washed and strained through canvas.

From the solid thus remaining, the silver is obtained by distilling off the mercury. The reactions involved are in the main as follows: —

$$CuSO_4 + 2\,NaCl = Na_2SO_4 + CuCl_2.$$
$$CuCl_2 + Ag_2S = CuS + 2\,AgCl.$$
$$2\,AgCl + 2\,Hg = 2\,HgCl + 2\,Ag.$$

Still other processes are also sometimes employed. So, when lead containing but little silver cools, the crystals that form are practically pure lead, and when these are removed, the remaining liquid is richer in silver. As this liquid cools further, more solid lead forms, after the removal of which the remaining solution is still richer in silver. By repeating this process, known as **Pattinson's process**, an alloy of lead relatively rich in silver remains behind, from which the silver is obtained by **cupellation.** This process consists of heating the lead-silver alloy in a current of air in a muffle furnace; the lead is thus oxidized to lead oxide, which melts and runs off or is volatilized, and the silver remains behind.

Silver is refined by electrolysis or by the sulphuric acid method. The latter consists of dissolving the silver in boiling hot, concentrated sulphuric acid and then diluting the solution with water. In this way, the noble metals, like gold, platinum, palladium, etc., remain behind, and the silver is obtained as silver sulphate in solution. From the latter the silver is precipitated by means of iron and then cast into molds. The electrolytic process of refining silver is similar to that of preparing pure copper by electrolysis. The impure silver is used as anodes. A solution of silver nitrate acidified with nitric acid serves as the electrolyte, and thin silver plates are used as cathodes, on which silver is deposited in the form of shining crystals that are continually rubbed off by a mechanical contrivance. These crystals of pure silver fall to the bottom of the vat, and after draining off the electrolyte and washing them, they are ready for further use. The electrolytic process of refining silver is much used at present. In the chemical laboratory pure silver is often made by heating pure silver chloride with soda, or by treating moist silver chloride with zinc.

The United States produces about 4000 tons of silver each year, which is somewhat over half of the world's annual production.

Silver, **argentum**, is the most abundant of the noble metals. It has been known to man since earliest times, and has been used for utensils and coins for many centuries. It is a pure white metal of high metallic luster. Its specific gravity is 10.6. At 962° it melts, and at 2050° it boils and may be distilled. Silver is very tough, ductile, and malleable, and may be beaten into very thin sheets, which transmit blue light. *It is the best conductor of heat and electricity known.* Molten silver absorbs about 20 times its volume of oxygen, which is again liberated when the metal cools, thus causing "spitting." Silver is softer than copper, but harder than gold. Copper is often added to silver to secure greater hardness and durability. **Sterling silver**, which is used for coins, spoons, dishes, and many other useful articles, is an alloy containing 90 per cent silver and 10 per cent copper. It is said to be 900 fine, pure silver being called **fine silver**, or silver that has a fineness of 1000. Silver also readily forms alloys with zinc, lead, mercury, tin, gold, and other metals. When alloyed with tin and mercury it forms amalgams which are used for filling teeth.

In the air, silver remains unchanged, but ozone oxidizes it to peroxide AgO. Molten nitrates or hydroxides of the alkalies do not attack silver, hence silver dishes are used in the laboratory in working with caustic alkalies or molten saltpeter. Hydrochloric acid attacks silver but slightly, a protective coating of silver chloride being formed. In hot concentrated sulphuric acid, silver readily dissolves, liberating sulphur dioxide: —

$$2\,Ag + 2\,H_2SO_4 = Ag_2SO_4 + 2\,H_2O + SO_2.$$

In nitric acid, silver is readily soluble even in the cold: —

$$3\,Ag + 4\,HNO_3 = 3\,AgNO_3 + 2\,H_2O + NO.$$

Nitric acid is the best solvent for silver. With sulphur, silver readily forms silver sulphide Ag_2S, which is a black powder, insoluble in dilute acids. Silver sulphide forms as a black or dark brown coating on silver spoons when in contact with the contents of eggs, for the latter contain sulphur. With the halogens, silver readily unites even at ordinary temperatures.

Oxides of Silver. — Silver monoxide, commonly called simply **silver oxide**, Ag_2O, is formed as an amorphous, dark brown precipitate when potassium or sodium hydroxide is added to a silver

nitrate solution. Above 250°, silver oxide decomposes into the metal and oxygen, a behavior which is similar to that of mercuric oxide. **Silver peroxide** AgO forms as a black compound when ozone acts on silver. It is also formed on a platinum anode when silver nitrate solutions are electrolyzed. **Silver suboxide** Ag_4O has also been prepared. Silver hydroxide is not known.

Halides of Silver. — These are formed by the action of halogens on silver, also by adding a halide to a solution of a silver salt, or by treating silver oxide with hydrohalogen acids.

Silver chloride is formed as a curdy, white precipitate when hydrochloric acid or another soluble chloride is added to a solution of silver nitrate. It is insoluble in water and nitric acid, but it dissolves in concentrated hydrochloric acid, also in ammonia water, alkaline chlorides, sodium thiosulphate, or potassium cyanide. Silver chloride is white, but on exposure to light it turns violet and then brown or black, probably because of the separation of finely divided silver. The salt melts at 151°. It is much used in analytical chemistry in the detection and estimation of silver and also of chlorine. Silver chloride readily absorbs ammonia, forming $AgCl \cdot 3\,NH_3$.

Silver bromide AgBr is obtained as a slightly yellowish precipitate by adding a soluble bromide to a silver nitrate solution. If a soluble iodide is added instead of the bromide, **silver iodide** AgI, a yellow precipitate, is produced. Both the bromide and the iodide of silver are also practically insoluble in water and dilute acids. The solubility of silver bromide in ammonia is less than that of the chloride; and the iodide is least soluble in ammonia. When exposed to light, the bromide and iodide of silver are partially decomposed, like the chloride. **Silver fluoride** AgF is very soluble in water, and consequently differs greatly from the other halides of silver. It may be obtained by adding hydrofluoric acid to silver oxide. The crystals are deliquescent and correspond to the formula $AgF \cdot H_2O$ or $AgF \cdot 2\,H_2O$.

Use of Silver Halides in Photography. — The fact that the halides of silver are decomposed when exposed to light forms the basis of modern photography. The sensitive dry plates or films are covered with a layer of gelatine containing finely divided silver bromide in suspension. When such a plate is

exposed to light in a camera, the silver bromide is acted upon more strongly in some places than in others, according to the intensity of the light reflected from the different parts of the object whose image is focused upon the plate. After being thus momentarily exposed to light, the plate exhibits no visible change. However, on now treating the plate with reducing solutions like ferrous salts, alkaline pyrogallic acid, or hydrochinone, silver is deposited from the bromide more rapidly and densely on those places where the light has acted more intensely, and less rapidly where the action of the light has been less intense. Thus these reducing solutions, or **developers**, as they are called, develop the picture, which is a so-called **negative**, for it is dark where the object was light, and light where the object was dark. The developing process must be stopped when a good picture of sharply defined outline has been secured. This is done by rinsing the developing solution from the plate and introducing the latter into a solution of sodium thiosulphate $Na_2S_2O_3$, commonly called hyposulphite of soda or "hypo." Thus the developing process is arrested, and the sodium thiosulphate dissolves the remaining unaltered silver bromide from the plate, forming a soluble sodium silver thiosulphate and sodium bromide, which are finally rinsed off: —

$$AgBr + Na_2S_2O_3 = NaBr + NaAgS_2O_3.$$

The film or the plate now consists simply of silver imbedded in gelatine and is said to be "fixed," for it may be exposed to the light without suffering further alteration thereby. The sodium thiosulphate solution is termed the "fixing bath." The pictures are printed by placing the negative upon paper covered with a sensitive film of silver chloride, bromide, or iodide, and then exposing this to the light. This yields a **positive**, for obviously the print is dark where the negative is light and *vice versa*. The prints must be "fixed" by the same process as the negative. Usually silver bromide papers are employed for printing. They are more readily acted upon by light than papers covered with a silver chloride film.

Silver Nitrate $AgNO_3$, also known as **argentic nitrate** and **lunar caustic**, *is the most important silver compound, for from it nearly all the other compounds are directly or indirectly prepared.* Silver nitrate is formed by dissolving silver in nitric acid.

It forms transparent, rhombic crystals which melt at about 200°, and are *extremely* soluble in water, although they are anhydrous and not at all deliquescent. At 0°, 100 parts of water dissolve 122 parts of silver nitrate, while at 100° nearly ten times that amount of salt is dissolved. In contact with organic matter, like the skin, cloth, or paper, silver nitrate turns black on exposure to light, owing to separation of metallic silver. Hence the salt is used in indelible inks. Silver nitrate has strong caustic properties, and hence is used in cauterizing sores and removing warts. For this purpose it is commonly cast into sticks, which are either pure silver nitrate or a mixture of the latter with potassium nitrate. It is in the form of such caustic pencils that silver nitrate is termed *lunar caustic* or *lapis infernis*. Silver nitrate is frequently used in analytical chemistry. It is poisonous, and its solutions have a disagreeable metallic taste. With ammonia, silver nitrate forms rhombic crystals of the composition —

$$AgNO_3 \cdot 2\,NH_3.$$

Silver Nitrite $AgNO_2$ is obtained as a sparingly soluble crystalline precipitate by adding potassium nitrite to a solution of silver nitrate. The salt is used in water analysis.

Silver Sulphate Ag_2SO_4 is commonly made by dissolving silver or silver carbonate in concentrated sulphuric acid. It forms rhombic crystals soluble in about 200 parts of water. In sulphuric acid it dissolves more readily, because of the formation of silver bisulphate $AgHSO_4$.

Silver Carbonate Ag_2CO_3 is obtained as a yellowish precipitate by adding soluble carbonates to solutions of silver salts. It dissolves in water charged with carbon dioxide. On heating silver carbonate, it decomposes : —

$$Ag_2CO_3 = 2\,Ag + CO_2 + O.$$

Silver Phosphate Ag_3PO_4 is a yellow, amorphous precipitate produced by adding sodium phosphate to a solution of a silver salt.

Silver Sulphide Ag_2S is obtained as a dark brown precipitate, when hydrogen sulphide acts on solutions of silver salts. It is insoluble in dilute acids.

Silver Cyanide AgCN is formed by adding potassium cyanide to a solution of silver nitrate. In excess of potassium

cyanide, silver nitrate is soluble, forming the double cyanide $KAg(CN)_2$. The latter is very important, for its solutions are used in silver plating. Silver cyanide is stable in the light, and is used in pharmaceutical practice for preparing dilute solutions of hydrocyanic acid by the following reaction :—

$$AgCN + HCl = AgCl + HCN.$$

The silver chloride being insoluble is filtered off.

Silver Plating. — This is commonly accomplished by electrolysis. The objects to be plated are first thoroughly cleaned, and then immersed in a bath consisting of a solution of **potassium silver cyanide** $KAg(CN)_2$, in which they serve as cathodes. The anode consists of a thick plate of silver. As the current passes, the objects are coated with a dense, white, well-adhering deposit of silver which can afterwards be polished. *Aqueous silver nitrate will not serve as the electrolyte in electroplating, for from such solutions crystalline, poorly adhering deposits are obtained.*

Silver mirrors are formed when a clean surface of glass is treated with an ammoniacal silver nitrate solution plus a reducing agent like formic aldehyde, glucose, or Rochelle salt.

Silver Fulminate AgONC is made like mercuric fulminate. It is even more explosive than the latter.

Analytical Tests for Silver. — Silver is very readily detected in its compounds. All silver salts of organic acids yield white metallic silver when ignited. Silver is precipitated from solutions of silver salts by copper, mercury, zinc, or iron. Solutions of silver salts yield insoluble silver chloride on treatment with hydrochloric acid. Silver chloride is soluble in ammonia, which is not the case with mercurous chloride or lead chloride. The last two salts are also insoluble in water, though lead chloride dissolves in boiling water. **Silver chromate** Ag_2CrO_4, a dark red precipitate, forms by adding a solution of either potassium chromate or bichromate to a soluble silver salt. Other characteristic precipitates are the carbonate, which dissolves in ammonium carbonate, and the phosphate, which is yellow; these have already been described. In potassium cyanide or in sodium thiosulphate solutions, silver salts are soluble. The fact that most silver compounds are affected by light is also characteristic.

Occurrence, Metallurgy, and Properties of Gold. — Gold is usually found in nature in the uncombined state in quartz veins and alluvial sands, though sometimes it occurs combined with tellurium as calaverite $AuTe_2$, petzite $(AuAg)_2Te$, and sylvanite $AgAuTe_2$. Native gold always contains some silver, frequently also copper, lead, iron, and other metals. Many samples of iron pyrites contain small amounts of gold. The chief localities are South Africa, Alaska, California, Colorado, Dakota, the Urals, and Australia.

Alluvial gold-bearing sands are usually washed with water, which carries away the light, loose material, leaving the heavier particles of gold behind. The latter is gathered by treatment with mercury; and from the gold amalgam thus formed, the mercury is removed by distillation from iron retorts. From quartz, gold is separated by pulverizing the material in stamping mills, and then running water bearing the finely divided ore over copper plates amalgamated with mercury. The latter thus catches and dissolves the gold particles. From time to time, the amalgam is removed and distilled to separate the gold from the mercury. The latter is used over and over again. Not all the gold is extracted from the ores by this **amalgamation process**, the "tailings" generally containing very finely divided particles of the metal. These are recovered by the **cyanide process**, which consists of treating the ore with a dilute solution of potassium cyanide (from 0.25 to 0.8 per cent), in which both gold and silver dissolve in presence of the oxygen of the air, thus:—

$$4\,Au + 8\,KCN + 2\,H_2O + O_2 = 4\,KOH + 4\,KAu(CN)_2.$$
$$4\,Ag + 8\,KCN + 2\,H_2O + O_2 = 4\,KOH + 4\,KAg(CN)_2.$$

These cyanide solutions are then subjected to electrolysis to obtain the gold, or the latter is precipitated by means of zinc, thus:—

$$2\,KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2\,Au.$$

If electrolysis is used, iron anodes and lead cathodes are employed. The latter are finally melted and cupelled, by heating them in a current of air in a muffle furnace. Thus lead is transformed to oxide and runs off, and gold remains. Auriferous pyrites ores are roasted, and then subjected to the **chlorination process**, which consists of treating the finely ground

ore with chlorine, thus forming soluble auric chloride $AuCl_3$. From the solution, gold is then precipitated by means of ferrous sulphate, thus:—

$$2\,AuCl_3 + 6\,FeSO_4 = 2\,FeCl_3 + 2\,Fe_2(SO_4)_3 + 2\,Au.$$

Gold from any of the above processes usually contains silver from which it must be parted. The **parting** is accomplished by treating the alloy in form of foil or granulated pieces with hot concentrated sulphuric acid which dissolves the silver and leaves the gold behind as a dark powder. This is finally melted with fluxes, like potassium nitrate or borax, to remove any further base metals that may still be present. Gold may also be separated from silver by electrolytic methods. In the process of **assaying** gold ores, the latter are heated with lead and fluxes like borax or soda. Thus gold and silver finally accumulate, dissolved in lead. This lead alloy, or "button," is then heated in a muffle furnace in a small dish called a cupel, made of bone ash, which absorbs the lead oxide formed, leaving the alloy of gold and silver. This is then treated with hot nitric acid which dissolves the silver and leaves the gold behind. This method of parting is called **quartation**, for it was formerly believed that in order that the separation be complete, the alloy must not contain more than 25 per cent gold. As a matter of fact, the alloy may contain up to 35 per cent gold and still the separation be successful.

Pure gold is a rather soft, bright yellow metal having a high luster. *It is the most malleable and ductile of all the metals*, and conducts heat and electricity well. It may be beaten into very thin leaves, which transmit green light. A grain of gold may be beaten into a leaf covering an area of about half a square meter. Gold may be obtained in regular octahedra or dodekahedra. Its specific gravity is 19.3. It melts at 1064°, and may be volatilized in the electric furnace. Chemically, gold is rather inert. In the air or in oxygen, it remains unchanged even at high temperatures. Gold is attacked by fused caustic alkalies and nitrates of the alkalies, aurates being formed. It is soluble in aqua regia, but not in nitric, hydrochloric, or sulphuric acid. Chlorine attacks gold, but sulphur does not. In potassium cyanide, it readily dissolves, as already stated. *On ignition, all compounds of gold are decomposed, leaving a residue of the metal.* The atomic weight of gold is 197.2.

Gold Alloys. — Gold forms alloys with many metals, like mercury, copper, silver, cadmium, tin, and lead. Pure gold is too soft for coinage, jewelry, and ornaments; hence it is alloyed with copper for these purposes. Indeed, *of the gold alloys those with copper are by far the most important ones.* They are harder, stronger, darker in color, and more readily fusible than pure gold. The gold coins of the United States consist of 1 part copper and 9 parts gold. It is customary to express the purity of gold in **carats.** Pure gold is called 24-carat gold; a gold alloy consisting of 8 parts copper and 16 parts gold is 16-carat; 14-carat gold contains 10 parts copper and 14 parts gold. For many articles of jewelry, it is necessary to use at least as low as 14-carat gold to secure sufficient rigidity.

Pure gold leaf in form of a wad is readily condensed to a solid piece by hammering, which fact is used by dentists in filling teeth with gold.

Gold has been known since earliest times and has always been regarded as an article of great value. Each year the United States produces nearly 160 tons of gold, representing a value of about $96,500,000. This is approximately one fifth of the world's annual output. The yield of the Transvaal mines is now greater than that of America. The production of gold has increased greatly in recent years. Only about 26 tons of gold were produced annually on the average during the first fifty years of the last century. Since 1850 there has been a steady increase in the production of gold.

Compounds of Gold. — On account of its inertness, gold forms but few compounds. There are **aurous** compounds in which gold is univalent, and **auric** compounds in which it is trivalent. When dissolved in aqua regia or when treated with chlorine, **auric chloride** $AuCl_3$ is formed. It consists of reddish-brown deliquescent crystals which, when heated to about 180°, decompose into chlorine and **aurous chloride** AuCl, which is white. On boiling aurous chloride with water, auric chloride and gold are formed: —

$$3\,AuCl = AuCl_3 + 2\,Au.$$

When auric chloride is evaporated with excess of hydrochloric acid, yellow prismatic crystals of **chlorauric acid** $HAuCl_4 \cdot 4\,H_2O$ are formed. With sodium chloride, auric chloride forms

sodium chloraurate $NaAuCl_4$ or $NaCl \cdot AuCl_3$, which is a salt of chlorauric acid. This salt is used in photography in dilute solutions as a **toning bath**, for silver prints immersed in it are colored slightly yellowish, due to the fact that silver decomposes the salt and so deposits a very thin layer of gold. The analogous bromides and iodides of gold are also known. They are rather unstable.

Aurous oxide Au_2O is a dark violet powder formed by the action of caustic alkalies upon aurous chloride. When heated, it yields gold and oxygen. **Auric oxide** Au_2O_3 is a brown powder. Auric hydroxide $Au(OH)_3$ is formed when caustic alkalies are added to auric chloride solutions. This hydroxide is soluble in excess of caustic alkalies, forming **aurates** like $KAuO_2$: —

$$Au(OH)_3 + KOH = KAuO_2 + 2\,H_2O.$$

By treating auric chloride or oxide with ammonia, a precipitate is formed which is called **fulminating gold**. It is very explosive when dry. Its composition is not known with certainty.

Aurous cyanide AuCN is a yellow, crystalline powder which is soluble in potassium cyanide, **forming potassium aurous cyanide** $KAu(CN)_2$. The latter is also obtained by dissolving gold in dilute potassium cyanide solutions in presence of air. When auric compounds are treated with potassium cyanide, **potassium auric cyanide** $KAu(CN)_4$ is formed. The solutions of these double cyanides of potassium and gold are used as baths in gold electroplating, which process is similar to silver plating. A gold plate serves as the anode, and the object to be plated is the cathode.

Auric sulphide Au_2S_3 is formed as brownish black precipitate when hydrogen sulphide is passed into cold solutions of auric salts. The precipitate usually contains free sulphur. Auric sulphide is soluble in alkali sulphides, sulpho-salts, like $(NH_4)_3AuS_3$, being formed. From hot solutions, **aurous sulphide** Au_2S is similarly precipitated. It has a steel-gray appearance and dissolves in water, from which it may be precipitated by adding hydrochloric acid.

Purple of Cassius consists of a finely divided, brownish purple precipitate of gold formed by adding stannous chloride to

solutions of auric chloride. The powder is used in coloring glass and in painting porcelain ware.

Analytical Tests for Gold. — On ignition with soda on charcoal, gold compounds yield a globule of gold. Ferrous sulphate precipitates gold from solutions of its salts. Other reducing agents, like oxalic acid and sulphur dioxide, also precipitate gold in brown, pulverulent form. Gold is readily displaced from its solutions by many other metals like copper, zinc, and iron. The purple of Cassius reaction already mentioned is also characteristic.

REVIEW QUESTIONS

1. Why do copper, silver, and gold occur in nature in the uncombined state? What other metals that you know of occur thus? What is meant by the terms noble metal, base metal?

2. Mention three important ores of copper and tell where they are found, also how metallic copper is obtained from them.

3. How much copper would be necessary to produce 100 tons of each of the following: gun metal, bell metal, Dutch metal?

4. What is the difference between brass and bronze? What is German silver?

5. What use is made of metallic copper?

6. How does metallic copper act toward: (*a*) nitric acid, (*b*) hot concentrated sulphuric acid, (*c*) dilute sulphuric acid? Equations.

7. What is a cupric compound? A cuprous compound? Give five illustrations of each.

8. What is the most common salt of copper? How is it prepared, and for what purposes is it used?

9. Mention six different ways of showing that a copper nitrate solution contains copper. Equations.

10. Mention four important silver ores and tell where the main silver mines of the world are located.

11. Explain two processes for refining silver.

12. Compare the action of silver, copper, and gold toward nitric acid, also toward sulphuric acid, writing the appropriate equations.

13. What is the most important compound of silver? Describe its properties and uses.

14. What is sterling silver? What use is made of it? How could you demonstrate that its composition is as you have stated?

15. What compounds of silver are used in photography? Upon what fact does their use depend?

16. What compounds of silver are insoluble in water and dilute acids? What silver compounds dissolve in water?

17. Explain the action of the fixing bath in photography. Equation.

18. What property have all photographic developers in common?

19. How much metallic copper would be required to completely decompose 20 grams of silver nitrate? Equation.

20. Why is silver plating done from a potassium silver cyanide solution, and not from one of silver nitrate?

21. In a solution containing the chlorides of gold, copper, and zinc, how demonstrate that these metals are present? Equations.

22. What is the composition of gold coins? How would you prove this? Equations.

23. What metals would precipitate gold from an auric chloride solution? Equations. How would a ferrous chloride solution act on one of auric chloride? Equation.

24. Where are copper, silver, and gold located in the periodic system of the elements? Explain.

CHAPTER XXVI

THE METALS OF THE EARTHS

Of the metals of the earths, aluminum is by far the most important. It has already been stated that boron is a trivalent element and that its compounds consequently bear some analogy to those of aluminum. Boron, however, exhibits but slightly basic properties, whereas aluminum is a basic element, though its hydroxide is also capable of acting as a weak acid in the formation of aluminates.

The other metals of the earths are gallium, indium, thallium, scandium, yttrium, lanthanum, and ytterbium. With the exception of thallium, these are all quite rare. In their compounds, these rare-earth metals are trivalent like aluminum.

Occurrence, Preparation, and Properties of Aluminum. — Aluminum is very widely distributed. *It is the most abundant of the metals* and enters into the composition of the earth's crust to the extent of nearly 8 per cent. Aluminum has a great affinity for oxygen, and so is never found in the uncombined state in nature. It occurs as an essential ingredient of practically all the common siliceous rocks. It is found particularly in feldspars, micas, chlorite, granites, slates, and clays. Oxide of aluminum occurs as corundum, also in form of sapphire or ruby. Bauxite is a mineral consisting of the hydrated oxides of aluminum and iron. **Cryolite,** which is found in Greenland, is a double fluoride of aluminum and sodium of the formula $AlF_3 . 3\,NaF$. Though widely distributed, *aluminum is not found in animals, and only in traces in some plants.*

Aluminum was formerly prepared by heating sodium aluminum chloride $NaCl \cdot AlCl_3$, or cryolite, with metallic sodium. It is now made in large quantities by electrolysis of a solution of aluminum oxide Al_2O_3 in molten cryolite. The containing vessel (Fig. 150) is made of graphitic carbon, which also serves as cathode. The anode consists of sticks of carbon placed vertically. Thus, as the current passes, oxygen is evolved on

the carbon anode and passes off. Aluminum is deposited at the bottom of the containing vessel and is tapped off from time to time. The heat generated by the current depositing the metal is sufficient to keep the electrolyte and the aluminum

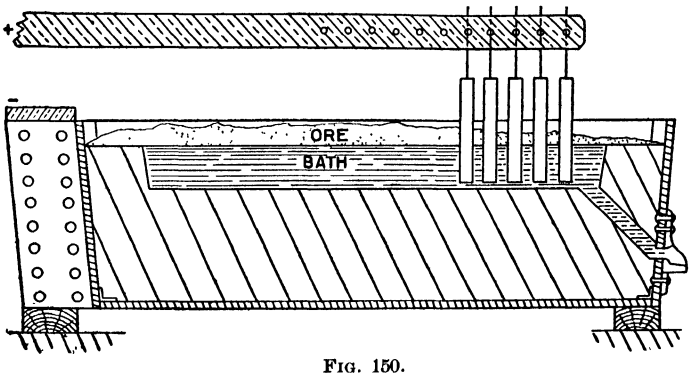


FIG. 150.

in a molten state. As the aluminum is deposited, more oxide is placed on top of the electrolyte, as shown in the figure. Large quantities of aluminum are now prepared, especially where water power is available, as at Niagara Falls and other localities. Over 36,000 tons of aluminum are used in the United States each year. Approximately two thirds of this amount is produced in this country.

Aluminum is a silver-white, lustrous metal of specific gravity 2.6 to 2.7; that is, it is about one third as heavy as iron. It melts at about 660°. It is very ductile and malleable and is a good conductor of heat and electricity. Aluminum is about as hard as silver. The hammered or rolled metal is denser than when cast, which is also in general true of other metals. Sufficiently large pieces of aluminum ring like a bell when struck. At a temperature slightly below its melting point, aluminum becomes brittle and crumbles when shaken or touched. At still lower temperatures, it is again pliable and may be welded and readily worked into desired forms. It is very difficult to solder aluminum, and consequently it cannot very well be used for many purposes. Chemically aluminum is relatively inert as compared with the metals of the alkalies, alkaline earths, and magnesium. It oxidizes but very slowly on exposure to the air or oxygen; for a thin, though resistant, coating of oxide forms on the metal, giving it a slightly bluish

hue. This film protects the aluminum from further oxidation and from attack by many acids. Thin pieces of aluminum, when strongly heated in the air or in oxygen, burn with a brilliant light, forming the oxide and some nitride. The metal may also be burned in a current of superheated steam, oxide and hydrogen being formed. In caustic alkalies, aluminum dissolves, yielding aluminates and hydrogen. Hydrochloric acid readily acts on aluminum, forming hydrogen and aluminum chloride, which is soluble. Nitric acid and dilute sulphuric acid are practically without action on aluminum, which is, however, soluble in hot, concentrated sulphuric acid with concomitant evolution of sulphur dioxide. The atomic weight of aluminum is 27.1; the metal is always trivalent.

Uses of Aluminum. — On account of the fact that aluminum is a good conductor of electricity, it is used for electric cables and wires, especially at times when copper is relatively high in price. Aluminum is used for cooking utensils, and many other useful articles. In finely divided form, it is used in aluminum paints. In the form of leaf, it is employed in stamping titles on the covers of books, for it does not blacken on exposure to the air as silver does. Aluminum is further employed in removing oxides from iron, and thus denser castings are obtained. **Aluminum alloys** are also in use. Besides the aluminum-bronze already mentioned, **magnalium**, consisting of 10 to 25 per cent magnesium and 90 to 75 per cent aluminum, is coming into use. It is lighter and much harder than aluminum and may be polished to a higher degree. With cadmium, aluminum forms a very tough alloy. Alloys with nickel, zinc, and other metals have also been studied.

On account of the great affinity which aluminum has for oxygen, it is used in preparing other metals from their oxides by the **Goldschmidt process**, which consists of heating together a mixture of powdered aluminum and the oxide to be reduced. Thus the oxides of iron, nickel, chromium, etc., are readily reduced; for example,

$$3\,Fe_3O_4 + 8\,Al = 4\,Al_2O_3 + 9\,Fe.$$
$$Fe_2O_3 + 2\,Al = Al_2O_3 + 2\,Fe.$$
$$3\,NiO + 2\,Al = Al_2O_3 + 3\,Ni.$$
$$Cr_2O_3 + 2\,Al = Al_2O_3 + 2\,Cr.$$

In practice the mixture of the oxide and aluminum powder is placed in a crucible and ignited by means of a ruse of magnesium ribbon or a mixture of either aluminum or magnesium and barium peroxide. The reaction, when once started, continues with great evolution of heat. The temperature attained during the reaction when ferric oxide is reduced by aluminum is about 3000°, which is quite sufficient to melt both the iron and the aluminum oxide formed. Upon this fact Goldschmidt has based his famous method of welding iron, which consists essentially of butting together the parts to be welded, surrounding the joint with an ignited mixture of oxide of iron, usually Fe_3O_4, and powdered aluminum. This mixure is called **thermite**. The heat developed by the reaction is sufficient to weld the iron securely. Thus car rails can be welded when in place, and many repairs on machinery, ships, etc., can conveniently be made. Thermite welding is consequently frequently used.

Many metallic sulphides, when heated with aluminum powder, may similarly be reduced to metal, aluminum sulphide being simultaneously formed.

Aluminum Oxide or **Alumina** Al_2O_3 is found in nature as corundum, ruby, or sapphire in hexagonal crystals. **Corundum** is colorless, **ruby** is red due to the presence of a little chromium, and **sapphire** is blue because it contains a trace of cobalt. Impure corundum is called **emery**. It contains ferric oxide, and is used as an abrasive material on account of its great hardness, which is but slightly below that of the diamond. Aluminum oxide results in the Goldschmidt reduction process, above described, also when the hydroxide of aluminum is strongly ignited. The oxide thus obtained is practically not attacked by acids. After fusion with bisulphate of potassium or with caustic alkalies, it may be dissolved in water, for thus aluminum sulphate or aluminates, which are soluble, are formed.

Aluminum Hydroxide $Al(OH)_3$ is found in nature as the mineral hydrargillit. **Diaspore** is a hydrated oxide $Al_2O_3 \cdot H_2O$, and **bauxite** is a hydrated oxide $Al_2O_3 \cdot 3\,H_2O$, containing ferric oxide. When an alkaline hydroxide is added to a solution of an aluminum salt, aluminum hydroxide is precipitated in the form of a gelatinous mass: —

$$AlCl_3 + 3\,KOH = 3\,KCl + Al(OH)_3.$$

Aluminum hydroxide is also formed when an alkaline carbonate is added to a solution of an aluminum salt: —

$$2\,AlCl_3 + 3\,Na_2CO_3 = 6\,NaCl + Al_2(CO_3)_3, \text{ and}$$
$$Al_2(CO_3)_3 + 3\,H_2O = 2\,Al(OH)_3 + 3\,CO_2.$$

The aluminum carbonate formed is at once completely decomposed by hydrolysis, as indicated. Aluminum hydroxide may be dehydrated by heat. At about 100°, $Al_2O_3 \cdot 2\,H_2O$, and at 300° $Al_2O_3 \cdot H_2O$ is formed; finally, on strong ignition all the water is driven off, thus leaving Al_2O_3.

The fact that a carbonate of aluminum does not exist shows the feebly basic character of aluminum hydroxide. Indeed, the latter is made on a large scale by fusing bauxite with soda, extracting the resulting mass containing sodium aluminate with water and passing carbon dioxide into the solution, thus: —

(1) $Na_2CO_3 + Al_2O_3 \cdot 2\,H_2O = 2\,NaAlO_2 + 2\,H_2O + CO_2.$
(2) $2\,NaAlO_2 + 3\,H_2O + CO_2 = Na_2CO_3 + 2\,Al(OH)_3.$

As the second equation indicates, sodium carbonate and aluminum hydroxide are formed simultaneously. The aluminates are therefore rather unstable salts, showing that aluminum hydroxide is but a feeble acid. Just as the zincates are formed by dissolving zinc hydroxide in caustic alkalies, so the **aluminates** may be obtained by dissolving aluminum hydroxide in caustic alkalies, thus: —

$$Zn(OH)_2 + 2\,NaOH = Na_2ZnO_2 + 2\,H_2O.$$
$$Al(OH)_3 + 3\,NaOH = Na_3AlO_3 + 3\,H_2O.$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2\,H_2O.$$

Like the zincates, the aluminates suffer hydrolysis to some extent: —

$$NaAlO_2 + 2\,H_2O \rightleftarrows Al(OH)_3 + NaOH.$$

Ammonia, being a weak base, does not react with aluminum hydroxide like sodium or potassium hydroxide.

The **aluminates** are salts formed by replacing the hydrogen atoms of aluminum hydroxide by bases. When aluminum hydroxide loses one molecule of water, $AlO \cdot OH$ or $HAlO_2$, results which may be regarded as **meta-aluminic acid**, analogous to metaboric acid $BO \cdot OH$ or HBO_2. Salts of meta-

aluminic acid, that is **meta-aluminates**, are found in nature and are known as **spinels**. These minerals generally crystallize in regular octahedra. Thus we have spinel $Mg(AlO_2)_2$, gahnite or zinc spinel $Zn(AlO)_2$, iron spinel or pleonast $Fe(AlO_2)_2$, and chrysoberyl $Gl(AlO_2)_2$. The latter is rhombic. The spinels are all very stable. They have been prepared artificially by heating the constituent oxides together, using boric anhydride as a flux. Insoluble aluminates may also be prepared by precipitation, so, for instance : —

$$CaCl_2 + 2\,NaAlO_2 = 2\,NaCl + Ca(AlO_2)_2.$$

It will be recalled that **calcium aluminate** is one of the products formed when cement sets. This aluminate hardens under water.

When aluminum hydroxide is precipitated in a solution containing coloring matter, the latter commonly unites with the precipitate, and thus the supernatant liquor remains clear. Suspended matter is also dragged down with the precipitate. *This fact is sometimes used in clarifying drinking water.* Pigments called **lakes** are made by dissolving dyestuffs in water together with an aluminum or tin salt, and then adding an alkali like soda ; thus precipitates are formed which consist of the coloring matter united with the hydroxide of aluminum or tin.

Many dyestuffs do not unite directly with cotton fibers, which, it will be recalled, are practically cellulose. Aluminum hydroxide does unite with cotton fiber, and as dyestuffs in turn unite with aluminum hydroxide, the latter may act as a means of fixing the dye to the fabric. This is done by first dipping the fabric in a solution of an aluminum salt, then treating with steam, whereby aluminum hydroxide is formed which adheres to the fiber, and finally immersing the cloth in the dye, when the latter unites with the aluminum hydroxide, forming an insoluble compound which is thus fixed on the goods. Sometimes salts of tin are similarly employed in fastening dyestuffs to fabrics. Substances that will serve this purpose are called **mordants**, from the Latin word meaning to bite. Besides alum and aluminum acetate, salts of tin, chromium, iron, and antimony are frequently employed as mordants. *Not all dyestuffs require the use of mordants, for many unite with the fiber directly.*

Again, though wool or silk more frequently unite directly with dyestuffs, they must, nevertheless, be treated with suitable mordants in many cases. It must be borne in mind that wool and silk are nitrogenous, organic compounds of animal origin, and are quite different chemically from cotton and linen, which consist mainly of cellulose.

Aluminum Chloride $AlCl_3$. — By dissolving aluminum or its hydroxide in hydrochloric acid and evaporating the solution, deliquescent crystals, $AlCl_3 \cdot 6\,H_2O$, form, which, on being heated, give off water and hydrochloric acid, leaving the oxide behind: —

$$2\,AlCl_3 \cdot 6\,H_2O = Al_2O_3 + 6\,HCl + 3\,H_2O.$$

Anhydrous aluminum chloride is made by heating aluminum in chlorine or by passing that gas over a heated mixture of carbon and alumina: —

$$Al_2O_3 + 3\,C + 3\,Cl_2 = 2\,AlCl_3 + 3\,CO.$$

The chloride sublimes and thus may readily be purified. It is very hygroscopic, and fumes in the air because hydrochloric acid is formed by hydrolysis when the salt is in contact with moisture. The chloride is used in the synthesis of organic compounds. With alkali chlorides, it forms double salts like $AlCl_3 \cdot NaCl$ and $AlCl_3 \cdot 3\,KCl$. **Aluminum fluoride** occurs in cryolite, which is an analogous double salt. **Aluminum bromide** $AlBr_3$ and **aluminum iodide** AlI_3 are colorless salts which are quite analogous to the chloride.

Aluminum Sulphide Al_2S_3 is formed by heating aluminum and sulphur together. It is a yellowish mass which is decomposed by water, forming the hydroxide and hydrogen sulphide. This behavior is similar to that of magnesium sulphide. Because of its complete hydrolysis by water, aluminum sulphide is not precipitated when ammonium sulphide is added to a solution of an aluminum salt. The precipitate consists of aluminum hydroxide.

Aluminum Sulphate $Al_2(SO_4)_3$ is formed by dissolving the hydroxide in sulphuric acid. On a large scale, it is prepared by treating kaolin or bauxite with sulphuric acid. On evaporating the solution, monoclinic crystals $Al_2(SO_4)_3 \cdot 18\,H_2O$ may be obtained. The salt is readily soluble in water. On heating, it loses both water and sulphur trioxide, leaving

aluminum oxide. Aluminum sulphate is used as a mordant. It is also used in **sizing paper**. With the exception of blotting paper and filter paper, all papers are sized so that they will be smooth and not absorb ink. **Rosin**, which consists essentially of a complex organic acid, **abietic acid** $C_{44}H_{64}O_5$, is dissolved in caustic soda, thus forming sodium abietate, or resin soap, which is added to the paper pulp, and this mixture is then treated with aluminum sulphate. Thus, sodium sulphate and insoluble aluminum resinate are formed. The latter acts as a binder, and gives the paper a smooth surface; for under the hot rollers the resinate is melted and pressed upon the fibers.

Alums. — Aluminum sulphate forms double salts with ammonium sulphate and the sulphates of the alkali metals. These double sulphates are readily obtained by adding a solution of the alkali sulphate to one of aluminum sulphate and evaporating. Crystals are thus obtained which are regular octahedra. The compounds all correspond to the general formula $M_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$, or $MAl(SO_4)_2 \cdot 12\,H_2O$, where M is either NH_4, K, Na, Cs, Rb, Ag, or Tl. These double salts are less soluble than aluminum sulphate. They are called alums. **Potassium alum** $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$ is **common alum**. It is prepared on a large scale by calcining the mineral alunite $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4\,Al(OH)_3$ at about 500° and extracting the mass with water, after having exposed the material to the action of the air and moisture for months. Alum is also made from clays, cryolite, and bauxite. Alunite occurs in large quantities in Hungary and in Italy near Rome. Alum dissolves in about 8 parts of water. Its solutions are astringent and have an acid reaction. Solutions of **aluminum acetate** $(C_2H_3O_2)_3Al$ act similarly. When alum is heated, it melts, loses water, and finally also some sulphur trioxide, thus leaving a somewhat **basic aluminum potassium sulphate** behind. This is commonly called **burnt alum**. On further heating, it is converted into potassium sulphate and alumina. **Ammonium alum** $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$ is also made on a large scale. It is cheaper than potassium alum. **Sodium alum** $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$ is more soluble than either potassium or ammonium alum; moreover, it does not crystallize readily and is consequently not made commercially. Alum is used as a mordant, also as an astringent in medicine, especially

as a mouth wash. The acetate is to be preferred for the latter purpose.

In the alums, the aluminum may be replaced by other trivalent elements like iron, chromium, manganese, gallium, and indium. The compounds so obtained are isomorphous with the alums. They are consequently also called alums, though they contain no aluminum. So we have **ferric ammonium alum** $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24\,H_2O$, **potassium chrome alum** $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\,H_2O$, **sodium manganese alum** $Na_2SO_4 \cdot Mn_2(SO_4)_3 \cdot 24\,H_2O$, etc. In general, the formula of an alum is $\overset{I}{M}_2SO_4 \cdot \overset{III}{M}_2(SO_4)_3 \cdot 24\,H_2O$, or $\overset{I}{M} \cdot \overset{III}{M}(SO_4)_2 \cdot 12\,H_2O$, where $\overset{I}{M}$ is a univalent metal or radical, and $\overset{III}{M}$ is a trivalent metal.

Aluminum Silicates are found in enormous quantities in nature. They are also very widely distributed. Thus **potash feldspar, orthoclase,** $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$, or $KAlSi_3O_8$, **soda feldspar, albite,** $Na_2O \cdot Al_2O_3 \cdot 6\,SiO_2$, or $NaAlSi_3O_8$, **lime feldspar, anorthite,** $CaO \cdot Al_2O_3 \cdot 2\,SiO_2$, or $CaAl_2Si_2O_8$, occur in granitic rocks, together with quartz and micas. The latter are also silicates of aluminum, containing potassium, magnesium, calcium, and sometimes iron. The mineral disthen is a pure aluminum silicate Al_2SiO_5, which occurs in rhombic crystals; it is also found in triclinic forms as andalusite. These two minerals are rather rare.

By the action of water and carbon dioxide of the air upon feldspars, the latter lose their alkali content, which is dissolved and enters the soil as soluble silicates or carbonates, thus supplying potash and lime needed for plant growth. A hydrous aluminum silicate $H_2Al_2(SiO_4)_2 \cdot 2\,H_2O$, called **kaolin**, remains as a **white clay.** The reactions of the weathering process of typical feldspars are in the main as follows: —

$$2\,KAlSi_3O_8 + 2\,H_2O = K_2Si_4O_9 + H_2Al_2(SiO_4)_2 \cdot H_2O.$$

$$CaAl_2Si_2O_8 + 2\,CO_2 + 3\,H_2O = Ca(HCO_3)_2 + H_2Al_2(SiO_4)_2 \cdot H_2O.$$

Ordinary clays contain ferric hydroxide, sand, and various silicates besides kaolin. Frequently calcium carbonate is also present. Clay containing a large amount of calcium carbonate is called **marl.**

When mixed with water, clay forms a plastic mass that can readily be molded into various forms as desired. On drying

and heating this material to higher temperatures (*i.e.* "burning" or "firing" it), it becomes hard, dense, and resistant without actually melting. These facts form the basis of making bricks, earthenware, and porcelain from clay. The rather impure clays are used for the manufacture of **bricks**, which get their color from the iron oxides contained in the clay. **Red pottery** is made from similar material. Light-colored **stoneware** and pottery requires a clay relatively free from iron; while fine white **porcelain** necessitates kaolin that contains no iron. Earthenware is frequently porous. Sometimes this porous material is covered with a glaze; and again, as porcelain, the material may be made perfectly vitreous throughout. Porous **earthenware** is made by simply shaping clay containing but little fusible material and firing it, as in making bricks, flowerpots, etc. If such articles are to be glazed, they are covered with a layer of fusible silicates, which is fired on. In the case of the cheaper grades of stoneware, glazed bricks, etc., this is accomplished by simply throwing salt into the kiln. At the high temperature that obtains, the salt is volatilized and decomposed as it comes in contact with the earthenware; hydrochloric acid and a readily fusible sodium aluminum silicate being formed. The latter covers the surface of the articles as a glaze. In **making porcelain**, the purest kaolin is mixed with finely pulverized feldspar and quartz. Of this mixture the dishes are shaped, and when they are finally fired in the kiln, the feldspar melts, fills the pores, and thus produces the translucent material known as porcelain. In actual practice, the articles are fired twice. After the first heating, they are dipped in water containing in suspension very finely ground material intended for the glaze. This material commonly consists of kaolin, together with enough finely ground feldspar to make a mixture that will fuse at a somewhat lower temperature than the ware of which the articles are composed. This fine material is taken up by the porous porcelain, which is then dried and fired again. As the feldspar melts, a smooth glaze is produced, and a mass that is vitreous throughout results.

Ultramarine is an important blue pigment which is manufactured in large quantities by heating together soda, sulphur, and clay, or, more frequently, sodium sulphate, carbon, and clay. The product, which is a silicate of sodium and aluminum

combined with sodium sulphides, is at first green and is called **ultramarine green.** This is also used as a pigment. On heating ultramarine green in a current of air, it turns blue, forming **ultramarine blue. Ultramarine violet** results when the blue is heated in a current of hydrochloric acid gas to about 175°, and **ultramarine red** is formed by the same process at about 145°. Only the green and blue ultramarines have much value in practice. The constitution of ultramarine has caused much discussion, and has not yet been finally settled. It is probable that ultramarine blue is $(Na_2Al_2Si_2O_8)_2 \cdot Na_2S_2$. It is found in nature as *lapis lazuli*, from which the pigment was first prepared. Ultramarine is stable towards light, and the action of the air and water; but acids readily destroy the color, liberating sulphur and hydrogen sulphide. Ultramarine blue is much used in paints and laundry blue. It is also employed in removing the yellow tinge of sugar, paper pulp, linen and cotton fabrics, and in making cotton prints and wall paper.

Analytical Tests for Aluminum. — Aluminum is precipitated as the gelatinous hydroxide from solutions by either potassium, sodium, or ammonium hydroxides, carbonates, or sulphides. Aluminum hydroxide is soluble in potassium or sodium hydroxides, but only slightly soluble in ammonium hydroxide. By means of hydrogen sulphide or carbon dioxide, solutions of aluminates are decomposed, yielding a precipitate of aluminum hydroxide. When alumina is moistened with a solution of cobalt nitrate and then strongly ignited, a blue mass $Co(AlO_2)_2$ results. This blue is known as **Thénard's blue** or **cobalt ultramarine.**

Gallium. — This is a rare metal whose atomic weight is 69.9. It was discovered in 1875 by Lecoq de Boisbaudran, who detected its presence in a sample of zinc blende from Pierrefitte in the Pyrenees, by means of the spectroscope. In 1869 Mendeléeff foretold the existence and described the properties of this element, which he called **eka-aluminum.** He was able to do this from the periodic system of the elements, in which the space now occupied by gallium was then vacant. Gallium receives its name from Gaul, the native land of its discoverer. Gallium is a hard, white metal which is stable in the air. It melts at 30°, and its specific gravity is 5.9. In its compounds, it is trivalent and analogous to aluminum, though a chloride of

the formula $GaCl_2$ is also known. The spark spectrum of gallium exhibits two characteristic lines in the violet, through which the element was discovered.

Indium, whose atomic weight is 114.8, is also a rare metal. It was discovered by Reich and Richter in 1863 by means of the spectroscope, in a sample of zinc blende from Freiberg. The metal receives its name from the bright indigo-blue line that characterizes its spectrum. Indium is a silver-white metal, softer than lead and very malleable. Its specific gravity is 7.4, and its melting point is 176°. Like gallium, it is stable in the air. In its compounds, it is commonly trivalent like aluminum, though indium dichloride $InCl_2$ and monochloride InCl are also known.

Thallium and its Compounds. — Thallium is a metal whose physical properties are similar to those of lead. It was discovered in 1861 by means of the spectroscope by Sir William Crookes, in the mud at the bottom of the lead chambers of the sulphuric acid factory at Tilkerode in the Harz. Thallium compounds yield a very characteristic green line in the spectrum, whence the name thallium, meaning a green branch. Crookesite, a selenide of copper, thallium, and silver contains about 17 per cent thallium. Many native sulphides of iron and copper contain small amounts of thallium, whence its appearance in the flues and lead chambers of sulphuric acid plants. In 1862 Lamy demonstrated that thallium is a metal. It oxidizes readily on exposure to air, and hence is kept under petroleum oil or glycerine. The atomic weight of thallium is 204.0, and its valence is either 1 or 3.

In **thallous compounds**, the metal is univalent and therefore analogous to the alkali metals. Thus we have TlOH, Tl_2O, TlF, TlCl, TlBr, TlI, $TlClO_3$, $TlNO_3$, Tl_2CO_3, Tl_2SO_4, Tl_2S, Tl_2PtCl_6, etc. Thallous chloride, bromide, and iodide are nearly insoluble in water, and so in this respect these compounds are similar to the corresponding ones of silver. Thallic chloride $TlCl_3$ is very soluble in water.

In **thallic compounds**, thallium is trivalent. Thus we have $TlO \cdot OH$, Tl_2O_3, $TlCl_3$, $Tl(NO_3)_3$, $Tl_2(SO_4)_3$, Tl_2S_3, etc.

Thallium readily dissolves in nitric or sulphuric acid, whereas, on account of the fact that thallous chloride is difficultly soluble, hydrochloric acid attacks the metal but slightly, it

being soon covered with a protective coating of the chloride. Thallium salts are readily recognized by means of the spectroscope. From neutral or faintly acid solutions of thallous salts, hydrogen sulphide precipitates black thallous sulphide, which is insoluble in water and acetic acid, but it readily dissolves in sulphuric or nitric acid.

The Rare-Earth Elements. — These are a series of metals that form compounds which are in general analogous to those of aluminum. The rare-earth metals are, as the name implies, of very rare occurrence. They are found in the complex and very rare minerals monazite, gadolinite, euxenite, samarskite, orthite, cerite, yttrotantalite, hjelmite, and several others which occur mainly in the Scandinavian peninsula, Finland, Greenland, France, Bavaria, and the United States. In general, the elements are trivalent, like aluminum.

Chemically the rare-earth metals deport themselves very much alike, which makes it extremely difficult to separate them. In general, their oxalates are insoluble, and their sulphates are soluble and readily form double salts with the sulphates of the alkalies. As the nitrates are decomposed by heat at different temperatures, this fact is used in separating the rare earths from one another. Fractional crystallization and fractional precipitation are also used to effect separations ; but these processes are laborious, and generally yield products that are, after all, not quite pure.

Scandium (Sc—44.1) was discovered in 1879 by Nilson and Cleve. Mendeléeff predicted the existence of this element in 1869. Compare gallium and germanium. He called it **ekaboron**, and described its properties. The element occurs in euxenite and gadolinite Volatilized in the electric arc, scandium chloride yields a bright characteristic spectrum of many lines. The oxide Sc_2O_3 is a white, earthy powder.

Yttrium (Y—89.0) occurs in the silicate gadolinite found at Ytterby, whence its name. Yttrium was discovered in 1843 by Mosander. Its oxide Y_2O_3 is a white, earthy powder of very high melting point. The chloride YCl_3 yields a bright spectrum containing many lines.

Lanthanum (La—139.0) was found in cerite in 1839 by Mosander. The name lanthanum comes from the Greek, meaning hidden. Like yttrium, lanthanum may be prepared by

electrolysis of its molten chloride. Lanthanum is a white, malleable metal not unlike iron in appearance. When heated, it burns to oxide La_2O_3, a white powder which readily absorbs water, forming $La(OH)_3$. Other compounds are $La_2(CO_3)_3 \cdot 3\,H_2O$, $La(NO_3)_3 \cdot 6\,H_2O$, $La_2(SO_4)_3 \cdot 9\,H_2O$, $LaCl_3$. The latter is deliquescent and readily forms $2\,LaCl_3 \cdot 15\,H_2O$; it shows a characteristic spectrum of many lines.

Ytterbium (**neoytterbium**) (Yb—172.0) occurs with scandium and yttrium in euxenite and gadolinite. Its compounds are in general like those of yttrium. In 1907 Urbain in Paris showed that the old ytterbium consists of two elements, neoytterbium (Yb—172.0) and **lutecium** (Lu—174.0). Auer von Welsbach, in Vienna, published the same discovery almost simultaneously. He named the two new elements **aldebaranium** and **cassiopeium**, and found their atomic weights to be 172.90 and 174.23, respectively. As Urbain's work appeared first, his nomenclature will probably be adopted.

Cerium (Ce—140.25) resembles lanthanum very much. It was discovered by Klaproth and also by Berzelius and Hisinger in 1803. The element is named from the planet Ceres, which had just been discovered. The mineral **cerite** contains about 60 per cent cerium. Cerium forms compounds in which the element is trivalent, like Ce_2O_3, $Ce_2(SO_4)_3$, and $CeCl_3$, but it also forms compounds in which it is quadrivalent, like CeO_2, $Ce_2(SO_4)_2 \cdot 4\,H_2O$, $Ce(OH)_4$, $CeF_4 \cdot H_2O$. The latter class of compounds indicates that cerium is closely related to other quadrivalent elements, and consequently probably belongs in the same group as silicon, titanium, zirconium, and thorium. Cerium may be prepared by electrolysis of the molten chloride. It is a steel-gray, very malleable metal of specific gravity 7.0. It readily burns in the air, forming a yellow powder, CeO_2. **Ceric hydroxide** $Ce(OH)_4$ is a red precipitate. In general, *cerous compounds are colorless, while the ceric compounds are yellow, brown, or red.* Cerium nitrate is now prepared from **monazite sand** found in North Carolina in considerable quantities. It is used together with thorium nitrate in making the mantles for Welsbach gas lights. The process of making these mantles consists essentially of knitting the mantle of cotton thread, and then dipping this into solutions of the nitrates of cerium and thorium. The mantle is then dried and calcined;

thus the thread is destroyed, and the nitrates are converted to oxides which adhere together. Such mantles are, of course, always frail, and consequently must be handled with care. As already mentioned, experience has shown that mantles consisting of 1 per cent cerium oxide CeO_2 and 99 per cent thorium oxide ThO_2 give the best efficiency. The light emitted from such mantles, when heated to incandescence by a Bunsen burner, is a brilliant white. Mantles containing different proportions of ceria and thoria are less efficient, and those made of other earths give a light of poorer quality and also lower intensity. The **Nernst lamp** consists of a filament of earths heated to incandescence by passing an electric current through it. At ordinary temperatures, this filament is practically a non-conductor; but on being heated, it conducts electricity and gives a bright light.

Praseodymium (Pr—140.6) and **neodymium** (Nd—144.3) were for half a century regarded as but one element, *didymium*. But in 1885 Auer von Welsbach separated it into praseodymium, which forms leek-green salts, and neodymium, which forms rose-violet salts. These elements occur with cerium and lanthanum, which they resemble. The absorption spectra of solutions of salts of the didymiums are especially characteristic.

Samarium (Sa—150.4) was discovered in Samarskite, a mineral from North Carolina, in 1878 by Delafontaine and also by Lecoq de Boisbaudran. Typical compounds are Sm_2O_3, $SmCl_3 \cdot 6\,H_2O$, $Sm_2(SO_4)_3 \cdot 8\,H_2O$, $Sm(NO_3)_2 \cdot 6\,H_2O$. These compounds are similar to those of lanthanum.

Erbium (Er—167.7), **terbium** (Tb—159.2), **thulium** (Tm—168.5), and **dysprosium** (Dy—162.5) are found associated with yttrium. Terbium also occurs in samarskite and in small quantities in gadolinite, which mineral also contains **gadolinium** (Gd—157.3). Europium (Eu—152.0) is another element about which but little is known.

The position of a goodly number of these elements in the periodic system is still unsettled. It is also quite probable that some of the rare-earth elements, especially those which have been studied but little, will be separated further.

REVIEW QUESTIONS

1. Why is aluminum called an earth metal? Where is it placed in the periodic system? Why? What other elements are classed with aluminum?

2. What properties of aluminum make it valuable in the arts?

3. Discuss the occurrence of aluminum in the earth's crust, also in plants and animals.

4. What is the chief ore from which metallic aluminum is prepared? How is this accomplished?

5. Describe how aluminum acts when treated with each of the following reagents: caustic alkalies, nitric acid, hydrochloric acid, sulphuric acid. Equations.

6. What is magnalium and what use is made of it?

7. What is thermite? Describe its uses and write the equation expressing the change that takes place when it is used.

8. Compare the action of aluminum and zinc on caustic soda, also on hydrochloric acid, writing the equations.

9. What is the chemical nature of: ruby, corundum, spinel, emery.

10. Write an equation indicating how aluminum hydroxide may be prepared. How does this compound act: (*a*) when used in clarifying drinking water, (*b*) when employed in making pigments called lakes?

11. What is a mordant? Give an illustration.

12. What use is made of aluminum sulphate in the paper industry?

13. What is an alum? Give the names and formulas of six different alums. What have they in common?

14. How does sodium alum act when treated with baking soda? Write the equation. What use is made of this fact?

15. Give the names and formulas of three different feldspars and write the equations showing how in the process of weathering they pass over into kaolin. What is the latter used for?

16. What is the difference between clay and kaolin? Between clay and marl? Between clay and sand?

17. Tell how earthenware and porcelain are made. What other silicate industries are there?

18. How is ultramarine blue prepared?

19. By what tests could you show that alum contains aluminum? Equations.

20. Why is thallium so called? Who discovered this element? Write the formulas of thallous and thallic chloride. Describe the physical properties of thallium.

21. What is meant by the term rare earths? Are any of the rare earths of practical importance? If so, state their use.

22. How much copper will be precipitated from a copper sulphate solution by 32 grams of metallic aluminum?

23. From 100 lb. of potassium alum how much aluminium oxide can be prepared?

24. How demonstrate that clay contains aluminum?

CHAPTER XXVII

LEAD AND TIN

GERMANIUM, lead, and tin are three metallic elements that exhibit a valence of two or four in their compounds, which are consequently analogous to those of carbon and silicon. The hydroxides of these metals increase in basicity with rise in atomic weight. These hydroxides, however, also have weakly acidic properties, for towards strong bases they may act as acids. Germanium forms a compound with hydrogen, GeH_4, but tin and lead do not.

Germanium (Ge — 72.5) is a very rare metal whose existence was foretold by Mendeléeff in 1871. He called the element **ekasilicon** and described its properties and fixed its atomic weight at about 73. In 1886 Clemens Winkler discovered germanium in the silver ore argyrodite $GeS_2 \cdot 3\,Ag_2S$, which occurs near Freiberg. The metal is also found in euxenite, samarskite, and confieldite. Germanium has properties which are practically the same as those predicted by Mendeléeff for ekasilicon. Germanium is a grayish white, brittle metal of specific gravity 5.47. It crystallizes in octahedra, and melts at about 900°. From the formulæ of the following compounds, the analogy of germanium to carbon and silicon is evident: GeH_4, GeF_4, $GeCl_4$, $GeHCl_3$, GeO_2, $GeOCl_2$, GeS_2, K_2GeF_6. Besides these, $Ge(OH)_2$ and GeS are also known.

Occurrence, Metallurgy, and Properties of Tin. — Tin occurs mainly in **cassiterite**, or tin stone, SnO_2, which crystallizes in the tetragonal system (Fig. 59), and is usually colored brown or black by oxides of iron and manganese. The metal has been known for a long time, for though it does not occur in the free state, its oxide is readily reduced by means of carbon. Tin was alloyed with copper to make bronze, even in ancient times. The Latin name of tin is stannum, whence the symbol Sn. It was also called *plumbum candidum* to distinguish it from lead, *plumbum nigrum*. Tin was obtained from the

mines at Cornwall in the days of the Roman Empire. Tin ores also occur in Saxony, Peru, Australia, Alaska, and the islands of Billiton and Banca east of Sumatra.

To extract tin from its ores, the latter are first roasted to expel any sulphur or arsenic present. The material is then treated with crude hydrochloric acid to remove iron, copper, etc., and lixiviated with water, after which the finely divided ore is mixed with carbon and heated in a furnace, thus: —

$$SnO_2 + 2\,C = Sn + 2\,CO.$$

The molten tin collects at the bottom of the furnace and is drawn off and cast into bars. It is purified by remelting it and collecting that portion which fuses at the lowest temperature, for this is freest from other metals. **Banca tin** is the purest; though German and English tin, **block tin**, also often is 98 to 99.9 per cent pure. The world's annual output of tin is about 130,000 tons, about two thirds of which comes from the East Indies.

Tin is a silver-white, lustrous metal of specific gravity 7.3. It melts at 232°, and boils at about 1600°. Tin is crystalline in character, and its bars, when bent, give a low, peculiar, crackling noise known as *tin cry*, which is due to the friction of the crystalline particles moving over one another. Tin is very ductile, malleable, and so soft that it may readily be cut with a knife. At 100°, the metal is still malleable, but this property decreases on raising the temperature further. At about 200°, tin is brittle and may be powdered. On cooling, molten tin always congeals in crystalline form. At low temperatures, tin gradually changes to a gray, brittle variety. This change takes place most rapidly at $-48°$, though it proceeds appreciably even at $-15°$. It is the cause of the *tin pest*, which consists of the disintegration of tin organ pipes and tin roofs and gutters in Russia, where winters are very cold. Above 20°, the ordinary malleable tin is the stable form, while below that temperature the gray, brittle variety is the stable modification.

In the air tin remains practically unchanged. When strongly heated, it burns with a white flame to SnO_2. In hot hydrochloric acid tin dissolves: —

$$Sn + 2\,HCl = SnCl_2 + H_2.$$

Hot concentrated sulphuric acid acts on tin, forming sulphur dioxide and stannous sulphate, $SnSO_4$: —

$$Sn + 2\,H_2SO_4 = SnSO_4 + 2\,H_2O + SO_2.$$

Cold, dilute, nitric acid acts on tin, forming stannous nitrate, thus: —

$$4\,Sn + 10\,HNO_3 = 4\,Sn(NO_3)_2 + 3\,H_2O + NH_4NO_3.$$

Concentrated nitric acid converts tin into metastannic acid (which see).

Uses of Tin. — Tin is used to a very large extent in making tin plate or **tinned iron.** This process consists of dipping thoroughly cleaned sheet iron in molten tin. The ordinary tin cans and other tin utensils are made of iron covered with a layer of tin by this dipping process. Copper is also often tinned in the same way.

Solder usually consists of 1 part tin and 1 part lead, but these proportions are often varied. An alloy of about 90 per cent tin, 8 per cent antimony, and 2 per cent copper is called **Britannia metal.** **Pewter** consists of 75 per cent tin and 25 per cent lead. **Bronzes** contain tin, copper, and sometimes also zinc, as stated under copper. Alloys of silver and tin are employed to make amalgams for filling teeth. Tin is recovered from old tin cans, etc., either by melting off the coating or more frequently by electrolysis. In this process, the cans placed in a wire basket are the anode, caustic alkali solution serves as the electrolyte, and an iron plate is used as the cathode. Much tin is saved in this way.

Chlorides of Tin. — **Stannous chloride** $SnCl_2$ is formed by dissolving the metal in hydrochloric acid. From the solution, monoclinic crystals $SnCl_2 \cdot 2\,H_2O$ are obtained, which are very soluble in water. This solution is a strong reducing agent. For instance, it readily reduces mercuric chloride to calomel and even to metallic mercury: —

$$2\,HgCl_2 + SnCl_2 = 2\,HgCl + SnCl_4.$$

$$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

Stannous chloride is hydrolyzed in solution. By treatment with much water a basic chloride of the composition $Sn(OH)Cl$ is precipitated: —

$$SnCl_2 + H_2O = Sn(OH)Cl + HCl.$$

Stannous chloride is used as a reducing agent in the laboratory and as a mordant in dyeing fabrics.

Stannic chloride $SnCl_4$ is made by the action of chlorine on tin or stannous chloride, or by treating stannic oxide or hydroxide with hydrochloric acid. It is a colorless, fuming liquid of specific gravity 2.28. It boils at 114°, and congeals at −33°. Tin tetrachloride is also known as *spiritus fumans Libavii*. With water, the chloride forms the hydrates $SnCl_4 \cdot 3\,H_2O$, *butter of tin*, $SnCl_4 \cdot 5\,H_2O$, and $SnCl_4 \cdot 8\,H_2O$. These are soluble in water. Stannic chloride readily forms double salts with other chlorides, like $SnCl_4 \cdot 2\,HCl \cdot 6\,H_2O$, or $H_2SnCl_6 \cdot 6\,H_2O$; $SnCl_4 \cdot 2\,KCl$, or K_2SnCl_6; $SnCl_4 \cdot 2\,NH_4Cl$, or $(NH_4)_2SnCl_6$. The latter is called **pink salt**. It is used as a mordant, as is also the hydrate $SnCl_4 \cdot 5\,H_2O$. Stannic chloride, on being boiled with water, yields a precipitate of **stannic acid**, thus :—

$$SnCl_4 + 3\,H_2O = 4\,HCl + H_2SnO_3.$$

In hydrocarbons, carbon disulphide, and many other organic and inorganic liquids $SnCl_4$ is soluble in all proportions. Compounds like $SnCl_4 \cdot PCl_5$, $SnCl_4 \cdot 2\,SCl_4$, $SnCl_4 \cdot 2\,NOCl$, $SnCl_4 \cdot POCl_3$ are also known. Indeed, stannic chloride enters into a large number of compounds.

Tin tetrabromide $SnBr_4$ and **tin tetraiodide** SnI_4 are also known.

Oxides of Tin. — **Stannous oxide** SnO is formed as a black powder by heating stannous hydroxide out of contact with oxygen. When ignited in the air, it burns, forming stannic oxide SnO_2. **Stannous hydroxide** is formed by adding sodium carbonate to a stannous chloride solution : —

$$SnCl_2 + Na_2CO_3 + H_2O = 2\,NaCl + Sn(OH)_2 + CO_2.$$

In potassium or sodium hydroxide, stannous hydroxide is soluble, but not in ammonium hydroxide, thus : —

$$Sn(OH)_2 + 2\,KOH = K_2SnO_2 + 2\,H_2O.$$

On boiling the solution, the **potassium** or **sodium stannite** is converted to stannate, with concomitant precipitation of tin, thus : —

$$2\,K_2SnO_2 + H_2O = K_2SnO_3 + 2\,KOH + Sn.$$

Stannic oxide SnO_2, or stannic acid anhydride, is obtained by burning tin in oxygen or in the air, or by igniting stannic acid. Stannic oxide is found in nature in quadratic crystals as cassiterite, the principal ore of tin. Stannic oxide as artificially prepared is a white or slightly yellowish powder, which is insoluble in water, acids, or alkalies especially after strong ignition. During ignition, the oxide turns darker in color, but it again changes to white on cooling. When fused with caustic alkalies, stannic oxide forms **stannates**, which are soluble, thus: —

$$SnO_2 + 2\,NaOH = Na_2SnO_3 + H_2O.$$

Stannic hydroxide is formed as a gelatinous precipitate by boiling tin tetrachloride with water, or by adding ammonia to the solution. Stannic hydroxide or **orthostannic acid** $Sn(OH)_4$ easily splits off water, and forms $SnO \cdot (OH)_2$ or H_2SnO_3, which is called **stannic acid**. This also gradually loses water so that neither $Sn(OH)_4$ nor $SnO \cdot (OH)_2$ have really been definitely isolated. It will be observed that stannic acid H_2SnO_3 is analogous to H_2CO_3 and H_2SiO_3. Stannic acid readily dissolves in concentrated sulphuric, nitric, or hydrochloric acid, and also in dilute solutions of caustic alkalies. With the latter it forms stannates, which dissolve. From these soluble stannates, the stannates of other metals may be prepared by precipitation; for as in the case of the silicates and carbonates, *only the stannates of the alkalies are soluble.* Sodium stannate Na_2SnO_3 is made by fusing cassiterite with caustic soda or by fusing tin with sodium carbonate and sodium nitrate. From its aqueous solutions, sodium stannate separates in monoclinic crystals $Na_2SnO_3 \cdot 3\,H_2O$. It is used as a mordant in calico printing, being termed **preparing salt.**

Concentrated nitric acid converts tin into a white, insoluble powder known as **metastannic acid**, which is a hydrated oxide of tin, whose composition, like that of stannic acid, varies slightly according to temperature and other conditions of preparation; being probably H_2SnO_4 or H_2SnO_3, thus: —

$$Sn + 4\,HNO_3 = H_2SnO_3 + H_2O + 4\,NO_2.$$

But metastannic acid is different from stannic acid, for it is insoluble in acids, and with alkalies it forms salts like $K_2Sn_5O_{11} \cdot 4\,H_2O$ and $Na_2Sn_5O_{11} \cdot 4\,H_2O$, **metastannates**, which

would indicate that the acid is dibasic and probably analogous to polysilicic acids. *On fusion with caustic alkalies, metastannic acid yields the stannates which are identical with those of stannic acid.*

Sulphides of Tin. — **Stannous sulphide** SnS is formed as a dark brown precipitate when hydrogen sulphide is conducted into a solution of a stannous salt. This precipitate is insoluble in dilute acids or solutions of the monosulphides of the alkalies; but when boiled with the latter and sulphur, or when treated with alkaline polysulphides, soluble **sulpho-stannates** are formed, thus: —

$$SnS + S + K_2S = K_2SnS_3.$$
$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

These sulpho-salts are decomposed by hydrochloric acid, yielding precipitates of stannic sulphide SnS_2, thus: —

$$K_2SnS_3 + 2\,HCl = 2\,KCl + SnS_2 + H_2S.$$
$$(NH_4)_2SnS_3 + 2\,HCl = 2\,NH_4Cl + SnS_2 + H_2S.$$

Stannic sulphide is a yellow, amorphous powder, which is also obtained by passing hydrogen sulphide into solutions of stannic salts. It is insoluble in dilute acids. On heating, it decomposes into stannous sulphide and sulphur. In alkaline sulphides it dissolves, yielding sulphostannates. Concentrated hydrochloric acid dissolves stannic sulphide, and concentrated nitric acid converts it into metastannic acid.

By heating tin and sulphur together, stannous sulphide is formed. Stannic sulphide cannot be thus obtained, for it decomposes into sulphur and stannous sulphide at the high temperature reached during the progress of the reaction. However, by heating together sulphur, ammonium chloride, and finely divided tin, stannic sulphide is obtained as a golden yellow, crystalline mass which is used for bronzing, being called **mosaic gold.**

Analytical Tests for Tin. — When mixed with sodium carbonate and ignited on charcoal, tin compounds are reduced, yielding bright globules of the metal. The behavior of stannous chloride toward mercuric chloride is often used to characterize tin. Furthermore, the reactions of the sulphides of tin, as given above, are of importance, as is also the fact that the hydroxides are precipitated by alkaline carbonates, and do

not dissolve in excess of the latter. Zinc precipitates spongy tin from solutions of tin salts. This may then be dissolved in hydrochloric acid and tested with mercuric chloride. In this way, tin may be distinguished from antimony.

Occurrence, Metallurgy, and Properties of Lead. — Lead, *plumbum*, is seldom found in the uncombined state in nature. It occurs chiefly as the sulphide PbS, which commonly crystallizes in cubes of the regular system, and is called **galenite.** The following ores are also found, though rarely and in smaller quantities: cerussite $PbCO_3$, wulfenite $PbMoO_4$, crocoisite $PbCrO_4$, bouronite $Cu_2S \cdot Sb_2S_3 \cdot 2\,PbS$, anglesite $PbSO_4$, pyromorphite $PbCl_2 \cdot Pb_3(PO_4)_2$. Galenite, or galena, is found in fairly large quantities in the United States, Great Britain, Germany, Spain, and Australia.

To obtain lead from galena, the latter is roasted so as to oxidize it in part to oxide and in part to sulphate, thus: —

$$2\,PbS + 3\,O_2 = 2\,PbO + 2\,SO_2, \text{ and}$$
$$PbS + 2\,O_2 = PbSO_4.$$

By then strongly heating this mixture of lead oxide, lead sulphate, and unchanged lead sulphide, out of contact with the air, lead is obtained, thus: —

$$2\,PbO + PbS = SO_2 + 3\,Pb, \text{ and}$$
$$PbSO_4 + PbS = 2\,SO_2 + 2\,Pb.$$

Lead may also be prepared from galena by heating the latter with iron, thus: —

$$PbS + Fe = FeS + Pb.$$

As the ferrous sulphide formed is much lighter than lead, it floats on top of the latter, and is run off like a slag. The molten lead can readily be drawn off from below. The separation of lead from silver, which commonly accompanies lead, has already been described. The world's annual production of lead is about 1,300,000 tons. The United States furnishes about one third of this amount.

Lead is a soft, malleable, bluish white metal, having a bright luster on freshly cut surfaces, which soon becomes dull on exposure to the air because of the formation of a film of oxide. The specific gravity of lead is 11.4. It melts at 327°, and

boils at about 1200° in vacuo. By heating lead in the air, the oxide is formed. Water in contact with the air acts on lead somewhat, forming lead hydroxide, which is slightly soluble. Waters containing calcium sulphate or bicarbonate act on lead, forming lead sulphate or carbonate. These salts are insoluble, and so form a coating that protects the metal from further action. Hence it is quite feasible to use lead pipes for conducting drinking water. Hydrochloric and sulphuric acids act on lead but slightly, because the resulting products, lead chloride and lead sulphate, are sparingly soluble. In nitric or acetic acid lead is readily soluble. Many other weak organic acids dissolve lead, hence it is unsuitable for cooking utensils. The atomic weight of lead is 207.10, and its valence is generally two, though in some compounds the element is quadrivalent. From solutions of its salts, lead is displaced by zinc, iron, and tin. When a strip of zinc is hung in a dilute lead acetate solution, a bulky, branching mass of lead, known as a **lead tree**, is formed thus: —

$$Zn + Pb(C_2H_3O_2)_2 = Zn(C_2H_3O_2)_2 + Pb.$$

Uses of Lead. — Lead has been known since earliest times. The Romans used it for water pipes, and Pliny distinguished between lead and tin. Much lead is used as lead pipes in plumbing. These pipes are readily made of hot, plastic lead by means of hydraulic pressure. In the sulphuric acid industry, lead is used for lining the chambers and making evaporating dishes and pipes. It is also employed in other chemical operations for containers. Sheet lead further serves for roofs and gutters. Alloyed with tin, lead forms solder, pewter, and Britannia metal, which have already been described. It also enters into the composition of Rose's metal and Wood's metal, which are alloys of low melting points. Type metal is an alloy of lead with antimony, which has been mentioned in connection with the latter. Lead used for **shot** and **bullets** contains from 0.2 to 0.4 per cent of arsenic. **Babbitt metal** consists of 70 to 90 per cent lead alloyed with tin and antimony. It is used for bearings in machines. Large quantities of lead are also used in making storage batteries. Besides this, much lead is consumed in the production of various lead compounds.

Oxides of Lead. — The following five oxides of lead are

known: Pb_2O, PbO, Pb_2O_3, Pb_3O_4, and PbO_2. **Lead suboxide** Pb_2O is a black powder, formed by the action of the air on lead, or by heating lead oxalate, thus: —

$$2\,PbC_2O_4 = Pb_2O + 3\,CO_2 + CO.$$

Lead oxide, or **plumbic oxide**, PbO is formed by burning lead in the air. It results as a by-product in the separation of lead from silver by cupellation. Lead oxide is also made by calcining the carbonate or nitrate. It is a yellow, amorphous powder; but when fused and allowed to cool, it forms a crystalline mass. This, when pulverized, is termed **litharge**. It is used in making glass of high refracting power, in glazing pottery, decorating porcelain, and preparing many lead compounds.

Lead hydroxide $Pb(OH)_2$ is formed by adding caustic alkali to a solution of a lead salt. Lead hydroxide is a strong base and is appreciably soluble in water, imparting a faintly alkaline reaction to the latter. With caustic alkalies, however, lead hydroxide exhibits acid properties, forming **plumbites**, thus: —

$$2\,NaOH + Pb(OH)_2 = Na_2PbO_2 + 2\,H_2O.$$

On boiling plumbic oxide with caustic alkalies, plumbites are also formed.

Lead sesquioxide Pb_2O_3 is an orange-yellow powder, obtained by the action of a hypochlorite on a solution of a plumbite.

Red lead, or **minium**, Pb_3O_4 is formed by heating plumbic oxide in the air to about 400°. It is a bright red powder, which is generally contaminated with some litharge, just as the latter always contains small amounts of minium. Red lead is used as a pigment in paints. When treated with nitric acid, it reacts thus: —

$$Pb_3O_4 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + PbO_2 + 2\,H_2O.$$

It is evident, then, that minium behaves like a mixture of $2\,PbO$ and PbO_2. However, it is probably a plumbate of lead, Pb_2PbO_4; and as nitric acid acts upon it, lead nitrate and *plumbic acid* H_4PbO_4 are formed. The latter, being very unstable, is decomposed at once into $2\,H_2O$ and PbO_2.

Lead peroxide PbO_2 is a brown powder, which is also formed by the action of hypochlorites upon lead salts in alkaline solution, and at the anode during the electrolysis of lead salts.

With sulphuric acid it forms lead sulphate and oxygen, and with hydrochloric acid lead chloride and chlorine, thus: —

$$2\,PbO_2 + 2\,H_2SO_4 = 2\,PbSO_4 + 2\,H_2O + O_2.$$
$$PbO_2 + 4\,HCl = PbCl_2 + 2\,H_2O + Cl_2.$$

In hot, concentrated solutions of caustic alkalies lead peroxide dissolves, forming **plumbates**, thus: —

$$2\,KOH + PbO_2 = K_2PbO_3 + H_2O.$$

Plumbates are salts of *metaplumbic acid* H_2PbO_3. They are analogous to carbonates, silicates, and stannates.

All oxides of lead when strongly ignited in the air are finally converted into litharge, thus: —

$$Pb_2O + O = 2\,PbO.$$
$$Pb_2O_3 = 2\,PbO + O.$$
$$Pb_3O_4 = 3\,PbO + O.$$
$$PbO_2 = PbO + O.$$

Halides of Lead. — **Lead chloride** $PbCl_2$ is a white salt obtained as a precipitate by adding a soluble chloride to a solution of a lead salt. It is sparingly soluble in cold water, but 100 parts of boiling water dissolve about 4 parts of the salt. On ignition in the air, lead chloride forms **lead oxychloride** Pb_2OCl_2. This oxychloride is also produced as $Pb_2OCl_2 \cdot H_2O$, Pattinson's white lead, by adding milk of lime to a hot solution of lead chloride: —

$$2\,PbCl_2 + Ca(OH)_2 = Pb_2OCl_2 \cdot H_2O + CaCl_2.$$

Lead tetrachloride $PbCl_4$ is a yellow oil of specific gravity 3.2, which congeals as a crystalline mass at $-15°$. It is formed by dissolving lead peroxide in well-chilled concentrated hydrochloric acid, or by passing chlorine into a cold solution of lead chloride in hydrochloric acid. On then adding ammonium chloride, the double salt $PbCl_4 \cdot 2\,NH_4Cl$ is obtained as a crystalline precipitate, which when treated with concentrated sulphuric acid at 0° yields lead perchloride as a yellow oil. The latter readily decomposes into $PbCl_2$ and Cl_2. At 105° this decomposition proceeds with explosive violence.

Lead bromide $PbBr_2$ and **oxybromide** Pb_2OBr_2 are analogous to the corresponding chlorides.

Lead iodide PbI_2 is a yellow precipitate formed by adding a

soluble iodide to a solution of a lead salt. It dissolves in about 200 parts of boiling water, from which it crystallizes in shining hexagonal scales. Like the iodide of mercury, it readily forms double salts with iodides of the alkalies.

Lead Nitrate $Pb(NO_3)_2$ is formed by the action of nitric acid on lead, lead oxide, or lead carbonate. It forms octahedra which are soluble in about 2 parts of water.

Lead Acetate $Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$ is made by dissolving lead or lead oxide in acetic acid. The salt forms prismatic crystals that readily effloresce. They are very soluble in water, and the solution has a sweetish taste, hence the salt is called **sugar of lead**, or *saccharum saturni*. Lead acetate solutions dissolve lead oxide or hydroxide, thus forming **basic lead acetate** $Pb(C_2H_3O_2)_2 \cdot (PbO)_x$, dilute solutions of which (about 2 per cent) are known as **lead water**. These basic lead acetate solutions readily become milky, due to the formation of lead carbonate with carbon dioxide of the air.

Lead Sulphate $PbSO_4$ is a white crystalline precipitate formed by adding a soluble sulphate to a solution of a lead salt. It is practically insoluble in water and dilute sulphuric acid. But it dissolves appreciably in hydrochloric and nitric acids, and fairly readily in concentrated sulphuric acid. It is also soluble in caustic alkalies, in sodium thiosulphate, and in ammonium acetate and other ammonium salts of organic acids.

Lead Sulphide PbS is found in nature as already stated. It is formed as a black precipitate when hydrogen sulphide is passed into a solution of a lead salt. In dilute acids it is insoluble also in sulphides of the alkalies; but when boiled with concentrated hydrochloric acid, it forms lead chloride and hydrogen sulphide. When boiled with dilute nitric acid, lead sulphide forms lead nitrate, while concentrated nitric acid oxidizes it to sulphate. The latter change also takes place slowly when moist lead sulphide is exposed to the air.

Lead Arsenate $Pb_3(AsO_4)_2$ is formed by treating a lead acetate solution with sodium arsenate. Lead arsenate is a white powder that is but sparingly soluble in water. Like Paris green, lead arsenate is used for exterminating potato bugs and other insects that infest cultivated plants.

Lead Carbonate $PbCO_3$ is found in nature, as already mentioned. It is formed as a white precipitate by adding lead

nitrate to a solution of ammonium carbonate. When a solution of a lead salt is precipitated with normal sodium or potassium carbonate, basic lead carbonates are obtained whose composition varies with the concentration and temperature of the solutions used.

White lead, which is used in paints, is a **basic lead carbonate,** commonly of the composition $Pb(OH)_2 \cdot 2\,PbCO_3$. It is formed by the action of carbon dioxide on basic lead acetate. **Thénard's method,** also called the French method, consists of passing carbon dioxide into a solution of basic lead acetate formed by dissolving lead oxide in lead acetate solution. Thus basic lead carbonate is precipitated, while neutral lead acetate remains in solution and can be used over again. This is a rapid, direct process, but it yields a crystalline or granular product which does not possess the desirable covering properties of white lead produced by the **Dutch process.** The latter has been in use for nearly three hundred years, and consists of allowing the vapors of vinegar and carbon dioxide to act slowly upon large surfaces of lead. To effect this, the sheet lead is loosely rolled together in spirals, each of which is placed in a small earthenware pot into which vinegar, 4 to 5 per cent acetic acid, has been poured. The lead rests on a shelf so as not to be in contact with the vinegar. Lead gratings or other forms of lead castings are sometimes used instead of sheet lead spirals. The earthen pots, which are about 20 cm. high and 12 cm. in diameter, are loosely covered and set in horse manure or spent tan bark. The acetic acid thus vaporizes and acts upon the lead, forming basic lead acetate, which is then acted upon by the carbon dioxide liberated during the process of fermentation of the manure or spent tan, resulting in the formation of white lead. Several weeks are required to complete the action. The fermentation process not only furnishes the required carbon dioxide, but also produces the heat necessary to vaporize the vinegar. An amorphous white lead of superior covering power is obtained in this way. Many **other processes** are in use, and some of them yield white lead of excellent quality. They all depend upon the action of acetic acid and carbon dioxide upon lead. **Electrolytic processes** have also been proposed; they depend upon the fact that when the electric current is passed between two lead plates dipping in a solution of sodium nitrate

or chlorate, and sodium bicarbonate, basic lead carbonate is precipitated. It is claimed that the product obtained is amorphous.

White lead is ground with linseed oil and used as a paint. The oil gives the paint a yellowish tinge which is usually dispelled by adding a trace of blue or black pigment. Barium sulphate, lead sulphate, and calcium carbonate, particularly the former, are used as **adulterants of white lead.** Their presence can readily be detected. White lead turns dark when exposed to hydrogen sulphide, or when sulphide pigments are mixed with it. It is also poisonous, and care must be exercised in its manufacture and use so that it will not get into the system. *All lead compounds are poisonous;* the readily soluble ones are, of course, the most dangerous. Painters and others that work with lead or its compounds are liable to lead colic, which is produced by the gradual absorption of lead compounds, by breathing the latter in form of fine dust, or by constantly handling them.

Analytical Tests for Lead. — When mixed with soda and heated on charcoal before the blowpipe, lead compounds yield globules of metallic lead, which upon oxidation are transformed to plumbic oxide. Lead sulphide, sulphate, hydroxide, chloride, and carbonate are all characteristic precipitates which may be obtained from solutions of lead salts as already stated. A lemon-yellow precipitate of lead chromate is produced by adding potassium chromate or bichromate to a solution of a lead salt.

REVIEW QUESTIONS

1. Compare the chemical properties of lead and tin. How are these metals related to: (*a*) germanium, (*b*) carbon and silicon?
2. How much carbon would be required to reduce one ton of cassiterite? Equation.
3. What are the characteristic physical properties of tin? Which prevents the formation of iron rust better, to coat iron with tin or with zinc?
4. Why is it not advisable to cover roofs with tin in cold countries?
5. How do the following act on tin: (*a*) concentrated nitric acid, (*b*) hot concentrated sulphuric acid, (*c*) hydrochloric acid? Equations.
6. Mention three alloys of tin and state their uses.
7. How form the tetrachloride of tin: (*a*) from metallic tin, (*b*) from stannous chloride?

8. What is a stannite? Give an example. What compounds of the following metals are analogous to the stannites: zinc, aluminum, antimony, lead.

9. Compare stannic acid with silicic acid and carbonic acid. Write the formulas of the compounds showing the relationship.

10. What two sulphides of tin are known? By equations show how they react with yellow ammonium sulphide.

11. Given a solution of stannous chloride, describe four different tests by means of which it could be shown that the solution contains tin. Equations.

12. What is the main ore of lead? By equations indicate how lead is prepared from this ore.

13. Describe the uses of metallic lead.

14. What alloys of lead are in common use?

15. What is litharge? How is it made and what is it used for?

16. What is a plumbate? Give an equation showing how sodium plumbate may be formed. Write the analogous equation for making sodium carbonate.

17. Write the formula expressing the composition of each of the following and state the use of each substance: sugar of lead, lead arsenate, white lead.

18. How test a paint to ascertain if it contains white lead?

CHAPTER XXVIII

CHROMIUM, MOLYBDENUM, TUNGSTEN, AND URANIUM

CHROMIUM (Cr — 52.0), molybdenum (Mo — 96.0), tungsten (W — 184.0), and uranium (U — 238.5) are related to the members of the sulphur family about as titanium, zirconium, cerium, and thorium are to the carbon and silicon group, or as vanadium, columbium, and tantalum are to the phosphorus group. The members of the chromium family form the trioxides CrO_3, MoO_3, WO_3, and UO_3, which are analogous to SO_3. Like the latter, they are acid anhydrides. With metallic oxides they form salts like K_2CrO_4, K_2MoO_4, K_2WO_4, which correspond to K_2SO_4. Again, the compounds MoO_2, WO_2, and UO_2 are analogous to SO_2. On the other hand, chromium often acts as a base, forming compounds that are analogous to those of aluminum and iron, as in $CrCl_3$, and $Cr_2(SO_4)_3$. The other members of the group do not form such salts, but they enter into other rather complicated compounds. This is particularly the case with uranium. Chromium is the most important member of the group. None of the elements of this family occur in nature in the free state.

Occurrence, Preparation, and Properties of Chromium. — Chromium is generally found in form of **chromite**, also called **chrome iron ore**, $FeO \cdot Cr_2O_3$ or $Fe(CrO_2)_2$, which crystallizes in octahedra and is isomorphous with spinel. Crocoisite $PbCrO_4$, first found in Siberia, occurs more rarely, though it was in this mineral that chromium was discovered in 1797 by Vauquelin. The name *chromium* was given the element because it forms colored compounds.

Metallic chromium may readily be prepared by Goldschmidt's process, consisting of igniting a mixture of chromic oxide and finely divided aluminum by means of a fuse of magnesium ribbon or a mixture of barium peroxide and aluminum powder. The reaction when thus started proceeds to completion. Chromium may also be obtained by reducing the oxide with carbon in the electric furnace.

Chromium is a steel-gray, hard, brittle metal of high metallic luster. Its specific gravity is 6.8. It requires the electric furnace to melt chromium. The metal may be polished, and it remains unchanged in the air. At high temperatures it burns in oxygen or in the air, emitting a brilliant light and forming Cr_2O_3. Chromium is not attacked by nitric acid; but in warm dilute hydrochloric or sulphuric acid it dissolves with evolution of hydrogen. Chromium is commonly bivalent, trivalent, or hexavalent.

Chromium is used in the steel industry for making chrome steel, in which process **ferrochromium,** an alloy of iron and chromium containing 60 per cent of the latter, is added to the steel. This ferrochromium is readily prepared by heating chromium ore with carbon in the electric furnace.

Chromic Oxide and Hydroxides. — With oxygen, chromium forms a **sesquioxide,** Cr_2O_3, which acts as a base, and a **trioxide,** CrO_3, which acts as an acid. These are the only oxides of chromium that are known with certainty, though **chromous hydroxide** $Cr(OH)_2$, in which the metal is bivalent, has also been prepared, being formed as a yellow precipitate when caustic alkali is added to a solution of chromous chloride.

Chromic oxide (chromium sesquioxide) Cr_2O_3 is a grass-green powder formed by ignition of chromic hydroxide, chromium trioxide, or ammonium bichromate. The oxide may be obtained in the form of very dark green, lustrous, hexagonal crystals by passing the vapors of **chromyl chloride** CrO_2Cl_2 through a red-hot tube, thus: —

$$2\,CrO_2Cl_2 = Cr_2O_3 + 2\,Cl_2 + O.$$

Amorphous chromic oxide dissolves readily in acids, but after strong ignition the latter scarcely attack it; and like highly heated oxides of iron or aluminum, chromic oxide is then usually fused with bisulphate of potassium in order to effect its solution. Chromic oxide is used as a pigment, **chrome green,** in paints. It also serves in coloring glass green.

Chromic hydroxide is formed as a grayish blue precipitate of the composition $Cr(OH)_3 \cdot 2\,H_2O$ when ammonia is added to a solution of a chromium salt. On drying this substance over sulphuric acid in a vacuum, a residue of very nearly the composition $Cr(OH)_3$ may be obtained. On heating the latter in

hydrogen to about 220°, chromous hydroxide $Cr(OH)_2$ is formed, which upon strong ignition yields chromic oxide and water. Potassium or sodium hydroxide also precipitates hydrated chromic hydroxide from solutions of chromium salts, but the precipitate always contains some alkali. In excess of potassium or sodium hydroxide, chromic hydroxide is soluble, forming **chromites**, thus: —

$$NaOH + Cr(OH)_3 = NaCrO_2 + 2\,H_2O.$$

This behavior is similar to that of aluminum hydroxide. However, on boiling solutions of chromites, they are decomposed, chromic hydroxide being precipitated, while aluminates are stable under similar treatment. **Insoluble chromites** are also known, chrome iron ore $Fe(CrO_2)_2$ being a compound of this character. With acids, chromic hydroxide forms chromic salts; indeed, it generally acts as a base.

Chromous Compounds. — In these compounds chromium is bivalent. The hydroxide, $Cr(OH)_2$, has already been mentioned. **Chromous chloride** $CrCl_2$ and **chromous sulphate** $CrSO_4 \cdot 7\,H_2O$ have been prepared by dissolving the metal in hydrochloric or sulphuric acid. Chromous chloride has also been made by heating chromic chloride in hydrogen. Chromous salts have been studied but little. They are strong reducing agents, for they readily pass over into chromic compounds.

Chromic Salts. — These are made by action of acids on chromic hydroxide. **Chromic chloride** $CrCl_3$ may also be prepared by the action of chlorine on heated chromium, or by passing chlorine over a red-hot mixture of chromic oxide and carbon. Thus prepared, the compound sublimes in violet leaflets that are almost insoluble in water. By ignition in the air these pass over into chromic oxide. On long-continued boiling the salt slowly dissolves; but when chromous chloride is added, even in traces, the action progresses much more rapidly, a green solution being formed from which by evaporation green, deliquescent crystals, $CrCl_3 \cdot 6\,H_2O$, may be obtained. The latter yield both water and hydrochloric acid on being heated in the air; consequently, to prepare the anhydrous chloride from them, they are heated in a current of chlorine or hydrochloric acid gas.

Chromic sulphate $Cr_2(SO_4)_3 \cdot 15\,H_2O$ is deposited from cold solutions in the form of violet crystals. The salt forms violet solutions at ordinary temperatures. On boiling these, they become green because a hydrolysis takes place, the exact nature of which has not yet been definitely determined. From the green solutions no crystals are obtainable; but on standing, these solutions slowly become violet again and deposit violet crystals. This peculiar behavior is also exhibited by other chromic salts.

Chrome alums are double salts which chromic sulphate forms with sulphates of the alkalies. They have the same general formula as other alums, and are isomorphous with them. **Potassium chrome alum** $KCr(SO_4)_2 \cdot 12\,H_2O$ is the commonest of these compounds, and is generally called simply **chrome alum.** It forms octahedra which are of a dark violet color, but appear reddish by transmitted light. They effloresce on exposure to the air. Their solutions exhibit color changes similar to those of chromic sulphate.

Chromates, Bichromates, and Chromium Trioxide. — The chief source of chromium is chrome iron ore, as already stated. When this is pulverized, mixed with potash and calcium carbonate, and roasted in contact with air, ferric oxide, potassium chromate, calcium chromate, and carbon dioxide are formed, thus: —

$$4\,Fe(CrO_2)_2 + 6\,K_2CO_3 + 2\,CaCO_3 + 7\,O_2 = 6\,K_2CrO_4 + 2\,CaCrO_4 + 2\,Fe_2O_3 + 8\,CO_2.$$

On lixiviating the mass with water, potassium and calcium chromates dissolve, and on adding potassium sulphate to the solution, calcium sulphate is formed, thus: —

$$CaCrO_4 + K_2SO_4 = CaSO_4 + K_2CrO_4.$$

On evaporating the clear solution of **potassium chromate** thus obtained, the salt crystallizes out in rhombic pyramids of lemon color which are isomorphous with potassium sulphate. Potassium chromate is soluble in about 2 parts of water. The solution has an alkaline reaction because of partial hydrolysis of the salt.

On adding sulphuric acid to a solution of potassium chromate, the latter turns orange-red and readily deposits large, red, triclinic crystals of **potassium bichromate** $K_2Cr_2O_7$. These are

soluble in about 1 part of water at 100°, whereas at room temperatures about 10 parts of water are necessary to effect their solution. The salt can consequently readily be purified by recrystallization. Potassium bichromate is analogous to potassium pyrosulphate $K_2S_2O_7$. On heating potassium bichromate, it melts and then decomposes: —

$$2\,K_2Cr_2O_7 = 2\,K_2CrO_4 + Cr_2O_3 + 3\,O.$$

When heated with concentrated sulphuric acid, chrome alum and oxygen are formed: —

$$K_2Cr_2O_7 + 4\,H_2SO_4 = 2\,KCr(SO_4)_2 + 4\,H_2O + 3\,O.$$

With hot concentrated hydrochloric acid, chlorine is evolved: —

$$K_2Cr_2O_7 + 14\,HCl = 2\,CrCl_3 + 2\,KCl + 7\,H_2O + 3\,Cl_2.$$

From these reactions it is clear that potassium bichromate is a strong oxidizing agent, each molecule yielding three oxygen atoms that are available to effect oxidations.

If, in the roasting of chrome iron ore with calcium carbonate and potash, soda is substituted for the latter, **sodium chromate** is produced. It is a yellow salt that may be obtained in deliquescent, prismatic crystals, $Na_2CrO_4 \cdot 10\,H_2O$, which are isomorphous with Glauber's salt. On treatment with sulphuric acid, sodium chromate may be transformed to **sodium bichromate** $Na_2Cr_2O_7 \cdot 2\,H_2O$, which forms red, triclinic crystals, soluble in about 1 part of water at ordinary temperatures. This salt is cheaper than potassium bichromate and hence is generally used in place of the latter in the industries. By adding potassium chloride to solutions of sodium bichromate, potassium bichromate may be obtained, for it is less soluble.

Gelatine treated with potassium bichromate solution darkens on exposure to light and becomes insoluble, probably because of the formation of chromic oxide and partial oxidation of the gelatine. This fact is used in photographic processes, and also in making a glue that gradually becomes insoluble. *Bichromates are used in dyeing and tanning, also as oxidizing agents in the laboratory and in the industries.* **Ammonium bichromate** $(NH_4)_2Cr_2O_7$ forms readily soluble red crystals which on ignition continue to oxidize with brilliant scintillations: —

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4\,H_2O + N_2.$$

Lead chromate $PbCrO_4$ is a bright yellow precipitate formed by adding either a soluble chromate or bichromate to a solution of a lead salt. It serves as a pigment in paints, being called **chrome-yellow.** It may be fused without decomposition. On cooling, it then forms a brown crystalline solid, which when heated with carbon compounds readily oxidizes the latter, hence its use in organic combustion analyses.

Barium chromate $BaCrO_4$ is a yellow precipitate prepared by adding a soluble chromate or bichromate to a solution of a barium salt. It is insoluble in acetic acid, but soluble in nitric or hydrochloric acid. It is also used as a pigment, under the name ultramarine yellow. **Calcium chromate** $CaCrO_4 \cdot 2\,H_2O$ is analogous to gypsum $CaSO_4 \cdot 2\,H_2O$. **Magnesium chromate** $MgCrO_4 \cdot 7\,H_2O$ is analogous to Epsom salt $MgSO_4 \cdot 7\,H_2O$. *With the exception of barium chromate, the chromates of the alkaline earths all dissolve in acetic acid, which fact is used in analysis. Chromates of the heavy metals are insoluble in water* and hence are readily prepared by precipitation. **Silver chromate** Ag_2CrO_4 and **mercurous chromate** Hg_2CrO_4 are characteristic red precipitates.

On adding concentrated sulphuric acid to a well-cooled concentrated solution of sodium or potassium bichromate, **chromium trioxide**, or **chromic acid anhydride**, CrO_3 separates out in form of beautiful, dark red, deliquescent, rhombic needles. Its aqueous solutions probably contain bichromic acid $H_2Cr_2O_7$, but the latter has not been isolated. On neutralization with alkalies, such solutions of chromic acid yield bichromates and chromates. *Chromium trioxide is a powerful oxidizing agent. It destroys organic tissues and oxidizes many compounds*, thus: —

$$2\,CrO_3 + 3\,H_2S = Cr_2O_3 + 3\,S + 3\,H_2O.$$

$$CrO_3 + 6\,HCl = CrCl_3 + 3\,H_2O + 3\,Cl.$$

$$2\,CrO_3 + 3\,SO_2 = Cr_2(SO_4)_3.$$

$$2\,CrO_3 + 3\,H_2SO_4 + 3\,C_2H_5 \cdot OH = Cr_2(SO_4)_3 + 3\,CH_3CHO + 6\,H_2O.$$

$$2\,CrO_3 + 3\,H_2SO_4 + 3\,(COOH)_2 = Cr_2(SO_4)_3 + 6\,H_2O + 6\,CO_2.$$

It should be borne in mind that *compounds of chromium are poisonous*, those that are readily soluble being most harmful.

Chromyl Chloride $CrO_2 \cdot Cl_2$ is analogous to sulphuryl chloride

$SO_2 \cdot Cl_2$. It is a dark red, fuming liquid commonly made by distilling a mixture of sodium chloride, sodium or potassium bichromate, and sulphuric acid, thus: —

$$4\,NaCl + Na_2Cr_2O_7 + 6\,H_2SO_4 = 6\,NaHSO_4 + 3\,H_2O + 2\,CrO_2Cl_2.$$

Water decomposes the compound: —

$$CrO_2 \cdot Cl_2 + H_2O = CrO_3 + 2\,HCl;$$

hence, in preparing it, a sufficient amount of sulphuric acid must be used to absorb the water formed during the reaction.

Analytical Tests for Chromium Compounds. — Because of their color, these compounds are readily detected. Chromous compounds readily pass over into chromic compounds. The latter yield a green coloration when heated in the borax or sodium metaphosphate bead. Caustic alkalies precipitate chromic hydroxide, which is soluble in an excess of the precipitant, but is again precipitated on boiling. Alkaline carbonates precipitate chromic hydroxide. Hydrogen sulphide produces no precipitate in solutions of chromic salts, but ammonium sulphide precipitates chromic hydroxide. The latter, like the hydroxide of aluminum, is scarcely affected by an excess of ammonium hydroxide. When fused with soda and saltpeter, chromic compounds yield chromates; these are characterized by their yellow color and by the characteristic insoluble precipitates which their solutions yield with silver nitrate, barium chloride, lead nitrate, and mercurous nitrate. Furthermore, when acidified with sulphuric acid, chromate solutions readily oxidize oxalic acid, alcohol, ferrous salts, etc., yielding green solutions of chromic sulphate.

Molybdenum. — This metal is found in **molybdenite** MoS_2, which looks like graphite, and in **wulfenite** $PbMoO_4$, which forms yellowish tetragonal crystals. On roasting molybdenite, it is converted to **molybdenum trioxide** MoO_3, a white crystalline powder which is the most stable oxide of molybdenum. This powder readily dissolves in caustic alkalies or ammonium hydroxide, forming **molybdates.** Of these **ammonium molybdate** $(NH_4)_2MoO_4$ *is an important reagent in analytical chemistry, for with phosphoric acid or phosphates in dilute nitric acid solution it yields a characteristic light yellow precipitate of* **ammonium phosphomolybdate** $(NH_4)_3PO_4 \cdot 11\,MoO_3 \cdot 6\,H_2O$. The

composition of the latter varies somewhat according to the conditions of precipitation. In dilute acids the compound is insoluble, but in alkalies or an excess of phosphoric acid it dissolves. On treating a solution of a molybdate with nitric acid, yellow crystals of **molybdic acid** $H_2MoO_4 \cdot H_2O$ separate out, which upon drying yield H_2MoO_4. Similarly when ammonium phosphomolybdate is treated with aqua regia, crystals of **phosphomolybdic acid** $H_3PO_4 \cdot 11\,MoO_3 \cdot 12\,H_2O$ are formed. This acid forms insoluble salts with salts of potassium, ammonium, and the alkaloids, and is consequently of value in analytical tests for the latter. It is known as **Sonnenschein's reagent.**

Molybdenum receives its name from the Greek word meaning lead, for molybdenite was regarded as graphite, which was called black lead. Scheele made molybdic acid in 1778 by treating molybdenite with nitric acid, thus showing that the mineral is not graphite. In 1790 Hjelm prepared the metal by heating the oxides or chlorides in a current of hydrogen, and Klaproth determined the true nature of wulfenite in 1797. Molybdenum may also be made by heating the oxide with carbon in the electric furnace. It is a hard, lustrous metal of specific gravity 9.1. Its physical properties resemble those of iron. Like the latter, it may be welded and tempered. Besides the compounds already mentioned, molybdenum forms the oxides Mo_2O_3 and MoO_2; the chlorides $(MoCl_2)_3$, $MoCl_3$, $MoCl_4$, $MoCl_5$; and the sulphides MoS_3 and MoS_4. It also forms a large variety of additional, rather complicated, compounds.

Tungsten. — This metal is found in the minerals **scheelite** $CaWO_4$, **wolframite** $(FeMn)WO_4$, and **stolzite** $PbWO_4$. By treating the pulverized ores with nitric acid, **tungsten trioxide** WO_3 is obtained as a yellow powder which is insoluble in acids. With caustic alkalies, it forms **tungstates** like Na_2WO_4 and K_2WO_4, which are soluble, and from whose solutions **tungstic acid** $H_2WO_4 \cdot H_2O$ is precipitated by means of acids. **Sodium tungstate** may also be made by fusing native tungstates with soda and lixiviating the mass with water. The salts $Na_2WO_4 \cdot 2\,H_2O$ and $Na_2W_4O_{13} \cdot 10\,H_2O$ are used as mordants. They are also employed in making fabrics fireproof. Tungsten forms the oxides WO_2 and WO_3; the chlorides WCl_2,

WCl_4, WCl_5, WCl_6, WO_2Cl_2, and $WOCl_4$; and the carbides W_2C and WC. In addition, tungsten enters into a very large number of complex compounds. **Phosphotungstic acid** is known as **Scheibler's reagent.** It consists of a compound of tungstic and phosphoric acids, which is analogous to phosphomolybdic acid.

Tungsten was discovered in 1781 by Scheele, and two years later the element was isolated by the d'Elhujar brothers. Tungsten may be made by igniting the oxides or chlorides in a current of hydrogen, by heating the oxides with carbon in the electric furnace, or by the Goldschmidt process. It is a hard, steel-gray, lustrous, brittle metal of specific gravity 19.13. Its melting point lies very high. On ignition, it burns to the trioxide. Tungsten is used in the steel industry, for its presence to the extent of 5 to 8 per cent in steel makes the latter very hard and tough. Tungsten is now also being used in making filaments for incandescent electric lamps, which have a higher efficiency than the lamps using a carbon filament.

Uranium.—The mineral pitchblende or **uraninite** $UO_2 \cdot 2\,UO_3$ or U_3O_8 constitutes the chief source of uranium, which, like molybdenum and tungsten, belongs to the rarer elements. The true nature of pitchblende was first recognized by Klaproth in 1789; but metallic uranium was not prepared till 1841, when Peligot obtained it by heating metallic sodium and uranous chloride together. The element is named after the planet Uranus, discovered in 1787. Metallic uranium may also be obtained by reduction of its oxides with carbon in the electric furnace, by heating the oxides with aluminum, or by electrolysis of the molten double chloride $UCl_4 \cdot 2\,NaCl$. Uranium is a very hard, white, lustrous metal, not unlike iron in appearance. Its specific gravity is 18.7; and its melting point is about 1500°. It has the highest atomic weight of all the elements known, namely, 238.5. Uranium shows variable valence in its compounds, which are very numerous. The maximum valence exhibited by uranium is eight.

On treating pitchblende with nitric acid, **uranyl nitrate** $UO_2 \cdot (NO_3)_2 \cdot 6\,H_2O$ may be obtained. This salt crystallizes in greenish yellow, rhombic prisms that show *fluorescence, a characteristic of many uranium salts.* By careful ignition, uranyl nitrate may be converted into **uranium trioxide** UO_3,

a dark yellow powder, which is uranic acid anhydride. On digesting uranium trioxide with nitric acid, **uranic acid** $UO_2(OH)_2$ or H_2UO_4 may be obtained as an amorphous, yellow powder. Towards strong acids, this acts as a base, forming the uranyl salts containing the bivalent radical **uranyl** UO_2. Thus we have **uranyl chloride** $UO_2 \cdot Cl_2$; **uranyl sulphate** $UO_2 \cdot SO_4 \cdot 3\,H_2O$; **uranyl nitrate** $UO_2(NO_3)_2 \cdot 6\,H_2O$; **uranyl acetate** $UO_2(C_2H_3O_2)_2$; **uranyl ammonium carbonate** $UO_2 \cdot CO_3 \cdot 2(NH_4)_2CO_3$; **uranyl ammonium phosphate** $UO_2 \cdot NH_4 \cdot PO_4$. The latter salt is obtained as a precipitate, insoluble in acetic acid, when uranyl acetate is added to a solution of a soluble phosphate containing ammonium chloride. This fact is sometimes used in the estimation of phosphoric acid.

By the addition of caustic alkalies to solutions of uranyl compounds, *uranates* are precipitated. These are not derivatives of H_2UO_4, but of $H_2U_2O_7$; that is, they are *diuranates*, analogous to pyrosulphates. So there are **potassium diuranate** $K_2U_2O_7 \cdot 3\,H_2O$ and **sodium diuranate** $Na_2U_2O_7 \cdot 6\,H_2O$. The latter is called **uranium yellow**, and is used in making a beautiful yellowish green, fluorescent *uranium glass*.

Besides the *uranyl salts*, uranium forms a series of *uranous compounds* in which the element is quadrivalent. So there are **uranous chloride** UCl_4, **uranous sulphate** $U(SO_4)_2 \cdot 8\,H_2O$, **uranous hydroxide** $U(OH)_4$, and **uranous oxide** UO_2. The latter may be obtained as a steel-gray crystalline powder by ignition of the trioxide in hydrogen; it was regarded as the element itself, till Peligot showed that this was erroneous. Uranous oxide is used in making a fine jet-black glass.

Uranium Carbide U_2C_3 may be made by heating uranium oxides with carbon in the electric furnace. It is harder than quartz. The sulphides, US_2 and UO_2S, are also known. The variable valence of uranium is readily apparent from the following list of its chlorides and oxides: UCl_3, UCl_4, UCl_5; UO_2, U_3O_8, UO_3, UO_4.

Compounds of uranium exhibit the phenomena of radioactivity which led to the discovery of radium as already stated. ***The radio-activity of uranium bearing minerals is proportional to their uranium content.***

REVIEW QUESTIONS

1. Why is chromium so named? What valence has this element in its compounds? Illustrate.

2. What other elements are classed with chromium in the periodic system? Why?

3. Is chromium an acid or base forming element? Illustrate.

4. Describe a simple way of preparing metallic chromium. Equation.

5. What is ferrochromium and what use is made of it?

6. Write the formulas of the oxides and hydroxides of chromium. Compare these compounds with the corresponding ones of aluminum.

7. How much chromium is there in 1000 grams of pure chrome green? What is the latter used for?

8. What is chrome iron ore chemically? How may it be decomposed?

9. Write the formulas of the following compounds: chromous chloride, chromic sulphate, chrome alum, potassium chromate, potassium bichromate, silver chromate, chromic acid anhydride, barium chromate.

10. By formulas show the analogy between the chromates, molybdates, and sulphates, also between the bichromates and pyrosulphates.

11. By means of an equation express the change that occurs when potassium bichromate is treated with hot, concentrated hydrochloric acid. How many available oxygen atoms has each molecule of a bichromate? Explain.

12. Why is it that potassium bichromate is the commonest chromium compound in the market? What is the compound used for?

13. How demonstrate that there is chromium in a piece of lead chromate? Give at least four different tests, writing the equations.

14. What use is made of ammonium molybdate in analytical chemistry? Discuss the importance of this reagent.

15. How may metallic tungsten be prepared? For what purpose is it used?

16. What is pitchblende? Why has this mineral attracted particular attention in recent years?

17. What can you say of the valence of the element uranium? How does its atomic weight compare with that of other elements?

18. How much metallic chromium could be made from 300 grams of chromium sulphate?

19. Given 700 grams of chromium hydroxide, how much chromic acid anhydride could be formed from it?

CHAPTER XXIX

MANGANESE

MANGANESE is a metal which forms quite a variety of compounds. The element is bivalent and basic in character in the **manganous compounds** which resemble those of the magnesium and iron groups. In **manganic compounds** manganese is trivalent, thus resembling aluminum, chromium, and trivalent iron. In its dioxide and the manganites, manganese is quadrivalent and shows analogies to tin and lead. Again, manganese exhibits similarities to sulphur and the chromium group by forming an acidic trioxide and manganates that are analogous to sulphates, chromates, molybdates, etc. Finally, the metal exhibits resemblances to the halogens in forming a heptoxide and permanganic acid and permanganates, which are analogous to chlorine heptoxide, perchloric acid, and the perchlorates. In the periodic system of the elements manganese occurs in group VII with the halogens, but it should be definitely stated that it is never univalent like the latter.

Occurrence, Preparation, and Properties. — Manganese is sometimes found uncombined in meteoric iron, otherwise it occurs in chemical combination in pyrolusite MnO_2, braunite Mn_2O_3, manganite $Mn_2O_3 \cdot H_2O$, hausmannite Mn_3O_4, manganese blende MnS, and rhodochrosite, or manganese spar, $MnCO_3$. The chief of these ores is pyrolusite. The main localities are Russia, Brazil, India, Germany, and the United States. In small amounts, manganese is very widely distributed in soils and rocks, also in traces in plants and animals. The annual output of manganese ores is about 800,000 tons, most of which comes from the Caucasus region. The United States produces but 5000 tons of manganese ores annually.

Manganese is prepared by heating its oxides with carbon in an electric furnace, or more readily by the Goldschmidt process of igniting the oxides with aluminum.

Manganese is a hard, steel-gray, brittle metal of specific gravity 8.0. In outward appearance it is not unlike cast iron. It melts at about 1300°. On exposure to moist air, it gradually

assumes a reddish hue due to superficial oxidation. From boiling water it evolves hydrogen. In dilute acids it readily dissolves, forming hydrogen and manganous salts. Manganese is non-magnetic. Its atomic weight is 54.93.

The **alloys of manganese** with iron are important in steel manufacture. The alloys usually employed are *spiegeleisen*, which contains from 10 to 20 per cent manganese, and **ferromanganese**, which contains from 20 to 80 per cent. Alloys of manganese and copper contain about 30 per cent manganese; they are called **manganese bronze**, are very hard, and possess great tensile strength.

Though pyrolusite MnO_2 was known for a long time, it was not until 1774 that its real nature was discovered by Scheele. In 1807 Gahn reduced the oxide, and so isolated the metal.

Oxides. — Manganese forms the following oxides: the *monoxide* MnO, the *sesquioxide* Mn_2O_3, the *protosesquioxide* Mn_3O_4, the *peroxide* MnO_2, the *trioxide* or manganic anhydride MnO_3, and the *heptoxide* or permanganic anhydride Mn_2O_7. Of these the first three are basic in character. Manganese dioxide yields manganous salts on treatment with acids, and half of its oxygen becomes available to effect oxidations. With strong bases, it forms **manganites**. The oxides, MnO_3 and Mn_2O_7, are acidic. *On ignition in the air, all oxides of manganese are finally changed to* Mn_3O_4, which is probably $Mn(MnO_2)_2$; and hausmannite is therefore analogous to the spinels, though its crystals are tetragonal.

Manganous oxide MnO is a green powder formed by heating higher oxides in hydrogen, or by ignition of manganous carbonate out of contact with the air. **Manganous hydroxide** is a white precipitate formed by the addition of caustic alkalies to solutions of manganous salts. It readily turns brown because of oxidation to **manganic hydroxide** $\dot{M}n(O\dot{H})_3$; the latter easily loses water and changes to $MnO \cdot OH$, which on careful ignition yields a brown powder, **manganese sesquioxide** Mn_2O_3. This forms manganous nitrate and **manganese dioxide** MnO_2 on digesting with nitric acid. By ignition of the nitrate, the dioxide may also be obtained, though on being strongly heated it loses oxygen and passes over into Mn_3O_4. Manganese dioxide is also produced at the anode when manganous salts are electrolyzed. It is a conductor of electricity, and like lead peroxide

it is frequently used as an anode in batteries. With hot hydrochloric acid, manganese dioxide yields manganous chloride and chlorine; while in cold hydrochloric acid a dark brown solution is formed. This probably contains $MnCl_4$, which decomposes into $MnCl_2$ and chlorine on warming. With lime, manganese dioxide forms **manganites** of the composition $CaO \cdot MnO_2$ and $CaO \cdot 2\,MnO_2$. These act like a mixture of CaO and MnO_2, of which fact advantage is taken in the *Weldon process* of again using $MnCl_2$ liquors for making chlorine. **Manganese trioxide** is an unstable, dark red mass. **Manganese heptoxide** Mn_2O_7 is a dark, reddish green, oily liquid obtained by treating potassium permanganate with concentrated sulphuric acid. The mixture must be carefully cooled with ice, for otherwise violent decomposition will occur.

Salts of Manganese. — *The stable salts in which manganese acts as a base are the manganous compounds.* In these the element is bivalent. They are obtained by dissolving any oxide or hydroxide of manganese with an acid. In the latter process, the higher oxides or hydroxides yield oxygen that is available to effect oxidations.

Manganous chloride $MnCl_2 \cdot 4\,H_2O$ forms pink, deliquescent, monoclinic crystals. The salt is obtained as a by-product when chlorine is prepared by the action of hydrochloric acid on manganese dioxide. Manganous chloride may be dehydrated by heating it in a current of hydrochloric acid gas. It is the only chloride of manganese that has been prepared in pure form. The double salt $MnCl_2 \cdot 2\,NH_4Cl \cdot H_2O$ may readily be made. It forms crystals of the isometric system, which on heating yield **anhydrous manganous chloride**, just as by heating magnesium ammonium chloride, anhydrous magnesium chloride is obtained.

Manganous sulphate $MnSO_4 \cdot 7\,H_2O$ separates from solutions at temperatures below 6° in form of pink monoclinic crystals that are isomorphous with other vitriols like $FeSO_4 \cdot 7\,H_2O$, $ZnSO_4 \cdot 7\,H_2O$, etc. Between 6° and 20° the salt crystallizes in triclinic crystals $MnSO_4 \cdot 5\,H_2O$, that are isomorphous with blue vitriol $CuSO_4 \cdot 5\,H_2O$; and above 25° orthorhombic crystals $MnSO_4 \cdot 4\,H_2O$ are obtained. Manganous sulphate forms double salts with alkali sulphates, like $K_2SO_4 \cdot MnSO_4 \cdot 6\,H_2O$. These sulphates are isomorphous with similar salts of magnesium, zinc, nickel, cobalt, and iron.

Manganous nitrate $Mn(NO_3)_2 \cdot 6\,H_2O$, is a deliquescent, pink salt which melts in its water of crystallization at about 25°.

Manganous carbonate $MnCO_3$ occurs in nature in reddish, hexagonal crystals as manganese spar. It is also formed as a white, insoluble precipitate by adding soluble carbonates to solutions of manganous salts. In water charged with carbon dioxide it dissolves, which behavior is similar to that of calcium carbonate.

Manganic chloride $MnCl_3$ is supposed to exist in the brown liquid obtained by dissolving manganese dioxide in cold hydrochloric acid. It has never been isolated.

Manganic sulphate $Mn_2(SO_4)_3$ is a dark green powder formed by heating manganese dioxide with concentrated sulphuric acid. It is unstable and readily passes over into manganous sulphate, sulphur dioxide, and oxygen on heating. With alkali sulphates, manganic sulphate forms double salts that are isomorphous with alum, like $K_2SO_4 \cdot Mn_2(SO_4)_3 \cdot 24\,H_2O$.

Manganates and Permanganates. — **Manganates** are salts of *manganic acid* H_2MnO_4, which has not been isolated. By fusing manganese dioxide with caustic potash, **potassium manganate** K_2MnO_4 is formed, as a green mass, thus: —

$$3\,MnO_2 + 2\,KOH = Mn_2O_3 + K_2MnO_4 + H_2O.$$

On treating the mass with water, a dark green solution is obtained, from which, on evaporation, greenish black, rhombic crystals of K_2MnO_4 are deposited. These are isomorphous with potassium sulphate and potassium chromate. *Manganates of sodium or potassium may be obtained by fusing any oxide or salt of manganese with sodium or potassium carbonate or hydroxide, plus sodium or potassium nitrate or chlorate.* The presence of the oxidizing agent, or even the action of the oxygen of the air, insures the more complete conversion of the manganese compound into manganate. Solutions of manganates are stable only when they contain an excess of caustic alkali. *On dilution with water, manganates suffer decomposition*, thus: —

$$3\,K_2MnO_4 + 2\,H_2O = 2\,KMnO_4 + 4\,KOH + MnO_2.$$

This change is effected more readily by passing carbon dioxide through the solution of the manganate: —

$$3\,K_2MnO_4 + 2\,CO_2 = 2\,KMnO_4 + 2\,K_2CO_3 + MnO_2.$$

The change may also be produced by other dilute acids or by the addition of chlorine.

The new salt thus formed is **potassium permanganate** $KMnO_4$. Its solutions have a beautiful purple-red color, and so in the reactions just mentioned the green solution of the manganate gradually changes through blue and violet to the characteristic purple color of the permanganate. Because of this change of color, Scheele called potassium manganate **chameleon mineral.** Sometimes potassium permanganate solution is called **chameleon solution**, for on treating it with hot, concentrated, caustic alkali, it again turns green, because of the formation of the manganate, thus: —

$$2\,KMnO_4 + 2\,KOH = 2\,K_2MnO_4 + H_2O + O.$$

Potassium permanganate forms very dark purple, lustrous crystals of the rhombic system. They are isomorphous with crystals of potassium perchlorate $KClO_4$. On heating potassium permanganate, it is decomposed: —

$$2\,KMnO_4 = MnO_2 + K_2MnO_4 + O_2.$$

When treated with concentrated sulphuric acid in the cold, permanganic anhydride Mn_2O_7 is formed, as already mentioned, thus: —

$$2\,KMnO_4 + H_2SO_4 = Mn_2O_7 + K_2SO_4 + H_2O.$$

This heptoxide is unstable. It gradually decomposes: —

$$Mn_2O_7 = 2\,MnO_2 + O_3.$$

At somewhat elevated temperatures, this reaction proceeds with explosive violence. The vapors of the heptoxide are violet. Paper, alcohol, ether, illuminating gas, and other combustible substances burst into flame when brought in contact with permanganic anhydride, because of the tremendous oxidizing power of the ozone that is being liberated. By dissolving permanganic anhydride in water at 0°, a purple red solution of **permanganic acid** $HMnO_4$ is obtained. This may also be made by treating a solution of barium permanganate with sulphuric acid, for thus barium is precipitated as barium sulphate. Though much more stable than manganic acid, nevertheless permanganic acid $HMnO_4 \cdot x\,H_2O$ gradually decomposes, especially on being heated or exposed to light, thus: —

$$2\,HMnO_4 = 2\,MnO_2 + H_2O + ?\,O.$$

Uses of Permanganates. — On account of their great oxidizing power, permanganates are used as disinfectants, and as oxidizing agents in many chemical processes. They also serve in the preparation and analysis of many substances in the laboratory. Potassium permanganate is commonly employed; though the cheaper **sodium permanganate** $NaMnO_4$, which does not crystallize, is also made and sold in solutions as *Condy's disinfecting fluid.* Wood alcohol is readily oxidized to formic aldehyde by potassium permanganate, which fact is used to produce formic aldehyde in fumigating infected houses, etc.

In alkaline or neutral solutions, potassium permanganate yields oxygen that is available for oxidation, with concomitant formation of manganese dioxide: —

$$2\,KMnO_4 + H_2O = 2\,KOH + 2\,MnO_2 + 3\,O.$$

Two molecules of permanganate thus yield three available oxygen atoms. The oxidation of wood alcohol to formic aldehyde would be expressed thus: —

$$2\,KMnO_4 + 3\,CH_3OH = 2\,KOH + 2\,MnO_2 + 3\,HCHO + 2\,H_2O.$$

In alkaline solutions potassium permanganate serves for the destruction of organic matter in the analysis of waters, fertilizers, etc., the nitrogen present in the substances being simultaneously liberated as ammonia.

When potassium permanganate is to be used in acid solution, sulphuric acid is commonly employed. Thus, when reducing substances are present, a colorless solution of manganous sulphate and potassium sulphate is produced. *In sulphuric acid solutions, two molecules of potassium permanganate yield five atoms of oxygen that are available for oxidation:* —

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O.$$

Since the oxidation of oxalic acid to carbon dioxide and water requires one atom of oxygen per molecule of oxalic acid, we have: —

$$(COOH)_2 + O = 2\,CO_2 + H_2O.$$

Consequently if the oxidation is effected by means of potassium permanganate, we have: —

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,(COOH)_2 = 10\,CO_2 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O.$$

Ferrous sulphate is converted to ferric sulphate, thus: —

$$2\,FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

Therefore, if the oxidation is carried on by means of potassium permanganate, we have: —

$$2\,KMnO_4 + 8\,H_2SO_4 + 10\,FeSO_4 = 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O.$$

With nitrous acid the reaction is: —

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,HNO_2 = K_2SO_4 + 2\,MnSO_4 + 5\,HNO_3 + 3\,H_2O.$$

Potassium permanganate and hydrogen peroxide mutually reduce each other, thus: —

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2.$$

This reaction is commonly used to determine the content of a solution of hydrogen peroxide by means of potassium permanganate.

Analytical Tests for Manganese. — Manganous sulphide MnS is precipitated as a flesh-colored, hydrous, amorphous substance, when ammonium sulphide is added to an aqueous solution of any compound of manganese. This sulphide readily turns dark on exposure to the air, because oxidation takes place. In dilute acid, even in acetic acid, manganous sulphide is readily soluble.

From solutions of manganous salts, soluble carbonates precipitate manganous carbonate, and caustic alkalies precipitate manganous hydroxide. The latter is soluble in solutions of ammonia or ammonium salts.

Amethyst-colored beads are produced by manganese compounds with either borax or microcosmic salt. Furthermore, when fused with a mixture of soda and saltpeter, a green manganate is obtained which, when dissolved in water and treated with carbon dioxide, yields the characteristic purple color of permanganate solutions.

REVIEW QUESTIONS

1. Justify the position which manganese occupies in the periodic system.

2. Compare the physical properties of manganese with those of chromium and iron.

3. Manganese may form manganous, and manganic compounds, also manganites, manganates, and permanganates. Give an example of each of these, writing the appropriate formula.

4. What is the main ore of manganese? How may the metal be obtained from it? What practical use is made of the ore itself?

5. On heating any oxide of manganese in the air, it finally passes over into Mn_3O_4. How do you account for this? What is the valence of manganese in Mn_3O_4?

6. What salts of manganese are commonest? Describe them and write their formulas.

7. What practical use is made of potassium permanganate? How may this compound be made from manganese dioxide? Equations.

8. How many available oxygen atoms are there in potassium permanganate? Give a concrete illustration demonstrating your answer.

9. How many grams of potassium permanganate would be required to oxidize 25 grams of oxalic acid crystals to carbon dioxide and water?

10. How would you prove that potassium permanganate contains manganese? How show that manganous sulphate contains manganese? What is the action of bromine on a solution of a manganous salt? Explain.

11. Explain how it is that the two oxidizing agents, potassium permanganate and hydrogen peroxide, will mutually decompose each other in sulphuric acid solutions, setting oxygen free. Write the equation.

12. How much available oxygen do 1000 grams of potassium permanganate contain when that salt is used for oxidation purposes in sulphuric acid solution?

13. From 256 lb. of manganese carbonate, how much manganese sulphide could be formed?

14. Discuss the occurrence of manganese compounds in nature.

15. How much oxalic acid will ten grams of potassium permanganate oxidize to carbon dioxide and water in sulphuric acid solution?

CHAPTER XXX

IRON, NICKEL, AND COBALT

THE atomic weights of the elements of this group are nearly alike, being Fe—55.84, Ni—58.68, and Co—58.97. Moreover, it will be recalled that the atomic weight of manganese, 54.93, is but little less than that of iron. The chemical similarities between manganese and iron have been mentioned. *Iron forms ferrous and ferric compounds. In the former it is bivalent, and in the latter trivalent.* Iron is also hexavalent, forming ferrates, which are analogous to manganates and chromates. The ferrous compounds are analogous to those of the magnesium group, also to cupric and manganous compounds, while the ferric compounds are analogous to those of aluminum and chromium. *Nickel forms but one series of salts.* In these the metal is bivalent. Nevertheless, a sesquioxide and a corresponding hydroxide of nickel are known, though salts of these are lacking. *Cobalt, like iron, forms two series of compounds, the cobaltous, in which the metal is bivalent, and the cobaltic, in which it is trivalent.*

Occurrence of Iron. — Iron is very abundant and widely distributed. In meteorites it is found uncombined, also in small grains in some of the crystalline rocks. Compounds of iron are found in plant and animal tissues, particularly in the chlorophyll of plants and the hemoglobin of the blood of animals. *Iron is necessary for plant and animal life*, though its real function in the vital processes is not understood. All soils and rocks contain compounds of iron. Ores of iron are found in enormous quantities. The most important of these are **hematite** Fe_2O_3, **magnetite**, or magnetic iron ore, Fe_3O_4, **limonite** $2\,Fe_2O_3 + 3\,H_2O$, and **siderite** $FeCO_3$. Iron is also found in combination with sulphur, as in pyrite FeS_2, but these compounds are not used for making metallic iron. In rocks, iron is found in the form of oxides and silicates; and so by the weathering of rocks iron gets into the soil and all natural waters, whence it enters plants and animals.

Metallurgy of Iron. — Metallic iron has been known to man for thousands of years. The Assyrians used iron knives and saws, the ancient Egyptians reduced iron ores and made steel, both Homer and Hesiod mention the forging of iron for weapons. Through the influence of the Romans iron came into more general use. Still, the metal was costly, because the processes of preparing it from ores were relatively difficult to carry out, imperfectly understood, and known to but few; and so iron was rather slow in replacing bronze for use in weapons and other implements.

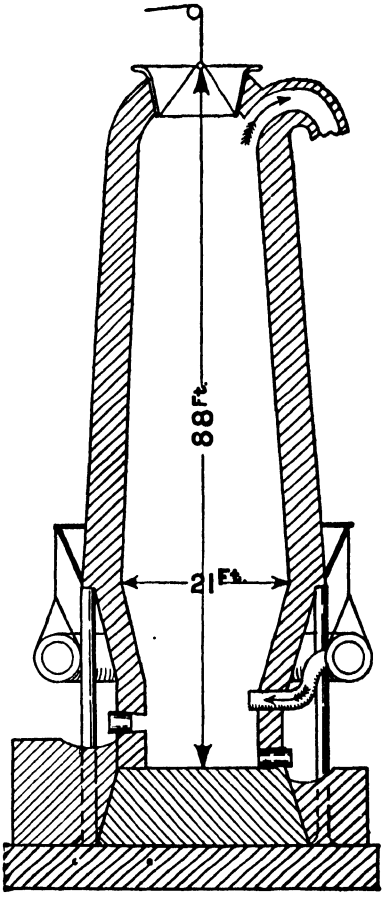


FIG. 151.

Iron is made by reducing its ores with carbon at high temperatures. The ores, which consist of the oxides, or carbonate, do not require preliminary roasting. The reduction is effected in blast furnaces, a cross section of a modern type of which is represented in Fig. 151. These furnaces are from 80 to 100 feet high, and have a diameter of about 20 feet where they are widest. They are lined inside with fire brick. The lower end of the furnace is provided with openings of tubes, the tuyeres, through which hot air can be forced into the furnace. The latter is heated and then charged from the top with ore properly mixed with coke and limestone. Instead of coke anthracite coal or charcoal may be used. The purpose of the limestone is to form calcium silicates, or so-called **slag**, with the sand present in the ore. If the latter contains carbonates of calcium and magnesium, or other basic materials.

sand is added instead of limestone to make the slag. In any case the material added to the ore to produce the fusible slag is termed the **flux**. The charge is carried to the top of the furnace by some form of mechanical conveyor, and is introduced through a bell trap, so arranged that while the material is put into the furnace practically no gases escape from the latter. As air heated to about 800° is blown up through the charge, the latter becomes very hot. In the lower part of the furnace carbon dioxide forms, due to the combustion of the coke. *The carbon dioxide as it rises through the hot layers of coke is reduced to carbon monoxide, and the latter acts on the ferric oxide and reduces it to iron*, thus: —

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2.$$

The gases, still rich in carbon monoxide, pass out through the vent at the top of the furnace, and are used as fuel to heat the air before it is blown into the furnace. Of late they are also frequently used to run gas engines. The slag and iron settle to the lower part of the furnace, forming two layers, the liquid slag covering the heavier molten iron. The iron is tapped off from below and run into molds of sand about every eight hours. In this way rough bars of cast iron called *pigs* are produced. The slag runs continually from a lateral opening above the iron. Blast furnace slag is now frequently used for making Portland cement. As the material in the furnace melts down, the latter is fed from the top, so that the process once started is continuous, furnaces remaining in operation for years at a time. In the upper parts of the furnace the temperature is not high enough to melt the iron, which is formed in a porous or spongy condition, and carried down with the slag to the lower and much hotter parts. Here it takes up carbon, forming iron carbide in part, which with the iron yields a mixture that melts at a much lower temperature than iron free from carbon. It is this iron containing carbon and other impurities that is tapped from the furnace and made into **pig iron**. The latter is essentially the same as cast iron, besides which we also have wrought iron and steel, as the main varieties of iron. *All kinds of iron used in practice contain carbon and various other impurities, pure iron being practically unknown.*

Cast Iron. — The melting point of cast iron varies from about

1050° to 1300°, according to its content of carbon and other impurities. Cast iron contains from 2.3 to 5 per cent carbon, besides smaller amounts of silicon, phosphorus, sulphur, and manganese. When cooled very slowly, most of the carbon in cast iron crystallizes out in the form of leaflets of graphite. This iron consequently appears dark gray on its fractured surface and is known as **gray cast iron.** It is used in making castings, for it has a low melting point, contracts uniformly on cooling, and can afterwards readily be worked with tools. On dissolving gray cast iron in hydrochloric acid, the graphitic carbon remains behind, while the carbon which was combined with the iron in the form of carbides is given off with the hydrogen, being evolved as hydrocarbon gases. Good gray castings contain about 2 to 3 per cent of graphitic carbon, and 1 to 1.5 per cent combined carbon.

On cooling cast iron rapidly, practically all the carbon remains combined with the iron, forming carbides. Such iron has a silver-white fracture and is known as **white cast iron.** It is very hard and brittle, and is consequently not employed for castings, but is converted into wrought iron. Cast iron containing from 5 to 20 per cent manganese takes up considerable amounts of carbon. Its fracture shows a coarsely crystalline structure, whence the iron is known as *spiegeleisen.* Ordinary cast iron contains from 0.5 to 4 per cent silicon, from 0.4 to 2 per cent phosphorus, and sulphur varying up to about 0.2 per cent. *Sulphur and phosphorus make iron brittle* and hence are quite objectionable.

Wrought Iron. — This is nearly pure iron, often containing less than 1 per cent of impurities. It is made by *puddling* cast iron. This process consists of heating the pig iron with iron oxide in a current of air on the hearth of a reverberatory furnace. Thus the impurities in the iron are oxidized. The carbon largely escapes as carbon monoxide. The silicon and phosphorus after oxidation unite with some of the iron, yielding a slag, which also contains the sulphur.

As the heating proceeds, the molten iron becomes more and more viscous. It is continually stirred or puddled so that the air may gain access to it. Finally, the mass becomes so thick that it can be worked up into a ball, which is then taken from the furnace and rolled, or hammered by a steam hammer.

Thus the slag is removed from the iron, and a malleable, ductile product is obtained which often contains less than 0.2 per cent carbon. Wrought iron melts at about 1600°, and is plastic enough to be welded at from 900° to 1100°. In **welding**, the two ends to be joined are brought to the welding temperature in a forge. Borax or sand is sprinkled over the parts, which are then again heated for a few moments till the borax or sand has formed a slag with the oxides of iron on the surface. This slag is a borate or silicate of iron. It protects the iron from oxidation. On now hammering the parts together, the slag flies off, and the iron coming into actual contact welds. *Because of its very low carbon content, wrought iron will not harden when rapidly chilled*, as does cast iron or steel.

By heating iron castings covered with pulverized iron ore for about 48 hours, and allowing them to cool slowly, they become sufficiently malleable for many purposes. The process abstracts some of the carbon from the iron, which then is called **malleable iron**. It is much cheaper than wrought iron, in place of which it is often used when possible.

Steel.—Steel contains more carbon than wrought iron, but much less than cast iron. It also contains practically no sulphur or phosphorus, and ordinarily runs low in silicon. The amount of carbon in steel varies from about 0.2 to 1.6 per cent. That which contains the least carbon, 0.2 per cent, approaches wrought iron in quality and is called **mild steel**. Steel used for building purposes is termed **structural steel**. It contains from 0.2 to 0.8 per cent carbon, whereas **tool steel** has a higher carbon content, namely from about 0.8 to 1.5 per cent. Like cast iron, steel may be hardened by heating and then suddenly cooling it. On the other hand, when such hardened steel is again heated to redness and cooled slowly, the material is soft. As in the case of cast iron, the heating and sudden chilling leaves the carbon in the combined condition and thus makes a hard steel; whereas on slow cooling, the carbon crystallizes out as graphite and so produces a soft, pliable product. By proper heating and cooling, steel of any desired hardness may be produced. This process is called **tempering**.

Pig iron is converted into steel by either the *Bessemer process* or the *open hearth* or *Siemens-Martin process*. In the **Bessemer process** the molten cast iron is poured into a converter (Fig. 152),

through whose perforated bottom compressed air is then blown into the metal; thus carbon, silicon, and phosphorus are oxidized. Molten *spiegeleisen* of known carbon content is then added in proper quantity to produce steel of the exact carbon content desired. The converter is mounted so that it can be tilted to pour out or receive its contents. The slag, which consists of silicates of manganese, iron, calcium, and sulphide of iron, is first poured off, after which the molten steel is run into molds to form **ingots**. These are afterwards rolled into rails.

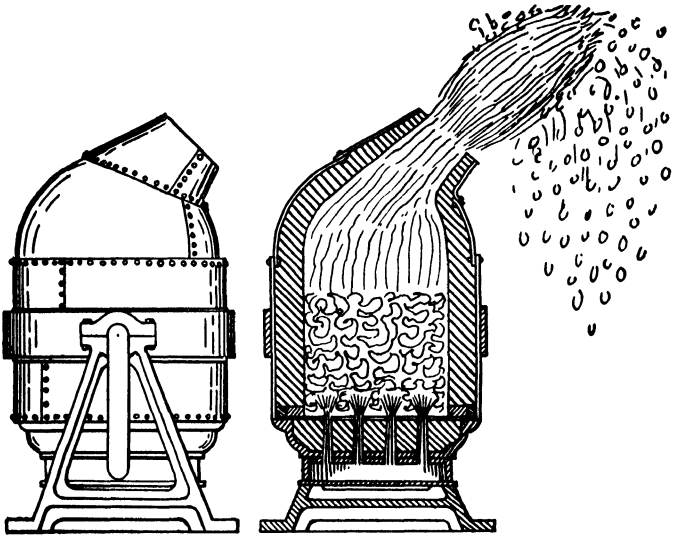


FIG. 152.

By means of a Bessemer converter about 20 tons of cast iron can be converted into steel in 20 to 30 minutes. The converter is made of iron and is usually lined with material similar to that of fire brick. *In case the cast iron is rich in phosphorus, this siliceous lining is replaced by one of calcium and magnesium oxides obtained by calcining dolomite.* This **basic lining** absorbs the phosphorus, yielding calcium and magnesium phosphates, which appear in the slag. This adaptation of the Bessemer process to the treatment of cast iron rich in phosphorus is know as the **Thomas-Gilchrist process**, and the slag produced by it is called the **Thomas slag**. *The latter, being rich in phosphates, is ground up and sold as a fertilizer.* Thus, ores rich in

phosphorus, which were formerly discarded as unfit for Bessemer steel, are very profitably turned to use.

The **open hearth** or **Siemens-Martin process** consists essentially of heating the cast iron together with rusty scrap iron or other iron oxide, commonly hematite ore, on the hearth of a special type of reverberatory furnace, using gas as fuel. The oxidation of the carbon in the cast iron thus proceeds at the expense of the oxygen in the iron oxide. The process is continued till a sample taken from the material shows that the oxidation has proceeded far enough to produce the steel desired. The molten mass is then run off into molds. The process requires about 8 hours for its completion; but it yields an excellent, uniform steel, and utilizes the carbon in the cast iron for the reduction of ores. Hence it is more economical than the Bessemer process, which it is rapidly displacing. Moreover, *if the cast iron is rich in phosphorus, a hearth lined with the oxides of magnesium and calcium may be used to absorb the phosphorus in form of phosphates;* with this modification the process is called the **basic open hearth process.**

The United States produces about 35,000,000 tons of pig iron annually, a large portion of which is converted into steel. Nickel, manganese, chromium, silicon, tungsten, and molybdenum are often added to steel in small proportions, thus forming alloys of mechanical properties that are desirable for certain special purposes.

Properties of Iron. — **Pure iron** may be made by strongly igniting ferric oxide in a current of hydrogen. If heated thus to not higher than 450°, the iron obtained contains hydrogen and is called **pyrophoric iron,** for it burns spontaneously on exposure to the air. **Electrolytic iron,** obtained by electrolyzing a ferrous sulphate solution, using a thick wrought iron anode and a thin iron foil as cathode, is also nearly pure; but it contains a few hundredths of one per cent of hydrogen, which renders it very hard and brittle. The melting point of pure iron has not been determined with certainty; it lies above that of wrought iron. The specific gravity of iron is 7.86. The metal is white, malleable, ductile, and fairly soft. It is attracted by a magnet, and becomes magnetic; but it loses its magnetism rapidly, while magnetized steel does not. Iron remains unchanged in dry air, while in moist air or in presence of air and salt solutions

it rusts, forming hydrated ferric oxide. This corrosion is hastened by local electrolytic action, and is generally guarded against by painting or tarring the exposed parts of the iron or steel. Dilute hydrochloric or sulphuric acid dissolves iron, forming ferrous chloride or sulphate and hydrogen, which in case of cast iron or steel is mixed with hydrocarbon gases and compounds of carbon, hydrogen, phosphorus, and sulphur that have a bad odor.

When dipped into very concentrated nitric acid and then rinsed, iron no longer dissolves in nitric acid, nor does it precipitate copper from solutions of its salts. The iron is said to be *passive*. It is thought by many that the phenomenon is due to a very thin, invisible coating of oxide on the iron, for when **passive iron** is scratched with a hard point, it at once dissolves rapidly in nitric acid. *Other metals, like chromium and nickel, also exhibit the phenomena of the passive state.*

Oxides and Hydroxides of Iron.— **Ferrous oxide** FeO is obtained as a black powder by heating ferric oxide in hydrogen or carbon monoxide to about 300°. On exposure to the air it readily oxidizes further.

Ferrous hydroxide $Fe(OH)_2$ is a white precipitate formed by adding caustic alkali to a solution of a ferrous salt. It readily oxidizes in the air, turning green and then brown.

Ferric oxide Fe_2O_3 is found in nature as *hematite ore. It is found in large quantities in the Lake Superior region, and is the most important of the iron ores.* It crystallizes in very dark red, hexagonal pyramids and prisms. When finely ground, ferric oxide is used as a pigment in paints under the name of **red ocher** or **Venetian red.** By ignition of ferrous sulphate or oxalate in the air, ferric oxide is obtained, which when finely ground is sold as a pigment or as **rouge** for polishing purposes. Ferric oxide is prepared in the laboratory by ignition of ferric hydroxide, which is obtained by precipitating a solution of a ferric salt with caustic alkali.

Ferric hydroxide $Fe(OH)_3$ is an amorphous, brown, flocculent precipitate to which alkali adheres very tenaciously. It dissolves to some extent in a concentrated solution of ferric chloride, forming a very dark brown solution of a basic ferric chloride; from this the chlorine may be removed in the form of ferric chloride by dialysis, thus leaving a dark brown, tasteless,

colloidal solution of ferric hydroxide or so-called **dialyzed iron** behind.

Hydrated ferric oxides occur in nature. Thus we have *limonite* $2\,Fe_2O_3 + 3\,H_2O$ or $Fe_2O_3 \cdot 2\,Fe(OH)_3$, also known as *brown iron ore; pyrosiderite* $FeO \cdot OH$, and *bog iron ore* $Fe_2O(OH)_4$. These may all be considered as dehydration products of $Fe(OH)_3$. **Yellow ocher** is an impure hydrated ferric oxide. It is used as a pigment in paints. Though the iron oxide pigments are not as bright in color as many others, yet they are valuable because they are permanent and cheap.

Ferrous ferric oxide Fe_3O_4 *also known as magnetic iron oxide, is formed as the final product of continuous strong ignition of any oxide of iron in the air.* In nature it occurs in black octahedra and dodecahedra as *magnetite ore.* It is often magnetic and is then called *lodestone.* The *hammer black* formed as a scale on iron when it is heated in the air is Fe_3O_4. Ferrous ferric oxide is isomorphous with spinel, and consequently probably is $Fe(FeO_2)_2$.

When iron turnings are fused with potassium nitrate, or when chlorine is conducted through a cold, concentrated solution of caustic potash containing ferric hydroxide in suspension, **potassium ferrate** K_2FeO_4 is formed. It may be obtained in the form of dark red crystals, which are, however, unstable. They decompose, yielding oxygen, ferric hydroxide, and caustic potash. **Barium ferrate** $BaFeO_4$ is more stable. The ferrates are salts of *ferric acid* H_2FeO_4, which, like manganic acid, is not known in the free state. *Ferrates are analogous to and isomorphous with sulphates and chromates.* When caustic alkali solutions are electrolyzed, ferrates are formed at the anode if the latter consists of iron.

Chlorides of Iron. — **Ferrous chloride** $FeCl_2$ is obtained as a white mass by heating iron filings in a current of hydrochloric acid gas. It may also be obtained in the form of green, monoclinic crystals $FeCl_2 \cdot 4\,H_2O$, from aqueous solutions carefully kept from the oxygen of the air, for the salt is readily oxidized, thus: —

$$6\,FeCl_2 + 3\,O = 4\,FeCl_3 + Fe_2O_3.$$

Ferric chloride $FeCl_3$ is obtained in the form of very dark green, lustrous, hexagonal crystals when iron is heated in a current of chlorine. The product may be sublimed. It is very

deliquescent. Ferric chloride may readily be formed by passing chlorine into a solution of ferrous chloride, by boiling the latter with aqua regia, or by dissolving ferric oxide or hydroxide in hydrochloric acid. On evaporation, a dark brown crystalline mass, $Fe_2Cl_6 \cdot 12\,H_2O$, is obtained. At higher temperatures different hydrates crystallize out and are in equilibrium with the saturated solution. This question has been carefully studied by H. W. Bakhuis Roozeboom, whose results are shown

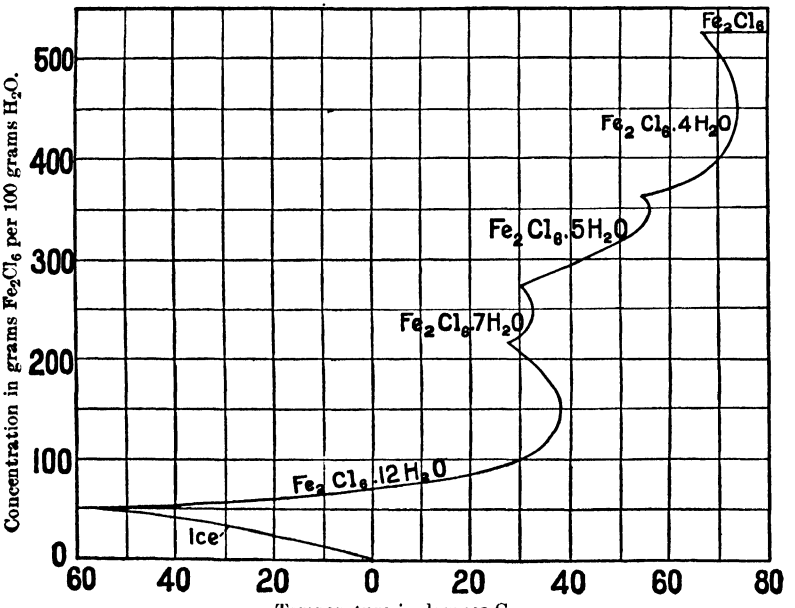


FIG. 153.

in Fig. 153, which gives the solubility curves of ferric chloride and indicates the ranges of temperature at which the different hydrates are in equilibrium with the solutions (compare the case of magnesium chloride, Fig. 136). Ferric chloride is used in medicine. The salt is soluble in alcohol, ether, and many other liquids besides water.

Ferrous bromide $FeBr_2$ and **ferric bromide** $FeBr_3$ are analogous to the corresponding chlorides.

Ferrous iodide $FeI_2 \cdot 4\,H_2O$ consists of bluish green, monoclinic crystals formed by heating iron filings and iodine together under water. The salt is used in medicine in sirup of ferrous iodide. Ferric iodide is not known.

Sulphides and Sulphates of Iron. — **Ferrous sulphide** FeS is formed by heating iron and sulphur together, or by adding ammonium sulphide to a solution of a salt of iron. If a ferric salt is used, a mixture of sulphur and ferrous sulphide is obtained, thus: —

$$2\,FeCl_3 + 3\,(NH_4)_2S = 6\,NH_4Cl + 2\,FeS + S.$$

Ferrous sulphide is also formed by warming finely divided iron with sulphur in water. The fused sulphide forms a black, brittle, crystalline mass on cooling; whereas the precipitated sulphide is black and amorphous. *Ferrous sulphide is soluble in dilute acids, hence it is not precipitated by hydrogen sulphide from acid solutions of salts of iron.*

Ferric sulphide Fe_2S_3 is a greenish yellow mass, obtained by fusing iron and sulphur, or ferrous sulphide and sulphur, together in proper proportions. It is not formed by precipitating ferric salts with ammonium sulphide; for the latter first reduces the ferric salt, and then precipitates ferrous sulphide.

Iron disulphide FeS_2 occurs in nature as pyrite and marcasite. It may be made artificially by carefully heating iron and sulphur together in proper proportions. *Pyrite* forms golden yellow crystals having a metallic luster. As pyrite, these crystals are cubes, octahedra, or pentagonal dodecahedra (Fig. 154); and as *marcasite*, they are orthorhombic.

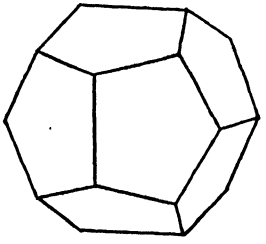


Fig. 154.

All sulphides of iron when roasted in the air finally yield sulphur dioxide and ferrous ferric oxide Fe_3O_4. On exposure to moist air the sulphides are gradually oxidized to sulphates.

Ferrous sulphate $FeSO_4 \cdot 7\,H_2O$, also called **green vitriol** or **copperas**, is formed by gently roasting pyrite so as to form ferrous sulphide, and then allowing the latter to oxidize to sulphate in moist air. From the mass the salt is readily extracted with water, and from the solutions green, monoclinic prisms, $FeSO_4 \cdot 7\,H_2O$ (Fig. 74), are obtained. These are isomorphous with other vitriols. The salt $FeSO_4 \cdot 5\,H_2O$ is also known. It forms triclinic crystals that are isomorphous with $CuSO_4 \cdot 5\,H_2O$ (Fig. 75).

Ferrous sulphate is used as a reducing agent, as a mordant,

as a disinfectant, and also in making **ordinary writing-ink**. The latter consists essentially of a solution of ferrous sulphate and extract of nutgalls, which contains tannin. Thus a ferrous tannate is formed, which on exposure to the air is oxidized to a ferric compound that is black and not readily soluble. Dextrine or gum arabic is generally added to ink to retard the precipitation of the ferric tannate as the ink stands in bottles. An antiseptic like carbolic acid or corrosive sublimate is often also introduced to prevent the growth of molds.

Ferrous sulphate forms double salts with alkali sulphates. Of these **ferrous ammonium sulphate** $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\,H_2O$ is of special importance. It is known as **Mohr's salt** and is used in chemical analysis. *On exposure to the air this salt does not oxidize as readily as ferrous sulphate.*

Ferric sulphate $Fe_2(SO_4)_3$ is formed by the oxidation of ferrous sulphate, or by dissolving ferric hydroxide in sulphuric acid. In an anhydrous condition it is a white mass. This dissolves in water, slowly yielding a brown solution. With alkali sulphates it forms ferric alums; examples of these are, $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24\,H_2O$ and $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24\,H_2O$.

Ferrous Carbonate $FeCO_3$ occurs in rhombohedral crystals in nature as siderite. It is formed as a white precipitate when alkali carbonates are added to solutions of ferrous salts. Ferrous carbonate, like calcium carbonate, is soluble in water charged with carbon dioxide, thus forming **ferrous bicarbonate** $Fe(HCO_3)_2$. On exposure to the air ferrous carbonate soon turns dark in color because of the formation of hydrated ferric oxide. *Ferric carbonate is unknown. When treated with sodium carbonate, ferric salts yield ferric hydroxide.* The reaction is similar to that of aluminum salts, thus: —

$$Fe_2(SO_4)_3 + 3\,Na_2CO_3 + 3\,H_2O = 3\,Na_2SO_4 + 2\,Fe(OH)_3 + 3\,CO_2.$$
$$Al_2(SO_4)_3 + 3\,Na_2CO_3 + 3\,H_2O = 3\,Na_2SO_4 + 2\,Al(OH)_3 + 3\,CO_2.$$

Cyanides of Iron. — The simple cyanides $Fe(CN)_2$ and $Fe(CN)_3$ are unknown, but many double cyanides of iron have been prepared. **Potassium ferrocyanide** $K_4Fe(CN)_6$, or $4\,KCN \cdot Fe(CN)_2$, is made by fusing together potash, scrap iron, and animal refuse, like blood, hoofs, horns, scraps of hides, etc., as stated in Chapter XIV. On cooling and leaching out the cake with water, a yellow solution is obtained

which deposits beautiful lemon-yellow, monoclinic crystals $K_4Fe(CN)_6 \cdot 3\,H_2O$. These are also known as **yellow prussiate of potash.** They readily lose water, and on further heating they decompose, yielding potassium cyanide, as already stated.

Potassium ferricyanide $K_3Fe(CN)_6$, or $3\,KCN \cdot Fe(CN)_3$, is formed by treating potassium ferrocyanide with chlorine, thus: —

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

The salt consists of dark red, rhombic prisms which readily dissolve in about three parts of water, yielding a greenish brown solution. The compound is also known as **red prussiate of potash.**

When treated with concentrated hydrochloric acid, a saturated solution of potassium ferrocyanide yields a white crystalline precipitate which is $H_4Fe(CN)_6$, *i.e.* the free **ferrocyanic acid.** Similarly, **ferricyanic acid** $H_3Fe(CN)_6$ may be obtained from $K_3Fe(CN)_6$.

While the alkali salts of these acids are soluble, the salts they form with the heavy metals are insoluble, and may consequently be obtained by precipitation from solutions. Copper ferrocyanide, for instance, is an insoluble ferrocyanide. It has already been described. When a ferric salt is added to a solution of potassium ferrocyanide, **ferric ferrocyanide** $Fe'''_4\,[Fe''(CN)_6]_3$ is formed as an indigo-blue precipitate called **Prussian blue:** —

$$4\,FeCl_3 + 3\,K_4Fe(CN)_6 = 12\,KCl + Fe'''_4\,[Fe''(CN)_6]_3.$$

If the ferric salt is added to a large excess of potassium ferrocyanide, **soluble Prussian blue** $K_2Fe'''_2\,[Fe''(CN)_6]_2$ is formed. Caustic alkali decomposes Prussian blue: —

$$Fe'''_4\,[Fe''(CN)_6]_3 + 12\,KOH = 3\,K_4Fe(CN)_6 + 4\,Fe(OH)_3.$$

Prussian blue is used as a pigment.

When a ferrous salt is added to a solution of potassium ferricyanide, **ferrous ferric cyanide** $Fe''_3\,[Fe'''(CN)_6]_2$ is precipitated: —

$$3\,FeSO_4 + 2\,K_3Fe(CN)_6 = 3\,K_2SO_4 + Fe''_3[Fe'''(CN)_6]_2.$$

This precipitate is also indigo-blue in color. It is known as **Turnbull's blue.** When treated with caustic alkali, it is decomposed into ferrous hydroxide and potassium ferricyanide.

Blue Printing. — When a ferric salt is added to a solution of potassium ferricyanide, a brown solution, but no precipitate, is formed. Paper treated with such a solution and dried in the dark is the sensitive paper used in blue printing. On exposing this paper to the light, the ferric salt is partially reduced to the ferrous state. When the paper is then washed with water, the insoluble Turnbull's blue formed remains, while the places protected from the light appear white, because the original mixture on the paper is simply dissolved away. As a rule, ferric ammonium citrate and potassium ferricyanide are used in making blue print paper. Ammonium hydroxide or caustic alkalies dissolve both Turnbull's and Prussian blue, and these serve as *inks* to write white characters on blue prints.

Other Compounds of Iron. — **Ferrous nitrate** $Fe(NO_3)_2$ and **ferric nitrate** $Fe(NO_3)_3$ have also been prepared. The latter is deliquescent and yields basic nitrates on boiling with water.

Ferrous phosphate $Fe_3(PO_4)_2$ is an insoluble white precipitate, while **ferric phosphate** $FePO_4$ is a yellowish white powder, insoluble in water and acetic acid.

Iron carbide Fe_3C, also called **cementite**, occurs in cast iron and steel as so-called combined carbon.

The **silicides** Fe_2Si and FeSi have been obtained in crystalline form. They are hard and brittle.

The **phosphides** Fe_3P and Fe_2P are known. Their presence in iron makes it very brittle.

Ferric acetate $Fe(C_2H_3O_2)_3$ is unstable and readily hydrolyzed, forming acetic acid and **basic ferric acetates**, which, being insoluble in acetic acid, enable the analytical chemist to precipitate iron from an acid solution. This is of consequence in separating iron from manganese, for instance.

Analytical Tests for Iron. — From solutions of both ferrous and ferric salts, ammonium sulphide precipitates black ferrous sulphide, which readily dissolves in acids.

In solutions of ferrous salts, which are almost colorless, hydroxides, carbonates, and ferricyanides of the alkalies produce characteristic precipitates that have already been described. In solutions of ferric salts, which are commonly brown, hydroxides, carbonates, and ferrocyanides of the alkalies also produce characteristic precipitates; while potassium sulphocyanate KCNS forms a deep red coloration of soluble ferric

sulphocyanide $Fe(CNS)_3$. In the borax bead, ferrous compounds yield a green, and ferric compounds a brown, coloration.

The fact that ferric salts may readily be changed into ferrous salts by many reducing agents, like nascent hydrogen, stannous chloride, hydrogen sulphide, etc., is frequently used in analytical chemistry. The change of ferrous salts to the ferric state by oxidizing agents like nitric acid, bichromates, or permanganates, is also often employed.

Occurrence, Preparation, and Properties of Nickel.—Nickel is found in meteoric iron. The chief ores of nickel are *nicollite* NiAs, *gersdorffite*, or nickel glance, NiAsS, and *garnierite* $Mg_2Ni_2H_4(SiO_4)_3 \cdot 4\,H_2O$. The chief localities are Ontario and New Caledonia.

The commercial production of nickel is a complicated process which will not be described here. Pure nickel may be obtained by igniting the oxides or the oxalate in a current of hydrogen; also by Goldschmidt's process, or by reducing the oxides with carbon.

Nickel is a silver-white, lustrous metal, of specific gravity 8.9. It melts at about 1485°. Nickel is malleable, ductile, and tenacious. It is but slightly altered on exposure to the air, and consequently it is frequently used in plating other metals. Nickel is but slowly attacked by sulphuric or hydrochloric acid; but nitric acid dissolves it readily. Like iron, nickel is magnetic, and exhibits the phenomena of passivity.

Nickel is used in many alloys. **German silver**, or **argentan**, an alloy of brass with nickel, has already been mentioned. **Manganine**, an alloy of nickel with copper and manganese, is used for resistance wires. **Nickel coins** contain 75 per cent copper and only 25 per cent nickel, which fact demonstrates the great power of nickel to impart its color to alloys. About three per cent nickel added to steel produces a product of great strength; and much nickel is used in making **nickel steel** for armor plates.

The Chinese have used nickel-copper alloys under the name *packfong* for many centuries. Through the work of Cronstedt and Bergmann, nickel was distinguished from other metals in 1751. Nickel coins came into use about fifty years ago.

Nickel Oxides and Hydroxides.—**Nickelous hydroxide** $Ni(OH)_2$ is an apple-green, amorphous precipitate, formed by adding

caustic alkali to a solution of a nickel salt. On ignition it yields a green powder, **nickelous oxide** NiO. **Nickelic oxide** Ni_2O_3 is a black powder obtained by careful ignition of the nitrate. **Nickelic hydroxide** $Ni(OH)_3$ is formed when a solution of a nickel salt is treated with an alkaline hypochlorite. It is a black precipitate.

Salts of Nickel. —*In these nickel is always bivalent.* The anhydrous salts are yellow or brown, and the hydrous salts and the solutions are green. Nickelic oxide acts like a peroxide on treatment with acids; there are no nickelic salts.

Nickelous chloride $NiCl_2 \cdot 6\,H_2O$ forms green, monoclinic crystals that readily dissolve in water.

Nickelous nitrate $Ni(NO_3)_2 \cdot 6\,H_2O$ consists of green, deliquescent monoclinic plates.

Nickelous sulphate $NiSO_4 \cdot 7\,H_2O$ forms green, orthorhombic prisms that are isomorphous with the other vitriols. It may also be obtained as $NiSO_4 \cdot 6\,H_2O$ in form of tetragonal crystals. It is readily soluble in water. The crystals effloresce on exposure to the air. With ammonium sulphate, nickel sulphate forms **nickel ammonium sulphate** $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6\,H_2O$, which is isomorphous with Mohr's salt. Nickel ammonium sulphate is soluble in about 17 parts of water. It is used in **nickel plating**, in which process a thick nickel plate is used as anode, and the thoroughly cleaned object to be plated is the cathode.

Nickelous cyanide $Ni(CN)_2$ is formed as a green precipitate by adding potassium cyanide to a solution of a nickel salt. In excess of potassium cyanide, the precipitate dissolves, forming $Ni(CN)_2 \cdot 2\,KCN \cdot H_2O$, which may be obtained as reddish yellow monoclinic crystals. On boiling, the solution remains unchanged; but on treatment with hypochlorites, black nickelic hydroxide is precipitated, which fact is used in separating nickel from cobalt.

Nickelous sulphide NiS is formed as a black precipitate when alkali sulphides are added to solutions of nickel salts. The sulphide is slightly soluble in excess of alkali sulphides, yielding a dark brown solution from which, by addition of acetic acid, the sulphide is again precipitated. Nickelous sulphide dissolves but slightly in dilute hydrochloric acid.

Nickel carbonyl $Ni(CO)_4$ is a colorless liquid boiling at 43°

and congealing at − 25°. It is formed by passing carbon monoxide over nickel obtained by reducing the oxide or oxalate by ignition in hydrogen. The vapors of nickel carbonyl are poisonous. The substance burns, depositing nickelous oxide and nickel. This compound is similar to iron carbonyl $Fe(CO)_5$, which is formed by passing carbon monoxide over finely divided iron under a pressure of about six atmospheres at 40° to 80°. An analogous compound of cobalt has not been made.

Occurrence, Preparation, and Properties of Cobalt.—Cobalt is found in meteorites and in *smaltite* $CoAs_2$ and *cobaltite* CoAsS, in which it is commonly associated with nickel, iron, and manganese. The principal localities are Canada, Sweden, Bohemia, Germany, and the Urals.

The metal is obtained by igniting the oxides or oxalate in a current of hydrogen. Cobaltous oxide is also reduced by mixing it with starch or flour and making small cubes of the paste formed, which are then embedded in pulverized carbon and highly ignited in a crucible. Thus the oxide is reduced, and the metal is obtained in form of cubes. Metallic nickel may be obtained similarly. Cobaltous oxide may be reduced by the Goldschmidt process.

Cobalt is a silver-white, malleable, tenacious metal of specific gravity 8.5. It melts at about 1500°. On exposure to the air, it soon acquires a reddish hue. Red-hot cobalt decomposes steam. The metal is magnetic. It dissolves in nitric acid, but other dilute acids attack it but slowly. The atomic weight of cobalt is 58.97 and its valence is either two or three. The cobaltous compounds are the more common. The metal itself is not used in the arts, but its oxides are used to color glass and porcelain blue. The fact that silicates are thus colored by cobalt ores has been known since ancient times, but the metal was not obtained till 1735, when the Swedish chemist Brandt prepared it. The word *cobalt* means goblin. This name was given to the ores of cobalt by the miners; for though these ores have a bright metallic luster suggesting a metallic content, it was not till relatively recent times that the metal was obtained from them.

Oxides and Hydroxides of Cobalt. — **Cobaltous hydroxide** $Co(OH)_2$ is a rose-red precipitate formed by adding caustic alkali to a solution of a cobaltous salt, and then boiling to

decompose the blue basic salt that is first precipitated. On igniting cobaltous hydroxide or carbonate out of contact with the air, **cobaltous oxide** CoO is obtained as a greenish powder. This is also formed by passing steam over red-hot cobalt. On heating cobaltous oxide in the air, **cobaltous cobaltic oxide** Co_3O_4, which is analogous to magnetite, is formed as a black powder. *This is produced as the final product by igniting any oxide of cobalt in the air.* It also results by calcining the nitrate. But if the latter is gently heated, **cobalt sesquioxide** Co_2O_3 is first obtained as a dark brown powder, which yields oxygen and Co_3O_4 on further ignition. **Cobaltic hydroxide** $Co(OH)_3$ is a dark powder formed by treating a solution of a cobaltous salt with hypochlorites. **Cobalt dioxide** CoO_2 is also known.

Other Cobalt Compounds. — The hydrous cobaltous salts are red, which is also true, as a rule, of their solutions at ordinary temperatures. The anhydrous cobaltous salts are generally blue, as are many of their solutions at higher temperatures. But few simple cobaltic salts are known.

Cobaltous chloride $CoCl_2$ is a blue crystalline powder obtained by heating cobalt in chlorine. From aqueous solutions, it may be obtained in form of deep red, monoclinic prisms of the composition $CoCl_2 \cdot 6\,H_2O$. The salt is also formed by dissolving cobaltous hydroxide or carbonate in hydrochloric acid. When the hydrous cobaltous chloride is heated, it turns blue, becoming red again as it absorbs water after cooling. So by writing on paper with a solution of cobaltous chloride (so-called **sympathetic ink**) the lines, which are at first invisible, become blue on gently heating the paper. On exposure to the air at ordinary temperatures, the salt again takes on water and the writing fades.

Cobaltous nitrate $Co(NO_3)_2$ forms red, deliquescent, monoclinic prisms.

Cobaltous sulphate $CoSO_4 \cdot 7\,H_2O$ is isomorphous with the other vitriols. It loses water readily on heating. The anhydrous salt is red and is not easily decomposed, even on strong ignition.

Cobaltic sulphate $Co_2(SO_4)_3 \cdot 18\,H_2O$ has been obtained at the anode by electrolysis of cobaltous sulphate.

Cobalt silicates result when glass or silica and potash are fused with an oxide or other compound of cobalt. The blue

glass that results is pulverized and used as a pigment under the name **smalt**. It serves well in decorating porcelain and glass, where it is afterwards fired in; but it is not satisfactory in oil or water paints.

Cobaltous sulphide CoS is obtained as a black precipitate by adding alkali sulphides to solutions of cobalt salts. Like the sulphide of nickel, cobaltous sulphide is insoluble in dilute hydrochloric acid. The sulphides Co_2S_3, Co_3S_4, and CoS_2 occur in nature.

Cobaltous carbonate $CoCO_3$ is a bright red powder. By adding alkali carbonates to solutions of cobaltous salts, red precipitates of basic carbonates form, which decompose and turn blue on boiling.

Cobalt silicides Co_2Si and CoSi have been made in the electric furnace. They are very hard crystalline substances.

Cobaltous cyanide $Co(CN)_2$ is formed as a reddish precipitate by adding potassium cyanide to a solution of a cobaltous salt. Cobaltous cyanide is soluble in an excess of potassium cyanide, forming **potassium cobaltous cyanide** $K_4Co(CN)_6$, which upon oxidation yields **potassium cobaltic cyanide** $K_3Co(CN)_6$. These compounds are similar to those of the corresponding double cyanides of iron. *Nickel does not form analogous double cyanides.*

Potassium cobaltic nitrite $3\,Co(NO_2)_3 \cdot 6\,KNO_2 \cdot 3\,H_2O$ is formed as a yellow precipitate when potassium nitrite is added to a solution of a cobaltous salt acidified with acetic acid. The precipitate separates out slowly. It is called **cobalt-yellow**. The reaction is used to separate cobalt from nickel. The latter does not form an analogous salt.

Cobalt amines are complex compounds which cobaltic salts form with ammonia. These compounds are made by treating solutions of cobaltous chloride with ammonia in sufficient amount to redissolve the cobaltous hydroxide that first forms. On standing in the air, these brown solutions absorb oxygen, thus becoming red. When hydrochloric acid is added to the red solution, brick-red crystals of **roseo cobaltic chloride** $CoCl_3 \cdot 5\,NH_3 \cdot H_2O$ are deposited. On boiling, the solution yields **purpureo-cobaltic chloride** $CoCl_3(NH_3)_5$, which forms a bright red crystalline powder, or brownish **luteo-cobaltic chloride** $CoCl_3 \cdot 6\,NH_3$, if much ammonium chloride is present in the strongly acid solution. Other cobaltous salts form similar

complicated compounds on treatment with ammonia. The three examples given must suffice here to indicate their general character, though the compounds are very interesting and have in recent years received careful study in connection with the subject of valence, particularly by A. Werner and S. M. Jörgensen.

Analytical Tests for Nickel and Cobalt. — When heated in the borax bead, cobalt compounds always give a blue coloration. Nickel compounds yield a brown bead in the oxidizing flame, and a milky bead in the reducing flame, for by the latter metallic nickel is formed. The reactions of salts of nickel and cobalt with alkali hydroxides, sulphides, hypochlorites, cyanides, and nitrites, as above explained, are used in the detection and separation of nickel and cobalt.

REVIEW QUESTIONS

1. Why is it that iron is the most useful of all of the metals?
2. What other metals are closely related to iron and are grouped with it in the periodic system? Why are these metals in the last column of the periodic system?
3. Write the formulas of the chlorides, sulphates, nitrates, and oxides of iron. Compare these with the formulas of the corresponding compounds of cobalt, nickel, manganese, chromium, aluminum, zinc and magnesium, by grouping the compounds of analogous composition.
4. What are the most important ores of iron? Write their formulas and the equations showing how iron is obtained from each of these ores.
5. Discuss the occurrence of iron: (1) in soils, (2) in plants and animals.
6. Why is limestone used in a blast furnace? Equation.
7. What are the main chemical differences between cast iron, wrought iron, and steel?
8. Why are phosphorus and sulphur especially objectionable in iron?
9. What occurs in the process known as the tempering of steel?
10. What is the chemistry of the use of borax or sand in welding? Equations.
11. Compare the essential features of the Bessemer process and the open hearth process of making steel.
12. Explain how phosphate fertilizer may be produced in connection with the production of steel.
13. Explain how blast furnace slag is employed in the Portland cement industry.
14. What is the chemical nature of the following: Venetian red, rouge, red ochre, yellow ochre, passive iron, Fool's gold, copperas, Mohr's salt, Prussian blue, cementite, electrolytic iron.

15. Explain the essentials of the process of blue printing. Equations. How write white characters on a blue print? Equation.

16. Mention four different ways of converting 10 grams of ferrous chloride into ferric chloride. How much of the latter would be formed? Write the equation in each case.

17. How demonstrate that a one per cent solution of ferrous sulphate contains iron? Equations. How show that a one per cent solution of ferric chloride contains iron? Equations.

18. What is the composition of a nickel coin? Of German silver? How prove that these contain nickel? Equations.

19. Why is nickel used: (1) in armor plates, (2) in plating iron, also copper and brass articles? How is the process of nickel plating conducted?

20. Compare the physical properties of nickel and cobalt.

21. What use is made: (1) of metallic cobalt, (2) of cobalt compounds?

22. Describe the chemical characteristics of cobaltous chloride.

23. What is sympathetic ink? Upon what fact does its use depend?

24. How test a compound for the presence of cobalt?

25. What is smalt, and what is it used for?

26. Given a solution containing a mixture of the chlorides of nickel and cobalt, how proceed to separate the nickel from the cobalt? Reaction.

CHAPTER XXXI

THE METALS OF THE PLATINUM FAMILY

THE metals of the platinum group and their symbols and atomic weights are: ruthenium (Ru—101.7), rhodium (Rh—102.9), palladium (Pd—106.7), osmium (Os—190.9), iridium (Ir—193.1), and platinum (Pt—195.2). These metals always occur together in nature in the form of alloys consisting of small corroded metallic bits or nuggets found in alluvial sands, chiefly in the Urals, California, Brazil, Australia, Borneo, and Sumatra. These alloys contain from 50 to 85 per cent platinum, several per cent iridium, and generally less than two per cent of each of the other members of the group. Gold, copper, iron, and other metals are also usually present. By careful washing of the sands, the particles of platinum ore are obtained as in the case of placer mining of gold. Though platinum ore usually occurs in the form of mere grains, larger nuggets weighing up to about eight kilograms have been found in rare instances.

It will be observed that ruthenium, rhodium, and palladium have approximately the same atomic weight; their specific gravities are also nearly alike, being 12.3, 12.1, and 11.5, respectively. Again, the second three metals, osmium, iridium, and platinum, have nearly the same atomic weight, which is about 90 units higher than that of the first three members. Osmium, iridium, and platinum also have about the same specific gravities, namely, 22.5, 22.4, and 21.5, respectively. It will be recalled that the atomic weights of iron, nickel, and cobalt are also nearly the same, and that these metals have specific gravities that differ but slightly from one another.

Extraction of Platinum from the Ores. The ores are freed from sand and other adhering impurities, and then treated with dilute aqua regia, which dissolves the gold, copper, and iron that may be present, leaving the platinum metals behind. On adding concentrated aqua regia to this residue, platinum, pal-

ladium, ruthenium, rhodium, and some of the iridium are dissolved. The residue left consists of osmium and iridium together with some ruthenium. From the solution, the platinum and iridium are precipitated by means of ammonium chloride as $(NH_4)_2PtCl_6$ and $(NH_4)_2IrCl_6$. There is usually but little iridium present in this precipitate. On ignition of the latter, metallic platinum, alloyed with a little iridium, is obtained as a spongy mass. As platinum containing minor amounts of iridium is excellent for crucibles, dishes, and other purposes, being stronger mechanically and more resistant towards reagents than pure platinum, this sponge is commonly used without further attempts at purification. From the filtrate containing palladium, rhodium, and ruthenium, these metals are precipitated by means of iron and then separated by special processes which will not be described here.

Ruthenium (Ru—101.7) was discovered by Claus in 1845. The element is named after the Ruthenians, a little Russian people in whose country the metal is found. Ruthenium occurs in the alloy of osmium and iridium, *osmiridium*, remaining as a residue when platinum ores are treated with concentrated aqua regia. Ruthenium is commonly prepared from this alloy. It is a brittle metal of steel-gray color. It melts above 2000°. When heated in the air, ruthenium oxidizes. The **oxides** RuO, Ru_2O_3, RuO_2, and RuO_4 are known. They are black powders. Ruthenium is not attacked by acids; even aqua regia acts but slowly on it, forming the **trichloride** $RuCl_3$. The **dichloride** $RuCl_2$ is known, but the **tetrachloride** $RuCl_4$ exists only in solutions. On fusing ruthenium with caustic potash and saltpeter, **potassium ruthenate** K_2RuO_4, readily soluble in water, is obtained, which fact is used in separating ruthenium from osmiridium.

Rhodium (Rh—102.9) was discovered by Wollaston in 1803. It receives its name from the red color of its chloride. The metal is silver-white, ductile, and malleable. It melts at about 2000°, and when pure it is not attacked by acids, not even by aqua regia, which, however, dissolves rhodium alloyed with platinum. By fusing rhodium with caustic potash and saltpeter and extracting the mass with nitric acid, oxides of rhodium are obtained. The **oxides of rhodium** are RhO, Rh_2O_3, and RhO_2; the **hydroxides** $Rh(OH)_3$ and $Rh(OH)_4$ are also known. The

red **chloride** RCl_3, formed by the action of chlorine on the metal, is the only one isolated. It is insoluble in water and acids. It forms soluble double salts with alkali chlorides. Rhodium chloride forms $RhCl_3 \cdot (NH_3)_5$ and other compounds analogous to cobalt amines. The double cyanide $K_3Rh(CN)_6$, which is analogous to $K_3Fe(CN)_6$, is also known.

Palladium (Pd — 106.7) was also discovered by Wollaston in 1803. It is named from Pallas, an asteroid discovered in 1802. While always present in platinum ores, palladium also occurs in alloys with gold in Brazil. Silver generally contains traces of palladium. It is a silver-white, ductile, malleable metal, which melts at about 1535°. *Palladium absorbs over* 300 *times its volume of hydrogen under ordinary conditions, at* 100° *about twice as much hydrogen is absorbed.* On electrolyzing water, using a palladium cathode, the latter absorbs nearly 1000 times its volume of hydrogen. The compound formed, **palladium-hydrogen**, is lighter than the metal; its composition varies with the conditions under which it is prepared. It gives off its hydrogen completely when heated to redness, though evolution of the gas begins even at 100°. The hydrogen liberated effects reductions like nascent hydrogen.

Palladium is soluble in nitric acid, in aqua regia, and in hot sulphuric acid. The **oxides** are PdO and PdO_2; both are black. The dioxide yields the chloride $PdCl_2$ and chlorine, when treated with hydrochloric acid, $PdCl_4$ being unknown. The following typical salts are also well known: —

$$Pd(NO_3)_2;\ PdI_2;\ PdSO_4;\ K_2PdCl_6;\ PdCl_2 \cdot (NH_3)_2.$$

Osmium (Os — 190.9) was discovered in 1804 by Tennant. It is found in platinum ores, in **osmiridium** and **iridosmium**, two alloys of osmium and iridium.

Osmium is a steel-gray, hard, brittle metal, which has *the highest specific gravity of all known substances*, 22.5. It melts in the electric furnace above 2500°. Osmium is oxidized to OsO_4 by aqua regia, nitric acid, or by ignition in the air. **Osmium tetroxide** forms white, monoclinic crystals that readily melt, and then boil at about 100°, emitting a very pungent vapor, from whose unbearable odor osmium gets its name. *Osmium tetroxide is used in hardening and staining histological specimens*, being commonly called **osmic acid** or perosmic acid.

Its use depends upon the fact that in contact with organic tissues, especially with fats, it is reduced, forming finely divided metallic osmium. The readiness with which osmium tetroxide is formed and its volatility serve in separating osmium from iridium and ruthenium, which also occur in osmiridium. The **chlorides** $OsCl_2$, Os_2Cl_6, and $OsCl_4$ are known, as are also **osmates** like $K_2OsO_4 \cdot 2\,H_2O$. The **oxides** are OsO, Os_2O_3, OsO_2 and OsO_4.

Iridium (Ir — 193.1) was also discovered by Tennant in 1804. It is a grayish white, rather brittle metal which melts at about 2200°. It is found in ores of platinum and in osmiridium. Its separation from osmium has been mentioned in connection with the latter. From platinum it may be separated by using the fact that the compound $(NH_4)_2IrCl_6$ is readily soluble in water. Aqua regia attacks pure iridium but slowly. The **oxides** are IrO, Ir_2O_3, and IrO_2. The **hydroxides** $Ir(OH)_3$ and $Ir(OH)_4$ and the **chlorides** $IrCl_2$, $IrCl_3$, and $IrCl_4$ are also known. Iridium gets its name from the fact that it forms compounds of various colors.

Platinum (Pt — 195.2) is a silver-white, tenacious, malleable, and ductile metal of specific gravity 21.47. The name platinum comes from platina, which is a diminutive of the Spanish *plata*, meaning silver. Platinum melts in the oxyhydrogen flame at about 1777°. At white heat it may be welded without the aid of a flux, for its surface is not covered with oxide. Even at high temperatures, platinum does not oxidize in the air. Aqua regia dissolves platinum, but the latter is not attacked by hydrofluoric, hydrochloric, sulphuric, or nitric acid. *Molten caustic alkalies and alkali nitrates, cyanides, or sulphides attack platinum, and it readily forms alloys with most of the heavy metals and also with silicon, boron, phosphorus, arsenic, and antimony.* These facts are of importance, for *the substances mentioned, and also such compounds as may yield these substances on ignition, must not be heated in platinum dishes. Platinum should also not be heated in a reducing flame*, for thus the metal takes up carbon and becomes brittle.

Platinum sponge is formed by ignition of ammonium platinic chloride; while **platinum black** is produced by electrolysis of platinic chloride solutions, or by adding finely divided magnesium, iron, or zinc to the latter. In finely divided form, *platinum*

absorbs about 300 times its volume of hydrogen or about one third that volume of oxygen. The gases are said to be *occluded* in the metal. On ignition they escape. The catalytic oxidations and reductions effected by finely divided platinum depend upon the fact that the latter absorbs the gases mentioned, which then act far more vigorously than when in the ordinary state. Thus Döbereiner's lamp (Fig. 155) depends upon the fact that when a jet of hydrogen is directed against a platinum sponge the latter is heated to redness and so lights the jet. The decomposition of hydrogen peroxide and the synthesis of SO_3 from SO_2 and O_2 are further typical instances of the catalytic action of platinum black.

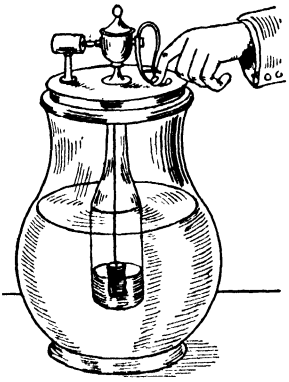


FIG. 155.

Besides being used for crucibles, dishes, and other utensils for chemical operations, much platinum is required for making various electrical connections. Platinum salts are used in photography.

There are two series of platinum compounds. In **platinous compounds** the metal is bivalent, while in **platinic compounds** it is quadrivalent. **Platinic chloride** $PtCl_4$ is formed by the action of chlorine on platinum at high temperatures, or by ignition of **chlorplatinic acid** $H_2PtCl_6 \cdot 6\,H_2O$, which results when platinum is dissolved in aqua regia. With the exception of **sodium chlorplatinate** Na_2PtCl_6 the alkali salts of chlorplatinic acid are insoluble in alcohol and sparingly soluble in water, *hence the use of chlorplatinic acid in separating sodium from potassium in analysis.* **Potassium chlorplatinate** K_2PtCl_6, or $PtCl_4 . 2\,KCl$, forms a golden yellow, crystalline precipitate. The crystals are small octahedra; they are isomorphous with **ammonium chlorplatinate** $(NH_4)_2PtCl_6$. When potassium chlorplatinate is ignited, potassium chloride and platinum remain; whereas when ammonium chlorplatinate is heated, the residue consists simply of spongy platinum. Either of these salts, which are also called potassium platinic chloride and ammonium platinic chloride, is readily formed by adding the alkali chloride to a solution of chlorplatinic acid or platinic chloride.

On heating chlorplatinic acid to 300°, or on passing chlorine over platinum sponge at about 245°, **platinous chloride** $PtCl_2$ is obtained as a grayish green, insoluble powder, which on ignition leaves platinum as a residue. **Potassium platinous chloride** K_2PtCl_4 is formed by reducing potassium platinic chloride with cuprous chloride. **Platinous hydroxide** $Pt(OH)_2$ is formed by treating platinous chloride with caustic alkali. On ignition of platinous hydroxide, **platinous oxide** PtO is formed, and finally platinum. **Platinic hydroxide** $Pt(OH)_4$ results when platinic chloride is treated with caustic alkali. By careful ignition of this hydroxide, platinic oxide may be obtained, which on strong ignition yields platinum. When platinic hydroxide is treated with an excess of caustic alkali, **platinates** are formed, thus: —

$$Pt(OH)_4 + 4\,NaOH = Na_4PtO_4 + 4\,H_2O.$$

Platinates also result when platinum is placed in molten caustic alkalies.

Platinous sulphide PtS and **platinic sulphide** PtS_2 are black precipitates, insoluble in acids, formed by adding hydrogen sulphide to solutions of platinous and platinic compounds, respectively. These sulphides are soluble in aqua regia. They also dissolve in alkali sulphides, with which they form sulpho-salts.

Analytical Tests for Platinum. — The sulphides described are characteristic. On heating any platinum compound with soda on charcoal, spongy platinum is obtained. This is soluble in aqua regia, and from the solution potassium chlorplatinate may be precipitated by adding potassium chloride.

REVIEW QUESTIONS

1. Name the metals of the platinum family and state how they may be divided into two distinct groups.
2. Besides these metals, what other noble metals are there? Why are these not grouped with the platinum metals in the periodic system?
3. How do the platinum metals occur in nature, and where?
4. Outline how platinum is extracted from its ores.
5. What physical and chemical properties make platinum an especially valuable metal: (1) in the chemical laboratory, (2) in the arts?
6. Write the formulas of the following compounds: platinic chloride, platinous chloride, potassium platinic chloride, osmic acid.

7. Explain what property of palladium makes this metal of special value in gas analysis.

8. What is so-called hard platinum? What use is made of it?

9. What use is made of osmic acid in histology?

10. Explain the action of platinum sponge: (1) in lighting a jet of hydrogen or illuminating gas, (2) in decomposing hydrogen peroxide, (3) in making sulphuric acid.

11. How is platinic chloride used in the detection and estimation of potassium? Equation.

12. Solutions of platinic chloride and ferric chloride are both yellow in color. In a solution containing a mixture of these salts how demonstrate the presence of both platinum and iron? Give three ways of doing this, writing the appropriate equations.

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