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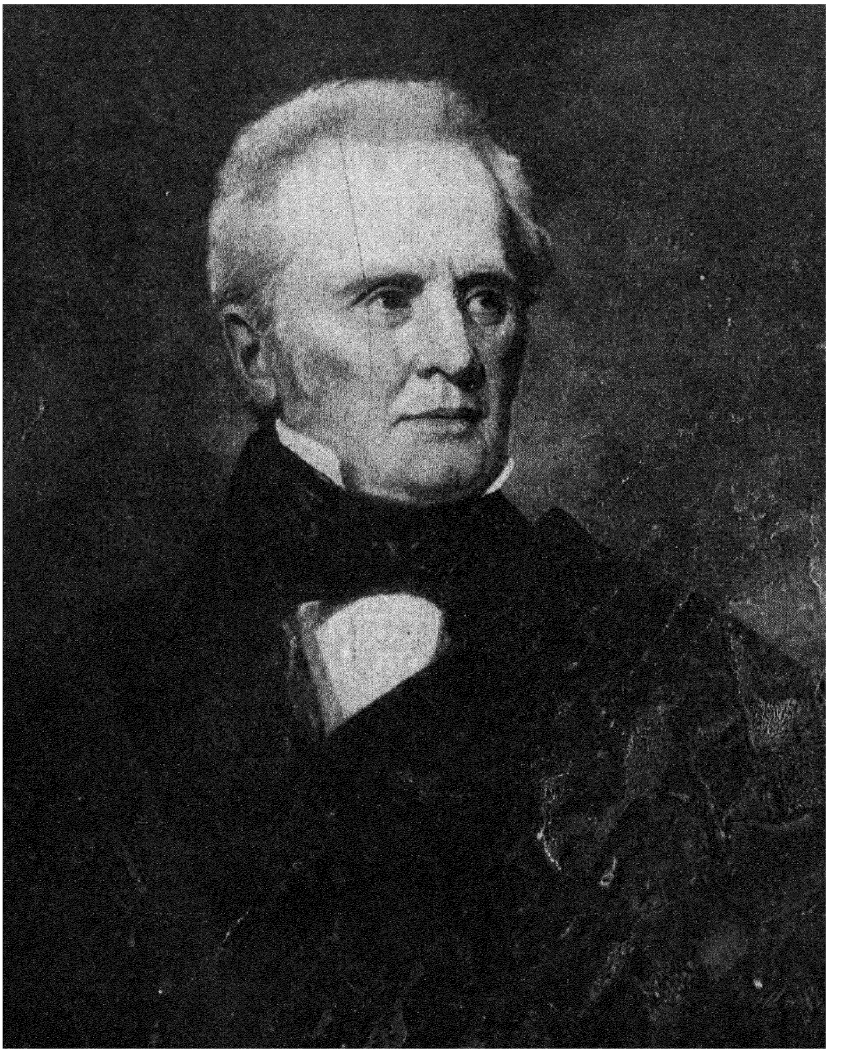

From a painting by Daniel Huntington

BENJAMIN SILLIMAN (1779–1864).

Professor of Chemistry at Yale College, 1802–1853
Eminent American Scientist and Teacher.

PRINCIPLES

OF

GENERAL CHEMISTRY

BY

STUART R. BRINKLEY

Associate Professor of Chemistry
Yale University

THIRD EDITION

NEW YORK
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1941

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PREFACE

The new edition of this text, like the preceding editions, is intended to meet the requirements of the general college course for students who have had a preparatory course in chemistry. In such courses it is necessary to review a number of topics, but the repetition involved should present a different and more advanced point of view with emphasis on the interpretation and significance of scientific data, not merely on the facts themselves. It should be assumed that students who choose a second course in chemistry are interested in the science and do not require artificial stimulus.

The order of the topics in the first part of the book has been modified in order to provide a sound basis for scientific reasoning. The atomic and kinetic theories are developed and applied in the interpretation of the chemical and physical properties of substances. The chemistry of oxygen and hydrogen is employed to present further applications of the atomic theory and to serve as a review of chemical equations, calculations and similar subjects. The halogens and the alkali metals are reviewed in the light of the concepts of atomic structure; and these topics afford a background of experimental data for the discussion of ionization and ionic reactions.

The chapters dealing with theoretical topics have been brought fully up to date. In the discussion of atomic structure, the experimental background which gives validity to the assumptions regarding the nature of the fundamental particles is indicated. The properties and reactions of the elementary substances are interpreted consistently in terms of the structures of the atoms. A chapter dealing with the nucleus of the atom, in which artificial radioactivity, transmutation of the elements, and nuclear fission are discussed briefly, is included in the latter part of the book. The complete ionization of salts follows as a natural consequence of the electronic changes which occur during the reactions of the active metals and non-metals with each other. The reduced

activity of the ions is attributed primarily to the forces of interionic attraction. The ionization of the molecular acids is based on their interaction with ionizing solvents. The Brönsted and Lowry definitions of acids and bases are developed and employed consistently. Oxidation-reduction in aqueous solution is discussed and represented in terms of the ion-electron half reactions so as to place continued emphasis on the ionic nature of these reactions. Such reactions in anhydrous media are balanced by the changes in oxidation numbers.

The theoretical material is grouped largely in the first half of the book; but a sufficiently extensive body of descriptive material is included to serve as a basis for the presentation of the theories in their true perspective. It is thus possible to secure a logical sequence of the topics dealing with atomic structure, ionization, and ionic equilibria including the common ion effect, complex ion formation, acids, bases, ampholytes, and hydrolysis. The early development of theoretical principles also clears the way for a rational discussion of the reactions involved in Qualitative Analysis in courses in which the laboratory work of the second semester deals with this subject.

The descriptive study of the elementary substances is based on the modern form of the periodic table. Brief discussion of the transition elements is included so that a more nearly complete view of the general relationships may be obtained. As in previous editions, the compound substances are classified into groups of similar substances: *e.g.*, acids, bases, and salts. The salts are grouped into four chapters on the basis of similarities in the anions which they contain. The discussion of the production of the metals from their ores is included, for the most part, in two chapters, in preference to scattering this related material by placing the production of each metal under the periodic group of which it is a member. This arrangement avoids much unnecessary repetition and emphasizes the principles which are involved.

Although emphasis is placed on the principles of the science, industrial applications and processes are included to indicate the importance of chemistry in the modern world. Figures showing the production and consumption of a number of substances, quoted from Chemical and Metallurgical Engineering and from

the Minerals Yearbook, 1940, United States Department of the Interior, Bureau of Mines, indicate the extent to which industry has become dependent on chemistry.

Lists of supplementary readings at the ends of the chapters suggest further study along historical, philosophical, and industrial lines, according to the interests of the students. The exercises direct the attention of the student to the main points in the chapter and emphasize scientific reading and the correlation of scientific knowledge. The data in the tables throughout the book and in the appendix are, for the most part, based on *International Critical Tabl s* (McGraw-Hill Book Co.); Latimer and Hildebrand, *Reference Book of Inorganic Chemistry* (The Macmillan Co.); Lange, *Handbook of Chemistry* (Handbook Publishers, Inc.); *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co.); and the scientific journals.

For many helpful suggestions the author wishes to express his appreciation to his associates in the courses in general chemistry in this University, Professors H. G. Dietrich, D. T. Keach, E. B. Kelsey, J. A. Timm, and Dr. A. D. Bliss; to Professors H. S. Harned and A. J. Hill; and to Professor J. B. Entrikin of Centenary College, Professor W. C. Sumpter of Western Kentucky State Teachers College, and Doctors R. B. Conklin and Donald D. Wright of Brooklyn College.

For photographs used in the sections dealing with "Atomic Structures" and the "Nucleus of the Atom," the author is indebted to Professor Carl D. Anderson, California Institute of Technology; Professor P. M. S. Blackett, Cavendish Laboratory; Professor Donald Cooksey, University of California; and Professor Ernest C. Pollard, Yale University. The courtesy of Miss Mary Trumbull Morse in permitting the use of the photograph of Benjamin Silliman, made from the painting by Daniel Huntington, is greatly appreciated. For the assistance given by furnishing pictures, charts, and diagrams and permitting their use in this book, the author's appreciation is expressed to those whose courtesy is acknowledged in connection with each of these illustrations.

STUART R. BRINKLEY

NEW HAVEN, CONNECTICUT
June, 1941.

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PRINCIPLES
OF
GENERAL CHEMISTRY

CHAPTER I

INTRODUCTION. VARIETIES OF MATTER

The aim of natural science is to secure complete and accurate knowledge of natural objects and phenomena. With such knowledge it would be possible to explain all changes which occur, and to predict the future behavior of the material universe. To only a limited extent has this knowledge been obtained; but progress has been so rapid as to indicate the path which science must follow to achieve its aim.

The Scientific Method. The first step in the scientific method is the accumulation of experimental data. Experimental facts are derived by the observation of phenomena which occur in nature and those which result from procedures planned by human agencies. These data must be as complete and accurate as the experimental methods permit. Isolated experiments lead to more or less unrelated specific facts; but properly planned and carefully executed experiments yield a series of related observations. Starting in this way with particular instances, it is possible to develop generalizations or laws. ***A scientific law is a statement which summarizes a large number of experimental observations.*** Since scientific laws are essentially descriptive, they are no more rigid than the experiments on which they are based and no more universally applicable than the experiments and calculations by which they can be tested.

After a series of scientific laws has been established, an *hypothesis* is set up in the attempt to explain the laws. This requires the imagination of a structure of matter and a mechanism of the observed changes, which aids in visualizing and interpreting the facts. Hypotheses which are found to interpret satisfactorily all of the facts involved and are supported by large additional amounts of experimental data are known as theories. ***A theory is a model, a mental picture, by which scientific laws are coordinated and interpreted.*** A theory differs from a law in that

it employs concepts which are not subject to direct observation and proof. As new facts are discovered, the inadequacy or incorrectness of an accepted theory may become apparent. Thus modifications in the theory are required, and theories may be supplanted by new ones which are more useful. Improvement in experimental methods and increase in the amount of knowledge serve as tests of the usefulness and validity of theories. It is assumed by all scientific workers that a theory which is firmly established provides a true model of the actual process; but it is also understood that changes in the model may become necessary.

Theories are useful, not only in the correlation and interpretation of the laws of science, but also in suggesting experiments which lead to the discovery of new facts. *By deduction* from accepted theories, experimental investigations are planned to test the validity of the theory, and in this way further knowledge is gained. If conclusions which are drawn logically from the assumptions of the theory cannot be verified by experiment, it becomes evident that the theory is not adequate, but requires modification. The scientific method requires both inductive and deductive reasoning. The great principles of science are reached by induction from classified knowledge. They are tested by experiments suggested to determine the accuracy of deductions from these principles. Additional data are accumulated which lead in turn to more accurate theories; and a more satisfactory and useful model is constructed for the interpretation of observations.

The method of reasoning and study by which science makes progress is important in other branches of knowledge also, because its logic appeals to the rational person. Many problems in other fields than chemistry may be attacked most effectively by the methods of science. The importance of the scientific method in the intellectual life of the past century has been stated clearly by Millikan.[1]

> "I think there can be no shadow of doubt that the great, characteristic feature of our times, the one thing that does distinguish our civilization from all that have preceded, is this discovery of the scientific method and the results that have followed upon its application. That discovery was indeed not made in our generation. It was made some three hundred years ago, but its cumulative effects

[1] R. A. Millikan, "Science and Humanism," *The Phi Beta Kappa Key* **7**, 650 (1931).

have come only within the last century. The method consisted in not starting with *a priori* postulates about the nature of reality or with any complete philosophic systems, such as all of the philosophers of the ancient world, idealists and atomists alike, had started with, and indeed had quarreled interminably over; in discarding likewise all intuitive axioms on the one hand and authority on the other such as had been the foundation of the medieval scholasticism of Thomas Aquinas and his successors; and appealing by the experimental method to the tribunal of brute facts."

Subdivisions of Science. The amount of knowledge dealing with different phases of science is now so great that it is not possible for any one person to master the whole of science. The specific vocabulary of one phase of science differs from that of another. The experimental procedures which are used in one field of science may not be suited to some other field. It is convenient, therefore, to group together the facts, laws, and theories dealing with the specific phases of science. *The physical sciences* deal with inanimate objects; *the biological sciences*, with living organisms and their products. As an aid to the study of science, further subdivisions are made in order to limit the field and make it possible to gain a clear understanding of scientific principles. Thus, chemistry, physics, and geology are physical sciences; botany, zoology, and physiology are biological sciences. One must not, however, overlook the fact that these subdivisions are made arbitrarily, and that these branches of science are portions of a body of knowledge in which there are no natural subdivisions. The sciences overlap, and it is important to integrate the branches of science as fully as one's knowledge permits.

Chemistry is the name given to that branch of science which deals with the different varieties of matter. Specific varieties of matter are investigated and the properties which lead to their identification are observed. Means of separating one variety of matter from another are developed. The composition of each specific variety of matter is determined; and changes in composition, together with the conditions which are necessary to bring about these changes and the relative amounts of energy accompanying the changes, are investigated. Scientific laws are formulated as an aid to this study, and theories are constructed for the interpretation of this specific knowledge. Chemistry is important as an exposition of the scientific method of thought.

Chemistry also has a practical aspect which is of fundamental importance in the modern world. A true understanding of the rôle of chemistry in the modern world can be gained only through the study of materials of outstanding importance and of the methods of science.

Matter. No single set of properties is sufficient for the description of matter. Many speculations regarding its ultimate nature have been advanced and have failed to withstand the test of rigid experiment. It is necessary, therefore, to accept the fact that matter is a fundamental reality, and that we have no general knowledge which permits us to say precisely what matter is. We may, however, study particular varieties of matter and learn a great deal about the nature of these specific substances, and about the units of structure which are common to all substances.

The quantity of matter in an object is its mass. The mass of an object is determined by its inertia, *i.e.*, the resistance which it offers to a change of motion. The relative masses of objects are measured by weighing them. The weighing of an object consists in measuring the attraction between that object and the earth. The intensity of the gravitational attraction between two bodies varies directly with their masses and inversely with the square of the distance between the centers of the bodies. Consequently, at the same distance from the center of the earth, the masses of two bodies are proportional to their weights. The object to be weighed is placed on the left pan of the balance and weights are placed on the right pan until the object is counterpoised. In this manner, the weight of the object is measured in the arbitrarily selected units of weight. The unit of mass is the *gram*, a one-thousandth part of the mass of the standard kilogram. The standard kilogram was intended to represent the mass of one cubic decimeter of water at 4° C., its temperature of greatest density; but this is not quite accurate. Nevertheless, one gram represents the mass of one milliliter, which is approximately one cubic centimeter, of water at 4° C.

Energy. Matter and energy are so closely interrelated that the study of the one involves a consideration of the other. Changes in matter are accompanied by changes in energy and occur in response to such changes. *The capacity to do work is called energy.* There are a number of different forms of energy. The kinetic

energy of an object is the energy which it possesses because of its motion; and the potential energy, the energy due to position. Heat, light, and electricity are forms of energy. *Chemical energy* is the energy which an object possesses because of its composition.

Different units are employed for the measurement of the different forms of energy. The unit of heat is the *calorie*, the amount of heat required to raise the temperature of one gram of water one degree, from 14.5° to 15.5° C. The unit of electrical energy is the *joule*, which is equal to the product of the quantity unit, one coulomb, multiplied by the intensity unit, one volt. Kinetic energy is dependent on the mass and velocity of the object. The kinetic energy, measured in ergs, is shown by the formula, $\frac{1}{2} mu^2$, in which m is the mass in grams and u the velocity in centimeters per second. Chemical energy is usually expressed in terms of the amount of heat to which it is equivalent, since changes in chemical energy are usually manifested in the form of heat.

It is a well-known fact that one form of energy may be transformed into another. Careful measurement of the amount of energy in such transformations leads to the generalization, the **Law of Conservation of Energy: In an isolated system, the total amount of energy undergoing transformation from one form to another is constant.** This means that all of the energy entering into a process reappears in other forms. This law, first stated by Helmholtz in 1847, is one of the most important and extensive generalizations in science. Energy which appears to be consumed is actually transformed into an equivalent amount of work or heat. Since energy may be dissipated as heat or transformed into work, it is apparent that there is a definite relation between work and heat. The equivalence of heat and work was established by Joule, whose experiments on the *mechanical equivalent of heat* led to the value:

$$1 \text{ calorie of heat} = 4.183 \times 10^7 \text{ ergs} = 4.183 \text{ joules.}$$

None of our machines will give a complete conversion of energy into useful work. Friction causes the transformation of other forms of energy into heat, which is conducted from one body to another, thus becoming dissipated so that it is no longer available for further transformation. In natural phenomena, the

transformations lead constantly to the degradation of energy in this way.

Substances and Their Properties. A substance is a specific variety of matter. It is *homogeneous;* that is, it has uniform composition throughout so that a sample from one portion of the substance has the same properties as a similar sample from some other portion, so long as the samples are kept in the same state. *A substance is characterized by a series of specific properties* by which it may be recognized and described. The physical state in which a substance exists at ordinary temperature and pressure is a prominent property. The boiling point and freezing point of a liquid and the melting point of a solid are important properties. Other common properties are color, odor, taste, density, solubility in water, and conductivity of heat and electricity. A crystalline solid has a definite structure.

The *chemical properties* of a substance are changes in composition which it undergoes when it is subjected to changes in conditions. Instability toward heat is a chemical property of some substances, such as potassium chlorate, which decompose when they are heated. Other chemical properties may involve the interaction of two or more substances. The combustibility of carbon in air is a chemical property of carbon involving its union with oxygen. The chemical properties of a substance are dependent on its composition and are manifested in changes in composition.

Classification of Substances. Different varieties of matter are classified according to their composition and properties. Some materials are homogeneous, while others are heterogeneous, *i.e.*, they do not have uniform composition throughout and can be separated into two or more components. Although the material as a whole is heterogeneous, a mixture is made up of several kinds of homogeneous particles. Each of the homogeneous materials of a single kind in any sample of matter is a *phase.* In a mixture of two pure solids there are two phases. In a mixture of the solid and liquid forms of a single substance, there are two phases; and, if the gaseous form of the same substance is also present with the solid and liquid, there are three phases in the system. Homogeneous materials may be classified into elements, compounds, and solutions.

Elements. There are a number of chemical substances which cannot be decomposed by any of the ordinary chemical changes, such as those which are effected through the application of heat, the passage of the electric current, and interaction with other substances. *These simple substances are called the chemical elements.* It has been found possible to transmute a number of the elements into other elementary substances. The significant distinction is not whether the substance can or cannot be decomposed, but that the element is a simple variety of matter in so far as chemical reactions are concerned. There are ninety-two elementary substances. One of them, designated as number 87, has not yet been obtained either in the elementary condition or in a pure compound. The production of another, number 85, in an elementary transmutation has been reported recently; but this element has not been separated from natural minerals. One or two additional elements have been reported as products of transmutation; but no evidence has been discovered of the existence of these additional elements in natural substances.

Abundance of the Elements. Only a small number of the elements are abundant. An estimate of the relative abundance of the elements in the outer portion of the earth, the sea, and the atmosphere has been made by F. W. Clarke and H. S. Washington.[1] A list of the twleve most abundant elements, which together comprise more than ninety-nine per cent of the matter in the outer ten miles of the solid earth, the ocean, and the atmosphere, is given in Table 1.

TABLE 1

ABUNDANCE OF THE ELEMENTS

Element	*Per Cent*	*Element*	*Per Cent*
Oxygen	49.52	Potassium	2.40
Silicon	25.75	Magnesium	1.94
Aluminum	7.51	Hydrogen	0.88
Iron	4.70	Titanium	0.58
Calcium	3.39	Chlorine	0.19
Sodium	2.64	Phosphorus	0.12

[1] F. W. Clarke and H. S. Washington, *The Composition of the Earth's Crust*, Department of the Interior, United States Geological Survey, *Professional Paper* **127**, 34 (1924).

It is to be noted that oxygen makes up approximately one half and silicon one fourth of the matter in the outer part of the earth, and that an unfamiliar element, titanium, occurs among the twelve most abundant, while other elements which are better known are not among the first twelve.

Compounds. The majority of the common substances are complex and may be decomposed into elementary substances. *Complex substances are called chemical compounds.* Compounds have properties which differ from those of the constituent elements. Compounds also have definite composition. This fact is expressed in the **Law of Definite Composition: The proportion by weight of the elements in a given pure compound is always the same.** This law was formulated by Proust in 1802 and received confirmation in the accurate experimental work of Stas about 1860.

A mechanical mixture is also complex but, unlike a compound, it is heterogeneous; and a mixture has no single set of properties by which it can be described. The composition of a mixture is not fixed and definite but the proportions of the components may be varied at will. Each of the substances in the mixture is unchanged in composition, and each retains its own characteristic properties.

Solutions. When one substance dissolves in another, for example, sugar in water, particles of the dissolved substance cannot be seen, nor can they be filtered out. The solution is of uniform composition. Nevertheless, the composition of the solution can be varied and, as the composition is changed, the properties are altered. Thus the density, the boiling point, and the freezing point of the solution are dependent on the relative proportions of the substances in solution. Although solutions, like compounds, are homogeneous, the properties depend on the composition of the solution. *Solutions, consequently, are homogeneous mixtures.*

EXERCISES

1. What is a natural science?
2. What factors are involved in the scientific method?
3. What is the significance of each of these factors?
4. Show how the scientific method involves both inductive and deductive reasoning.

5. How is the adequacy of a theory determined?
6. What is the significance of the following: mass; weight; energy?
7. Name and define units of mass, heat energy, electrical energy, and chemical energy.
8. What is meant by conservation of energy; the mechanical equivalent of heat?
9. What are substances? Name several properties which are used in the description of substances.
10. Distinguish fully between elements, compounds, mechanical mixtures, and solutions.

SUPPLEMENTARY READINGS

In his study of chemistry, the student should from the start form the habit of making use of the Library to read other books so as to broaden his knowledge of the topics under consideration. He should endeavor to discover some phase of each subject which appeals to him enough to cause him to wish to read further. At the end of each chapter a list is given to suggest further reading. In connection with this section, an historical survey, such as is given in one or more of the following books, should prove interesting.

Dampier-Whetham, *A History of Science* (The Macmillan Company, 1930), Chapters I–III.

French, *The Drama of Chemistry* (The University Society, Inc., 1937).

Jaffe, *Crucibles* (Simon and Schuster, 1930), Sections I and II.

Read, *Prelude to Chemistry* (The Macmillan Company, 1937).

Lenard, *Great Men of Science* (The Macmillan Company, 1933).

Findlay, *The Spirit of Chemistry* (Longmans, Green and Company, 1934), Chapters I and II.

Gregory, *Discovery* (The Macmillan Company, 1923).

Boyle, *The Sceptical Chymist* (Everyman's Library).

Lucretius, *De Rerum Natura*, Translated by W. E. Leonard (Everyman's Library).

Findlay, *A Hundred Years of Chemistry* (The Macmillan Company, 1937).

CHAPTER II

CHANGES IN SUBSTANCES. THE ATOMIC THEORY

Changes take place continuously in the natural substances about us and other changes are caused by planned experiments. The study of these changes in matter is an essential part of the science of chemistry. The weight relations involved in chemical changes are especially important, because they serve as the basis of the fundamental laws and theories of the science. The development of the atomic theory on the foundation of exact experimental data, the testing and confirmation of some of the postulates of this theory in the light of new data, and the modification of the theory to bring it into accord with new discoveries give a clear insight into the scientific method.

Physical Changes. *A physical change is one in which some of the properties of a substance are altered without change in the composition.* The changes in state in which a liquid evaporates or a solid melts are physical changes. The differences in the properties of substances in the different states are due to differences in the amount of energy associated with the ultimate particles of the substance. This results in differences in the position of these particles with respect to one another. No change in composition occurs during such changes in state. Similarly, when sugar dissolves in water it loses its characteristic crystalline structure and becomes dispersed into very minute particles. These particles, however, are still particles of sugar; and the solid may be recovered in its former structure by the evaporation of the water.

Chemical Changes. *A chemical change or chemical reaction is one in which the composition of the substance is altered.* The heating of potassium chlorate leads to its decomposition with the formation of two substances: the white solid, potassium chloride, and the colorless gas, oxygen. Each of these substances has its own specific properties. Consequently, an abrupt change in properties accompanies a chemical change. Each substance pos-

sesses a specific amount of energy, for a fixed weight, at a definite temperature. Therefore, a chemical change is accompanied by a definite change in energy, which is equal to the difference in the chemical energy of the initial substances and the products. Since compounds have definite composition, it follows as a necessary consequence that **the proportions by weight of the substances entering into and produced from a chemical reaction are fixed and definite.** This generalization, called the **Law of Definite Proportions,** is simply a restatement of the Law of Definite Composition discussed in the preceding chapter.

The Law of Conservation of Mass. A belief in the indestructibility of matter was a part of Greek philosophy; but during the Middle Ages, the view that matter is actually destroyed during some changes, such as the burning of wood, became accepted. Until the time of Lavoisier, 1743–1791, mistaken notions about combustion and many other chemical reactions were common, because of the lack of enough exact data to lead to the correct conclusions. Lavoisier is credited with having led the way in making quantitative methods the basis of chemical experimentation. In 1785, he stated the **Law of Conservation of Mass** as an experimental generalization: **The sum of the masses of the substances entering into a chemical reaction is equal to the sum of the masses of the products.** The significance of this law may be illustrated by the following experiment. Two substances which react with each other are placed in solutions in opposite limbs of a sealed U-tube, and the tube with its contents is counterpoised on the balance, Fig. 1. The tube is now removed from the balance and tilted so as to mix the solutions and allow a reaction to occur. It is then replaced on the balance; and it is found that no change in weight can be distinguished, although the composition of the substances has changed.

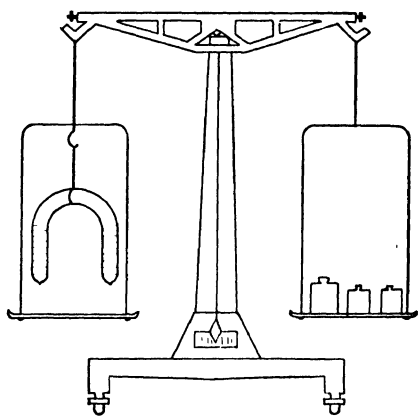


FIG. 1

ANTOINE LAURENT LAVOISIER (1743–1794)

As a result of his public activities, Lavoisier aroused the enmity of Marat during the French Revolution. He was tried by the Revolutionary Tribunal in May, 1794, convicted, and executed the following day.

Lavoisier brought to his experimental work the ability to reason in a clear and logical manner. His major interest in chemical problems was from their quantitative aspects. His work showed the true nature of combustion and respiration and may be considered the beginning of the scientific study of chemistry.

The laws of conservation of mass and of conservation of energy have been verified by a large amount of experimental work. Their truth is necessary if the quantitative experiments, upon which the foundations of chemistry as an exact science rest, are to have any significance. Modern theoretical research has shown that a change in mass must accompany the emission of energy. Since, however, the change in mass which accompanies the energy change in an ordinary chemical reaction is so small that it is not detected by weighing the substances, these laws may be accepted with complete confidence. A conservation principle which includes both matter and energy is taken to be rigidly accurate.

Equivalent Weights. The law of definite composition is a generalization which is applicable to specific substances, but indicates no relation between different substances. A generalization of broader application describes the reaction ratios of elements in different compounds. This generalization may be stated as the **Law of Equivalent Weights: The weights of two substances which are equivalent to the same weight of a third substance are equivalent to each other.** It may be shown by experiment that 1.008 g. of hydrogen and 35.46 g. of chlorine are each held in combination by 8 g. of oxygen, and that hydrogen and chlorine may combine with each other in the ratio of 1.008 g. to 35.46 g. The weight of magnesium that combines with 8 g. of oxygen is 12.16 g.; and this same weight of magnesium displaces 1.008 g. of hydrogen from a solution of hydrochloric acid, and combines with 35.46 g. of chlorine. These relations are shown graphically in Fig. 2.

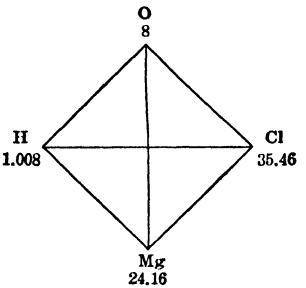


FIG. 2

In order to express all equivalent weights in a series of related numbers, it is necessary to choose arbitrarily a basis of the system. Since most of the elementary substances combine directly with oxygen, this substance has been selected as the most convenient standard. Eight units of weight for oxygen is the smallest quantity that can be selected without giving an amount less than one unit for hydrogen. Consequently, although other standards

have been used, the present basis for the system of equivalent weights is eight parts by weight of oxygen. ***The equivalent weight of an element is the weight of that element which is chemically equal to eight parts by weight of oxygen.*** The gram equivalent is the equivalent weight expressed in grams.

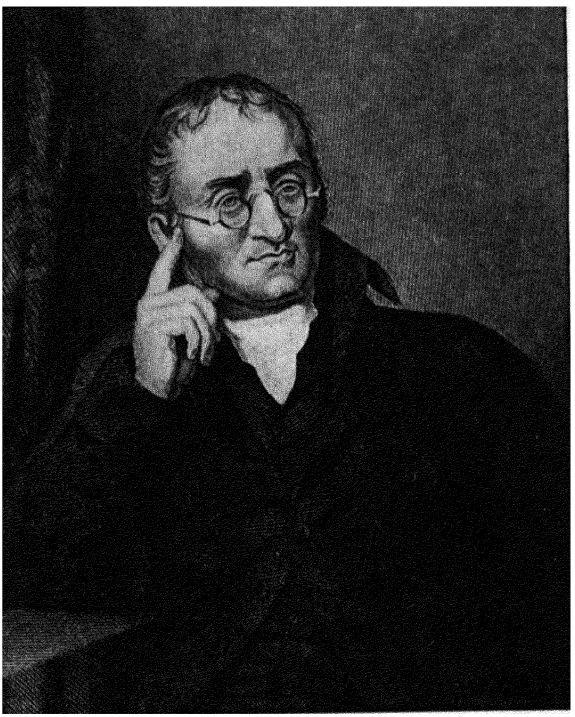
The equivalent weights of substances are determined by first finding experimentally the reacting ratio and then recalculating the data to the standard basis. Magnesium oxide is found to contain 60.32% of magnesium. This means that 39.68 parts by weight of oxygen combine with 60.32 of magnesium. This ratio is next reduced to the new one with 8 parts by weight of oxygen as the base.

$$\frac{60.32}{39.68} = \frac{x}{8}$$

$$x = \frac{60.32}{39.68} \times 8 = 12.16$$

A list of equivalent weights gives a ratio in which the substances may react, if they react at all. The relation of the equivalent weights of the elements to their atomic weights will be discussed in a later paragraph dealing with atomic weights. Likewise, the relation of the equivalent weights to the molecular weights of compounds will be discussed subsequently. Whether substances actually react or not, or react in more than one ratio, is specific information obtained from the study of the substances involved.

The Law of Multiple Proportions. Many of the elements may react with others in more than one ratio so as to form two or more compounds containing the same elements. Thus, there are two common oxides of carbon, carbon monoxide and carbon dioxide. In carbon monoxide, the equivalent weight of carbon is 6, while in carbon dioxide it is 3. These numbers show the weight of carbon combined with 8 parts by weight of oxygen in the compounds. It is obvious that the equivalent weight of carbon in the one oxide is twice that in the other. In 1803, John Dalton proposed the generalization known as the **Law of Multiple Proportions: If two or more elements yield a series of compounds, the different weights of one element held in combination by a fixed weight of another are in the ratio of small whole numbers.** This conclusion was advanced by Dalton on theoretical grounds as a necessary deduction from the



JOHN DALTON (1766–1844)

Dalton was not a highly gifted experimenter, and for financial reasons it was often necessary for him to work with very crude apparatus. His method of attack was based on his knowledge of mathematics and physics. He formulated several important laws and stated the fundamental concepts of the atomic theory, which, somewhat supplemented, are accepted today. His work is a good example of the scientific method of attack. By reasoning inductively on the basis of experimental facts, he formulated laws and theories and then devised experiments to test and substantiate the concepts of his theories. He also devised a system of atomic weights which, although containing many inaccuracies, was based on the fundamental idea that an interrelated series of relative weights for the elementary substances could be obtained.

atomic theory; but he was not able fully to prove its accuracy. Complete proof from a large number of investigations has now established the truth of the generalization.

The Atomic Theory. The laws describing the weight relations which are observed during chemical reactions lead logically to the idea that there is a unit particle of each elementary substance which is not changed during chemical reactions. At various times in the development of natural science, speculations about the nature of matter have involved the notion of an indivisible particle. Leucippus and Democritus in the fifth century B.C. and Lucretius in the first century B.C. set forth this view as a part of their general schemes of philosophy. Isaac Newton in 1675 suggested that chemical changes result from the separation and recombination of minute particles. John Dalton, 1766–1811, is commonly considered to be the first to devise an atomic theory for the quantitative interpretation of the laws of chemical combination. Dalton first advanced the atomic theory in 1803 and published it in his *New System of Chemical Philosophy* in 1808.

The important assumptions of Dalton's Atomic Theory may be summarized in the following form:

All matter is composed of minute particles, atoms, which are not subdivided in chemical reactions.
Atoms of the same element have identical properties and mass.
Atoms of different elements have different properties and mass.
Atoms of different chemical elements combine in a simple integral ratio during chemical reactions.

The law of conservation of mass is satisfactorily interpreted by the assumption that atoms merely undergo rearrangement during chemical reactions, and no atoms are divided or lost. If no change in the mass of the atom occurs during such rearrangements, it is obvious that there is no change in the total mass of the system. *The law of definite composition or definite proportions* is likewise fully explained, for a given compound always contains the same relative numbers of atoms of its constituent elements, and each variety of atom has characteristic weight. *The equivalent weights of the elements* depend on the weights of the individual atoms and the numerical ratio in which they react. If carbon and oxygen react in an atomic ratio of one to two, and carbon and hydrogen in a ratio of one to four, then it might be expected that

hydrogen and oxygen should react in an atomic ratio of two to one. It is evident that the ratio in which the atoms combine differs when two elements react to form two different compounds. In each compound, however, the ratio of combination is constant. Hence, it follows that the same number of atoms of one element may combine with two or more specific numbers of atoms of the other. In the compounds carbon monoxide and carbon dioxide, discussed previously, it may be concluded that the number of atoms of carbon in combination with the same number of atoms of oxygen is twice as great in carbon monoxide as in carbon dioxide. This conclusion is drawn from the fact that the equivalent weight of carbon in the monoxide is twice that in the dioxide. *The law of multiple proportions* is, therefore, a necessary consequence of the atomic theory. The confirmation of the accuracy of the law of multiple proportions, advanced by Dalton as a deduction from the theory, furnishes strong support of the theory.

Modifications in the Atomic Theory. The most important assumption of Dalton's atomic theory is that compounds are formed by the union of atoms of the elements in simple integral ratios. It is now fully established that atoms are complex particles which may be decomposed. The atoms of the radioactive elements spontaneously disintegrate, and atoms of many of the elements have been decomposed by experimental techniques since the first elementary decomposition was effected by Rutherford in 1919. Nevertheless, the atom is the reactive unit of elements and it does go through chemical reactions virtually unchanged in so far as its mass is concerned. It is now known that all atoms of a particular element do not necessarily have the same mass; but more commonly elements are made up of atoms having different masses. The different atoms of the same elementary substance have identical chemical properties and are usually present in the same proportions in natural compounds of that element. Consequently, the average mass of the atoms as determined by experiment is as definitely fixed as though all of the atoms had precisely the same mass. It has also been found that two atoms of the same mass may react differently, thus showing that atoms of two different elements may have the same mass. It is now known that the properties of elements depend on their atomic

numbers, a term which will be discussed in Chapter VI, rather than on atomic masses.

Having considered these points, it may seem that the atomic theory has been completely overthrown. This is not true, however, for the usefulness of the theory in the interpretation of chemical behavior has not been destroyed by these discoveries, and its essential postulates are now established more firmly than ever. Modifications in the statement of the theory have been made to place emphasis more properly on the true significance of its assumptions. The fundamental ideas in the atomic theory may be stated in the form: ***There is a reactive unit of each element, the atom, which is characterized by a constant average mass.*** Dalton made no distinction between atoms of elementary substances and unit particles of compounds; and it was not until the introduction of the term *molecule* by Avogadro in 1811, that the distinction between physical and chemical units became clear. The first great modification in the theory came with the recognition of this difference.

The Law of Reacting Volumes of Gases. The amounts of gaseous substances are commonly measured by volume rather than by weight. The same weight of a gas may occupy varying volumes depending on temperature and pressure. Therefore it is necessary that the volume measurements be made at specified temperature and pressure in order that they may represent definite amounts of substances. When measured in this way, it is found that a simple relation exists between the volumes of reacting gases and gaseous products. Hydrogen and chlorine unite with each other in a volume ratio of one to one, but the volume of the hydrogen chloride formed is equal to double that of either the hydrogen or the chlorine. Two volumes of hydrogen unite with one volume of oxygen to form two volumes of gaseous water. One volume of nitrogen unites with three volumes of hydrogen to form two volumes of ammonia. One volume of oxygen reacting with an excess of solid carbon yields two volumes of carbon monoxide. On the basis of observations such as these, Gay-Lussac, in 1808, advanced the generalization known as the **Law of Combining Volumes of Gases: The volumes of gases taking part in chemical reactions, either as reactants or as products, bear a simple ratio to each other if the measure-**

ments are made under the same conditions of temperature and pressure.

According to the atomic theory, there is a simple ratio between the numbers of atoms of the elements involved in a chemical reaction. It seems, therefore, that there should be a simple relation between the number of atoms in equal volumes of different gaseous substances under the same conditions of temperature and pressure. The supposition, at one time favored by Dalton, that equal volumes of gases contain the same number of atoms under the same conditions, appeared to lead to contradictory conclusions. In the reaction of hydrogen with chlorine, one volume of hydrogen is observed to combine with an equal volume of chlorine to produce a volume of hydrogen chloride that is twice as great. According to the supposition just made, this would mean that one atom of hydrogen unites with one atom of chlorine to produce two compound atoms of hydrogen chloride, in terms of Dalton's theory. Since each ultimate particle of the compound contains some hydrogen and some chlorine, this conclusion would require the division of the hydrogen and chlorine atoms. This conclusion is contradictory to the postulate of the atomic theory that atoms are the ultimate chemical units of the elements. Consequently the assumption that equal volumes of gases contain the same number of atoms under the same conditions was considered untenable.

Avogadro's Hypothesis. In 1811, Avogadro advanced the assumption, which seems from the discussion of the preceding paragraph to be demanded, that the physical unit of gases may contain more than one atom. ***The smallest particle which can exist separated from other like particles, as in the gaseous state or in solution, is called a molecule, the physical unit of a substance.*** Molecules of elementary substances may contain one atom or more than one atom, but the atoms are alike. Molecules of compounds contain atoms of two or more different varieties. The supposition which explains Gay-Lussac's law in terms of the atomic theory now follows as **Avogadro's Hypothesis: Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.** The reaction of hydrogen with chlorine may now be interpreted. Since one volume of hydrogen combines with one volume of

chlorine to form two volumes of hydrogen chloride, two molecules of hydrogen chloride are formed from one molecule each of hydrogen and chlorine. Each molecule of hydrogen chloride contains both hydrogen and chlorine. Hence, it is necessary to conclude that the molecules of hydrogen and chlorine are each divisible into two identical parts. Each of these molecules is considered to be diatomic, since no evidence exists to indicate the presence of more than two atoms per molecule. The atoms become associated to form molecules of the compound during chemical reaction. Similar reasoning based on the reaction of hydrogen with oxygen leads to the conclusion that the oxygen molecule is diatomic and that the molecule of water contains twice as many atoms of hydrogen as of oxygen.

Atomic Weights. The unit which is used as the basis for expressing the weights of atoms is equal to one sixteenth of the average weight of the oxygen atoms. Other units have been used in the past; but the oxygen basis has been generally accepted since 1905. The selection of oxygen as the standard atom and the assignment of the number 16 to represent its weight is a matter of convenience. On this basis all atomic weights are greater than one, and the values of the atomic weights of all of the elements are more nearly integral numbers than on any other standard. ***The atomic weight of an element is the average weight of the atoms of that element measured in units, each equal to one sixteenth of the average weight of oxygen atoms.*** The atomic weights of elements show the relative weights of their atoms. The atomic weight of chlorine is 35.46, *i.e.*, the ratio of the weights of chlorine and oxygen atoms is 35.46 to 16.

The atomic weights of the elements, shown in the Table of Atomic Weights printed on the inside front cover of this book, are determined by experiment. We have seen that the equivalent weights of elements depend on the weights of the atoms and the numerical ratio in which they combine with the element chosen as the basis of the system. The weight ratio in which hydrogen and oxygen combine is 1.008 parts by weight of hydrogen to 8 of oxygen. The atomic ratio is two atoms of hydrogen to one of oxygen. Therefore, it is necessary to conclude that the number of atoms in 1.008 parts by weight of hydrogen is twice the number of atoms in 8 parts by weight of oxygen. The ratio of the weights

of the individual atoms of these two elements is thus shown to be 1.008 for hydrogen to 16 for oxygen. The atomic weight of each element is an integral multiple of its equivalent weight.

Molecular Weights. Since molecules are composed of atoms, the weight of a molecule is equal to the sum of the weights of the atoms in it. Therefore, molecular weights are expressed in the same units as atomic weights. ***The molecular weight of a substance is equal to the weight of one molecule of that substance measured in atomic weight units.*** The molecular weight of a substance expresses the ratio of the weight of a molecule of the substance to the weight of an atom of oxygen taken as 16.

An equivalent weight of a compound is the weight which is chemically equal to 8 parts by weight of oxygen: *i.e.*, the weight which contains, furnishes, or combines with 8 parts by weight of oxygen, 1.008 parts by weight of hydrogen, 35.46 parts by weight of chlorine, or an equivalent weight of some other element. The equivalent weight of a compound is determined by the variety of the chemical reactions into which it enters, as well as by its composition. Since molecular weights are based on the oxygen standard, the molecular weight of a compound is an integral multiple of its equivalent weight. Molecular weights are determined experimentally by devising methods of weighing the same number of molecules of different substances and reducing these weights to the standard basis.

The Gram Atom and the Mole. In even the smallest weight of substances commonly employed in chemical experiments, there are millions of atoms and molecules. The weights of materials involved in chemical reactions are proportional to the weights of the atoms and molecules themselves, or to some multiple of these weights. It is usually convenient to express the reacting weights of substances in ordinary units of weight. One gram of each of two elements contains different numbers of atoms; but the weights of two different elements which are proportional to the weights of the individual atoms contain the same number of atoms. Similarly, weights of two substances which are proportional to their molecular weights contain the same number of molecules. The units of weight commonly used in chemical calculations are the gram atom and the mole. ***The weight in grams which is numerically equal to the atomic weight is known as the***

gram atom; and the weight in grams which is numerically equal to the molecular weight is the mole. The atomic weight of oxygen is 16 and one gram atom is 16 g. Similarly, the molecular weight of oxygen is 32 and one mole is 32 g. The actual number of atoms in one gram atom of any element, commonly called the Avogadro number,[1] is 6.064×10^{23}. Therefore, the gram atom of any element is equal to the weight in grams of 6.064×10^{23} atoms of that element. Similarly, the mole is equal to the weight in grams of 6.064×10^{23} molecules of the substance.

Symbols and Formulas. *Symbols* are used to represent the atoms of the elements. The symbol is often the first letter in the name of the element; but some additional letter in the name is required to distinguish many of the elements: *e.g.*, C, carbon; Ca, calcium; Cl, chlorine; Co, cobalt; Cr, chromium. Some symbols are based on Latin names: *e.g.*, Cu, cuprum, copper; Au, aurum, gold; and Ag, argentum, silver. The symbol is frequently used as an abbreviation for the name of the element; but the symbol also has quantitative significance. The symbol Cl represents the element chlorine, and signifies one atom, one atomic weight, and one gram atom of this element.

Formulas represent the molecules of substances. Formulas are written through the use of the symbols of the constituent elements, with subscripts to denote the number of atoms in one molecule, if the number is more than one. Thus, the formula of oxygen is O_2; of carbon dioxide, CO_2; and of sulfuric acid, H_2SO_4. The symbol itself is commonly employed to represent elementary solids. Each symbol retains its complete significance when written

[1] Large numbers are conveniently expressed as powers of the base 10. Thus, 3×10^4 means that 10 is raised to the fourth power, 10,000, and this number is multiplied by 3, giving 30,000. The same number may be written 30×10^3 or 0.3×10^5. The number, 6.064×10^{23} is equal to 606,400,000,000,000,000,000,000. Negative exponents are used to represent very small fractions. They represent the fraction resulting from the division of the coefficient by the number obtained when the base is raised to the power indicated. Thus, 3×10^{-5} represents $3/10 \times 10 \times 10 \times 10 \times 10$, or 3/100000, or 0.00003. The multiplication of exponential numbers consists in multiplying the coefficients and adding the exponents.

$$3 \times 10^5 \times 3 \times 10^3 = 9 \times 10^8$$
$$2 \times 10^{-6} \times 2 \times 10^{-8} = 4 \times 10^{-14}.$$

In division, the coefficients are divided and the exponents subtracted.

$$9 \times 10^{10} \div 3 \times 10^2 = 3 \times 10^8$$
$$8 \times 10^{-10} \div 4 \times 10^{-3} = 2 \times 10^{-7}.$$

For addition and subtraction, the numbers must be converted to the same power of the base. The coefficients are then added or subtracted in the usual manner. This is equivalent to "lining up the decimal point."

$$3.4 \times 10^5 + 2\,6 \times 10^4 =$$
$$3.4 \times 10^5 + 0\,26 \times 10^5 = 3.66 \times 10^5.$$

in a formula, and formulas show the composition of substances. The formula H_2SO_4 represents one molecule, one molecular weight, and one mole of the substance, sulfuric acid. It expresses the fact that a molecule of this substance contains two atoms of hydrogen, one of sulfur, and four of oxygen. It represents 98.076 units by weight of sulfuric acid, and shows that 98.076 g. of this substance contain 2.016 g. of hydrogen, 32.06 g. of sulfur, and 64 g. of oxygen. Even though the molecule may not exist as a physical particle, as in many crystalline salts, it is customary to use the formula to show the composition of the substance. The formula NaCl shows that one mole, 58.46 g., of common salt contains one gram atom, 35.46 g., of chlorine and one gram atom, 23 g., of sodium, even though crystalline salt is not characterized by molecular constitution.

Percentage Composition from the Formula. The per cent of each of the elements in the compound may be calculated from the formula and atomic weights. The per cents of hydrogen, sulfur, and oxygen in sulfuric acid are, respectively:

$$\frac{2.016}{98.076} \times 100 = 2.05\,\% \text{ of hydrogen}$$

$$\frac{32.06}{98.076} \times 100 = 32.70\,\% \text{ of sulfur}$$

$$\frac{64.0}{98.076} \times 100 = 65.25\,\% \text{ of oxygen.}$$

Derivation of the Formula from the Percentage Composition. The composition of a compound may be determined by analysis and may be expressed as the ratio of the weights of the constituent elements. This ratio is often stated in per cents but it may also be shown in an atomic ratio, that is, in a formula. To derive the formula, the composition of the substance must be determined and the atomic weights of the elements must be available in the Table of Atomic Weights. From the data, the ratio of the gram atoms of the elements in the compound is calculated. This ratio is then reduced to the simplest integral ratio. An example will serve to illustrate the calculations. It is found by experiment that 10 g. of a certain compound contain 2.91 g. of sodium, 4.05 g. of sulfur, and 3.04 g. of oxygen. First,

the number of gram atoms of each element in the specified weight of that element is calculated.

2.91 g. ÷ 23 g. = 0.126 gram atom of sodium
4.05 g. ÷ 32 g. = 0.126 gram atom of sulfur
3.04 g. ÷ 16 g. = 0.19 gram atom of oxygen

These numbers of gram atoms which are combined with each other in 10 g. of the compound are then reduced to the simplest integral ratio.

Na	S	O
0.126 | 0.126	0.126 | 0.126	0.126 | 0.19
1	1	1.5

The simplest integral ratio is 2 : 2 : 3, and the simplest formula is $Na_2S_2O_3$. The simplest formula in agreement with the analytical data is the *empirical formula*. Any multiple of this formula, such as $Na_4S_4O_6$, would agree with the per cents of the elements in the compound. In order to establish the true molecular formula, it is necessary to determine by experiment the molecular weight of the substance. If the molecular weight of this substance is found to be approximately 158, then the formula $Na_2S_2O_3$ is established, because multiples of the formula require multiples of the weight corresponding to the empirical formula.

Valence. Deriving formulas by the procedure outlined in the preceding paragraph is a tedious task; but, after determining a number of formulas in this way, it is possible to deduce an important principle which serves as an aid in writing correct formulas. It will be noticed from such a list of formulas that the numerical ratios of the atoms in the molecules of different compounds vary. It will also be observed, as might be expected from the system of equivalent weights, that one or more definite capacities for holding other elements in combination is characteristic of the atoms of all of the elements. This capacity, known as the *valence*, seems to be inherent in the atom, so that a specified element shows the same valence whether it be in combination with any one of a number of different elements. Since none of the atoms shows a lower capacity for holding others in combination than the hydrogen atom, the basis of the valence system is the hydrogen atom. ***The valence of an element is a number showing the combining capacity of its atoms measured in terms of hydrogen atoms.*** If an

element forms no hydrogen compounds and does not displace hydrogen, its valence may be determined indirectly by finding the combining ratio of its atoms with those of some other element whose valence is known. Since valence is a measure of the combining ratio exhibited by an atom, an elementary substance is considered to be in a zero valence state.

Elements, such as sodium, hydrogen, and chlorine, which exhibit a valence of one are *monovalent.* Those having a valence of two are *divalent, e.g.,* oxygen, magnesium, and calcium. The elements having a valence of three are *trivalent* and those having a valence of four are *tetravalent.* There are many instances in which an element may have more than one valence. There are a number of compounds which contain groups of atoms capable of acting as units in a series of chemical reactions. Such groups of elements are *compound radicals* and a valence is assigned to the group as a whole on the same basis as to individual atoms in binary compounds. Thus, the sulfate radical (SO_4) is a divalent radical and its hydrogen compound has the formula H_2SO_4.

The valences of some of the elements are considered to be positive while others are considered to be negative. Definite experimental evidence supports this practice in many instances. The basis for ascribing positive or negative character to the valences is discussed in Chapter VI. There are also many instances in which the distinction between positive and negative nature of the valences is more or less arbitrary. Nevertheless, it is convenient to employ the idea in all instances, particularly in those reactions in which radicals are formed or decomposed and in which the valences of simple radicals change. ***The term oxidation number will be used to designate not only valence in the sense already discussed, but also the arbitrary number assigned to each element in its complex radicals.*** The sulfate radical as a group has an oxidation number of 2 −. This number is not assigned to the oxygen or to the sulfur, but to the group as a unit. Each oxygen atom in all of its familiar radicals with few exceptions is arbitrarily assigned an oxidation number of 2 −. This number is taken as a basis of reference in calculating other oxidation numbers. The sum of the oxidation numbers of the four atoms of oxygen in the radical is 8 −. But the entire radical has an oxidation number of only 2 −. Hence, it is necessary to

assign the sulfur atom in the radical an oxidation number of 6 + so that the sum of the oxidation numbers of all of the atoms in the radical may be equal to the oxidation number of the radical, 2 −. The oxidation numbers of several of the common elements and radicals are shown in Tables III and IV in the Appendix.

The equivalent weight of an element expresses the weight ratio in which it reacts with an arbitrarily set standard; and the oxidation number, the number of atoms of a standard its atom holds in combination or may replace in compounds. It is necessary, therefore, that there be a simple relation between the atomic weight, equivalent weight, and oxidation number of an element. The equivalent weight of any element is the weight equivalent to one oxidation number unit and is equal to the atomic weight divided by the oxidation number.

Formula Writing. The formulas of compounds show the relative numbers of the atoms of the constituent elements. In writing formulas, the numbers of atoms of the different elements represented by subscripts must be such that the algebraic sum of the oxidation numbers is equal to zero. If two elements which combine with each other have the same oxidation numbers, but one is positive and the other negative, they combine in the atomic ratio, 1 : 1. Thus, the oxidation number of hydrogen is 1 + and of chlorine 1 −, so that the formula of hydrogen chloride is HCl. Similarly, zinc has an oxidation number of 2 + and sulfur in the sulfides a number of 2 −, and the formula of zinc sulfide is ZnS. If the combining elements have different oxidation numbers, the correct ratio is obtained through the use of the lowest common multiple of the two numbers. The oxidation number of aluminum is 3 + and of oxygen 2 −. The lowest common multiple of these two numbers is 6. Two atoms of aluminum are required to give a total of 6 + units, and three atoms of oxygen for a total of 6 −. The formula of the oxide of aluminum is, consequently, Al_2O_3. The oxidation numbers of compound radicals are used in the same manner as those of atoms or simple radicals. The oxidation number of the sulfate radical (SO_4) is 2 −. The formulas of sulfuric acid, zinc sulfate, and aluminum sulfate are, respectively, H_2SO_4, $ZnSO_4$, and $Al_2(SO_4)_3$.

In order to write correct formulas, it is necessary to know which elements are present in a given substance and the oxidation

numbers which these elements exhibit in this compound. Since formulas represent the actual composition of substances, formulas purporting to represent substances which do not exist are meaningless even though the valence relationships are properly observed.

EXERCISES

1. What differences distinguish physical changes and chemical changes?
2. State the important assumptions of Dalton's atomic theory and show how two of its assumptions have been modified.
3. Show how the assumptions of this theory account for the facts stated in each of the laws of chemical combination.
4. What is the basis for Avogadro's hypothesis concerning the numbers of molecules in gas volumes?
5. Cite the argument to show that the molecule of nitrogen contains at least two atoms. What is the reason for believing that the nitrogen molecule contains only two atoms?
6. What is meant by the equivalent weight, the atomic weight, the molecular weight? What is the relation between these weights?
7. Calculate the equivalent weight of each of the elements in combination with oxygen in the following compounds:

(*a*) Calcium oxide	Ca	71.43%	O	28.57%
(*b*) Carbon dioxide	C	27.27%	O	72.73%
(*c*) Sulfur dioxide	S	50.00%	O	50.00%
(*d*) Zinc oxide	Zn	80.34%	O	19.66%
(*e*) Phosphorus pentoxide	P	43.68%	O	56.32%

8. Iron yields two simple oxides, formed under different experimental conditions. Ferrous oxide contains 77.73% of iron; and ferric oxide, 69.94% of iron. Calculate the equivalent weight of iron in each of these oxides. What is the ratio between these two equivalent weights of iron? What law does this illustrate?
9. Calculate the simplest formula corresponding to the analytical data given for each of the compounds in question 7.
10. What is meant by the term "valence"? Learn the valences of the atoms and radicals shown in Tables III and IV in the Appendix.

SUPPLEMENTARY READINGS

Dampier-Whetham, *A History of Science*, Chapter IV.
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CHAPTER III

STATES OF MATTER. THE KINETIC THEORY

The fact that matter exists in the solid, liquid, and gaseous states is well known from common observation. The state of matter in which a substance is found at ordinary temperatures and pressures is characteristic of the substance, so that most substances are commonly observed in only one state. The transformation of a substance from one state to another takes place under definite conditions of temperature and pressure. The temperature at which two forms of a substance, either in the same state or in different states, may exist together in equilibrium under specified conditions of pressure, usually one atmosphere, is called the *transition temperature*. The description of the *transition point* for any particular change requires the statement of both the temperature and pressure under which the two forms may remain in equilibrium. The transition temperatures for water under a pressure of one atmosphere are close enough to ordinary temperatures so that the transitions from one state to another are brought about easily and are of great importance. Oxygen, hydrogen, and nitrogen were long considered to be "permanent gases" because no one had been able to liquefy or freeze them. Hydrogen was first liquefied by Dewar in 1898 and helium by Onnes in 1908. The transition temperatures for these substances are so low that they are commonly observed only in the gaseous state. The transition of the metal tungsten from the solid to the liquid state occurs at such a high temperature that the solid is the familiar form of this element. Three states of matter are common for most substances, although great changes in temperature and pressure may be necessary to bring about the transitions in a number of instances. There are, however, some substances which decompose before the necessary conditions are reached so that only one or two of the states of matter may be possible for them. The physical properties of substances in different states differ

greatly, and different substances in the same state have certain properties in common. This is especially noticeable for matter in the gaseous state, so that the properties of gases will be discussed first.

THE GASEOUS STATE

A gas has no definite volume or shape but expands to fill completely and uniformly a closed vessel in which it is placed. Gases may be mixed in any proportions to produce a homogeneous mixture, if no chemical reaction occurs. The gases in a mixture show no tendency to separate, even though their densities may differ greatly. Matter in the gaseous state is characterized by low density, high compressibility, great expansibility, and rapid diffusion.

FIG. 3

Gas Pressures. Gases exert the same force on each unit of the area of the walls of the vessel in which they are inclosed. The pressure depends on the concentration of the gas in the vessel and on the temperature. The pressure of the atmosphere may be measured by the use of a barometer, Fig. 3. The average pressure of the atmosphere at sea level is equivalent approximately to that of a column of mercury 760 mm. in height, or a weight of 1033 g. per square centimeter; and this pressure is chosen as a unit and called a pressure of *one atmosphere*. Atmospheric pressure varies from day to day and from place to place on the surface of the earth, so that a pressure equal to one atmosphere is an arbitrarily selected unit.

The Gas Laws. Some of the properties of gases are entirely independent of their composition and are subject to quantitative description. The gas laws describe the relation to one another of the temperature, pressure, and volume of a specific quantity of a gas. The generalizations do not hold strictly for any known gas under great changes in temperature and pressure, but they are sufficiently accurate for practical use when the changes are not great.

The Relation of the Volume to the Pressure of a Gas. Since gases are highly compressible, the volume of a given weight

of a gas depends on the pressure. It is found that doubling the pressure applied to a gas sample reduces the volume to one half, if there is no change in the temperature, Fig. 4; and that reducing the pressure to one half causes the volume to become doubled. In 1662, Robert Boyle published the results of his experiments dealing with the relation between the volume and pressure of a gas sample. These results are summarized in the generalization known as **Boyle's Law: At constant temperature, the volume of a given mass of a gas varies inversely with the pressure.** The law is stated mathematically in the expression,

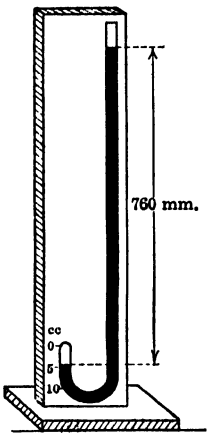


FIG. 4

$$V \propto \frac{1}{P} \text{ (constant temperature).}$$

This relation is shown graphically by the curve in Fig. 5, in which V represents the volume in liters and P the pressure in atmospheres.

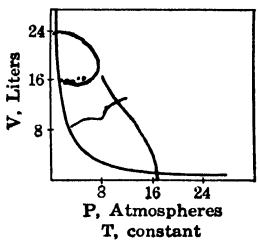


FIG. 5

The Relation of the Volume to the Temperature of a Gas. Gases expand when they are heated, thus becoming less dense. Careful measurements show that the change in the volume of any gas sample is equal to 1/273 of its volume at 0° for each degree change in temperature,[1] if constant pressure is maintained. Should this uniform change in volume continue during the cooling of a gas to very low temperatures, the gas sample would have no volume at − 273°, because its contraction in volume would be equal to 273/273 of its volume. This relation for four different gas samples is shown graphically in Fig. 6. It is observed that the curves all appear to intersect at − 273°. This point represents *the absolute zero of temperature*, − 273.18° (the exact value), at which a sample of a gas would theoreti-

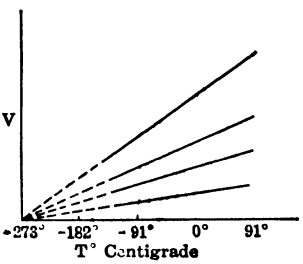


FIG. 6

[1] The temperature scale employed throughout this book is the *centigrade* scale, unless otherwise stated.

cally have no volume. Since all known gases liquefy at temperatures above − 273° (in round numbers), no physical significance can be attached to the zero volume of a gas. Temperatures on the centigrade scale are converted to the absolute scale, designated by A or by K for Lord Kelvin. The relation of the two scales is shown in Fig. 7. The variation of the volume of a gas with changes in temperature was measured independently, in 1801, by Charles and by Gay-Lussac. Hence, the generalization describing this relation is known as **Charles' Law and as Gay-Lussac's Law: At constant pressure, the volume of a given mass of a gas varies directly with the absolute temperature.** Mathematically, this relation is

$$V \propto T \text{ (constant pressure).}$$

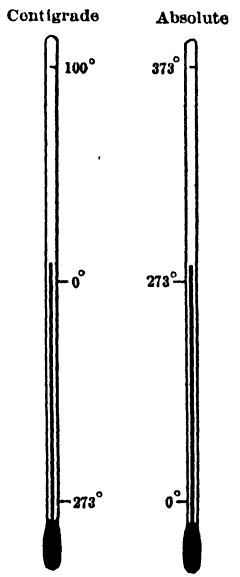


FIG. 7

The curve in Fig. 8 shows the variation in the volume of a gas with changes in the absolute temperature.

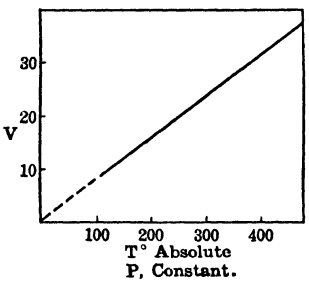


FIG. 8

The Relation of the Pressure to the Temperature of a Gas. The effect of changes in temperature upon the pressure exerted by a gas may be derived from a consideration of the laws of Boyle and Charles. Suppose that a gas sample is inclosed in a cylinder with a movable piston and that a constant pressure of one atmosphere is applied to the piston, Fig. 9. If the temperature is raised from 0° to 273°, the piston will move to permit the expansion of the gas to double its former volume, according to Charles' law. In order now to force the gas back into its former volume while holding the temperature constant, it is found necessary to double the pressure on the piston, according to Boyle's law. **At constant volume, the pressure exerted by a given mass of a gas varies directly with the absolute temperature.**

The General Gas Law. From the gas laws discussed separately above, it is possible to derive a general equation relating the weight and volume of a gas to the temperature and pressure.

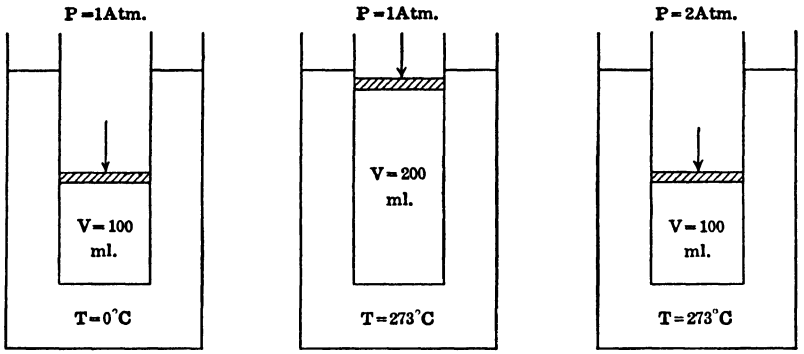


FIG. 9

If the mathematical expressions which show the relations stated in Boyle's and Charles' laws are combined, the following expression is obtained:

$$V \propto \frac{T}{P}.$$

Introducing a proportionality factor,

$$V = K\frac{T}{P},$$

or

$$PV = KT.$$

If this equation is applied specifically to one mole of a gas, the molar gas constant, R, may be substituted for the proportionality factor, K,

$$PV = RT.$$

The factor, n, representing the number of moles of the gas, is now introduced, so as to increase the generality of the equation.

$$PV = nRT.$$

The numerical value of the molar gas constant may be calculated from experimental data. One mole of any gas is found to occupy 23.414 liters at 0°, 273.1° A., and a pressure of one atmosphere. If these numbers are substituted in the equation,

$$R = \frac{PV}{nT} = \frac{1 \text{ atmosphere}}{1 \text{ mole}} \times \frac{22.414 \text{ liters}}{273.1^\circ}$$

$$= 0.08207 \text{ liter-atmosphere per mole per degree.}$$

In the application of this equation in solving problems dealing with weights and volumes of substances in the gaseous state, it must be observed that the weight is expressed in moles, the volume in liters, the pressure in atmospheres, and the temperature on the absolute scale. As an example to illustrate the application of the equation, the calculation of the volume occupied at 20° and 740 mm. by 10 g. of oxygen is shown. The weight of the oxygen is 10/32 of one mole; the pressure is 740/760 of one atmosphere; the temperature 293°; and the volume will be found in liters.

$$V = \frac{nRT}{P} = \frac{10/32 \times 0.08207 \times 293}{740/760} = 7.717 \text{ liters.}$$

Partial Pressures of Gases in a Mixture. It may be shown by experiment that the gas laws describe the changes in volume with changes in temperature and pressure for gas mixtures also. In 1801, Dalton investigated the changes taking place when gases which do not react with each other are mixed. The results of his experiments are stated in the **Law of Partial Pressures: The pressure exerted by a gas mixture is equal to the sum of the partial pressures of the components of the mixture. The partial pressure of each gas in the mixture is the pressure that it would exert if it were present alone in the containing vessel.** If 100 ml. of oxygen, measured at 760 mm., are transferred to an evacuated flask of 500 ml. capacity, the pressure in the flask is found to be 152 mm., provided that the temperature is constant. If now 100 ml. of nitrogen, also measured at 760 mm., are admitted to the same flask, the total pressure becomes 304 mm.

Slightly soluble gases are usually collected over water. When the liquid stands at the same level both inside and outside of

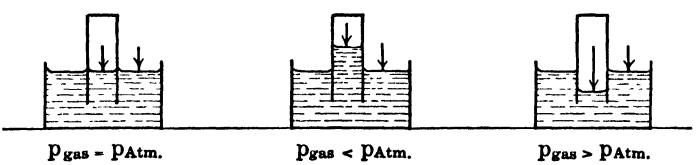


FIG. 10

the collecting tube, the total gas pressure is equal to the atmospheric pressure. This is shown diagrammatically in Fig. 10. The

gas collected in this manner is saturated with water vapor, and a portion of the pressure of the gas in the tube is due to water vapor. The pressure of saturated water vapor is definite at each temperature and increases with rise in temperature. The pressures of saturated water vapor at different temperatures are shown in Appendix II. Suppose that a sample of oxygen is collected over water at a temperature of 20° and a pressure of 760 mm. The sum of the partial pressures of water and oxygen is equal to the total pressure, Fig. 11.

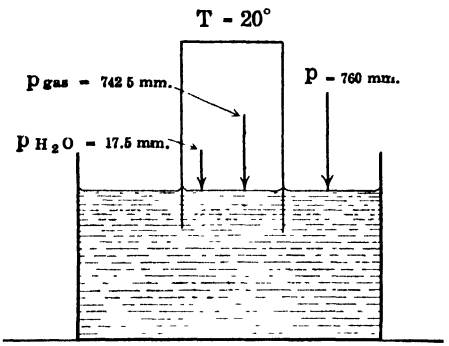


FIG. 11

$$P_{O_2} + P_{H_2O} = P = 760 \text{ mm.}$$

At 20°, the pressure of saturated water vapor is 17.5 mm. Hence,

$$P_{O_2} = 760 \text{ mm.} - 17.5 \text{ mm.} = 742.5 \text{ mm.}$$

If dry oxygen were present in this volume, the pressure would be 742.5 mm., not 760 mm.

Correction of Gas Volumes for Changes in Temperature and Pressure. Since the volume occupied by a given mass of a gas varies with changes in temperature and pressure, *standard conditions* are selected; and it is customary to state gas volumes under these conditions. The standard conditions are a pressure of 760 mm., one atmosphere, and a temperature of 0°, 273° A. The actual measurements may be made under other conditions, and the volumes corrected to standard conditions by calculations based on the application of the gas laws. The volume under standard conditions is equal to the measured volume multiplied by two conversion fractions, one for the temperature change and the other for the pressure change. These fractions are arranged according to Boyle's and Charles' laws with the larger number in the numerator if the change gives a larger volume, and the smaller in the numerator if the change gives a smaller volume. Suppose that the volume of a gas sample is 150 ml. at 20° and 752 mm. The

volume, V, which it would occupy at standard conditions, is calculated in the following manner:

$$V = 150 \times \frac{752}{760} \times \frac{273}{293} = 138.1 \text{ ml.}$$

If, however, the gas is collected over water, the partial pressure of the gas, rather than the total gas pressure in the container, must be used in making the correction.

Partial pressure of the gas $= 752 - 17.5 = 734.5$ mm.

$$V = 150 \times \frac{734.5}{760} \times \frac{273}{293} = 135 \text{ ml.}$$

As an additional example, the calculation may be made of the volume of a gas saturated with water vapor at some temperature and pressure other than standard conditions. Suppose that the volume of a given quantity of a dry gas under standard conditions is 200 ml., and that the volume which it would occupy when collected over water at 20° and 757.5 mm. is to be calculated.

Partial pressure of the gas $= 757.5 - 17.5 = 740$ mm.

$$V = 200 \times \frac{760}{740} \times \frac{293}{273} = 229 \text{ ml.}$$

The Diffusion of Gases. Two gases which are introduced into the same container diffuse rapidly so that a uniform mixture of the two soon occupies the whole vessel. The uniform dispersion of the gases occurs even though one of the gases may be much more dense than the other. Some gases, however, diffuse much more rapidly than others. In 1832, Graham measured the relative rates of diffusion of a number of gases and found: **The rates of diffusion of gases at the same temperature vary inversely as the square roots of their densities.** Density is defined as the mass per unit volume; but the weight of one milliliter of a gas is so small that the weight of one liter is commonly called the density of the gas. The densities of oxygen and hydrogen are in the ratio of sixteen to one and the rates of diffusion in the ratio of one to four.

The Kinetic Theory of Gases. The uniform behavior of gases subjected to changes in temperature and pressure indicates that all gases have similar structure. The theory of gas structure

to account for the observed behavior on a mechanical basis was first proposed by Bernoulli in 1738. It has been supplemented by additional experimental data and has been verified beyond reasonable doubt. The fundamental assumptions of this theory, *the Kinetic Theory of Gases*, may be stated in the following form:

Gases are composed of separate particles, molecules. Relative to their sizes, these molecules are very far apart.

The molecules of gases are in rapid motion, colliding with each other and with the walls of the containing vessel.

The molecules of gases are perfectly elastic, and no loss of kinetic energy results from molecular collisions.

The molecules of gases exert no appreciable attraction for one another at ordinary pressures.

The motion of the gas molecules is a manifestation of heat energy. The average kinetic energy of the molecules of a gas is proportional to the absolute temperature.

The great compressibility of gases indicates a porous structure in which the molecules themselves occupy an inappreciable part of the total volume of the gas. The compression of a gas simply involves crowding the molecules somewhat more closely together. *The pressure exerted by gases* is due to the impacts of the moving molecules on the walls of the containing vessel. The fact that the pressure of an inclosed gas does not diminish on long standing shows that the molecules rebound from each collision with other molecules and with the walls of the vessel with undiminished kinetic energy.

The average distance through which a molecule moves between collisions is called its *mean free path.* This distance averages about one thousand times its own diameter, when the pressure is approximately equal to ordinary atmospheric pressure. Because of the rapidity with which gas molecules move and the relatively large amount of free space between the molecules, gases *diffuse* rapidly into each other to produce uniform mixtures. The great *expansibility* of gases is explained by the fact that the molecules are in rapid motion and the kinetic energy of the molecules is so great that the forces of molecular attraction are relatively insignificant.

The Gas Laws Interpreted by the Kinetic Theory. Since pressure depends on the impacts of the moving molecules on the

walls of the containing vessel, an increase in pressure causes the molecules to be crowded closer together, Fig. 12. Consequently, there are a greater number in unit space. Doubling the number of molecules in unit volume doubles the number of impacts in unit time upon unit area of the walls of the container. In this way, the pressure is doubled as described by Boyle's law. Due to the fact that the molecules of gases actually do have some volume and exert some forces of attraction, particularly when the pressures are high, Boyle's law does not describe the behavior of gases in an exact manner.

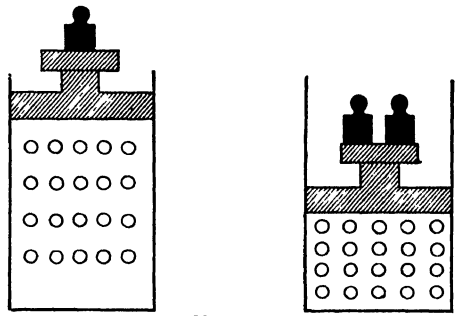


FIG. 12

In gas mixtures the molecules of the gases do not appreciably affect each other, unless a chemical reaction takes place. The average kinetic energy of the molecules of different gases is the same at the same temperature. Hence, the pressure of a gas at fixed temperature depends on the total number of molecules present, and the partial pressure of each gas depends on the fraction of the total number of molecules which its molecules represent. Thus, Dalton's law of partial pressures is satisfactorily interpreted.

Gas pressure is due to the kinetic energy of the molecules. The kinetic energy of a body of mass, m, and velocity, u, is represented by the expression $\frac{1}{2}\ mu^2$. Changes in temperature alter the kinetic energy of the molecules by changing the velocity at which they move. If the temperature is raised, the molecules of the gas not only strike the walls more frequently, but the force of each impact is greater. The absolute zero of temperature indicates cessation of molecular motion. The kinetic energy of gas molecules is proportional to the absolute temperature. Hence, according to Charles' law, the volume of a gas at constant pressure is directly proportional to the absolute temperature.

At the same temperature and pressure, the light molecules of a gas of low density have the same average kinetic energy as the heavy molecules of a gas of high density. Hence, it is clear that the lighter molecules travel with the greater velocity. From a

study of kinetic relations, the fact may be derived that the velocities of the molecules of two different gases at the same temperature vary inversely as the square roots of their densities. The relative rates of diffusion depend on the relative velocities at which the molecules of different gases move. The velocity of the hydrogen molecule at 0° is 1.84 kilometers, approximately 1.15 miles, per second; and the velocity of the oxygen molecule is about 0.46 kilometer per second. For comparison, the velocity of sound at 0° is 0.331 kilometer per second; and the earth's orbital velocity, about 29.8 kilometers per second.

The Kinetic Equation and the Gas Laws. It has been shown in the preceding paragraph that deductions drawn from the kinetic theory are qualitatively in accord with the gas laws, and thus the basis for the confirmation of the assumptions of the theory is indicated.

Quantitative deductions from the kinetic theory are based on the fundamental kinetic equation. Let us imagine that a cubical vessel, Fig. 13, of such size that the length of an edge is l cm., contains n molecules of a gas each having the mass m. According to the kinetic theory, the volumes of the molecules are insignificant compared to the distances between them, the molecules exert negligible attraction for each other, and the molecules rebound from all collisions without loss of kinetic energy. At a fixed temperature, the average kinetic energy of all of the molecules in the sample is the same, although all of the molecules do not have exactly the same kinetic energy. The average velocity of all of the molecules may be represented by u. The motion of the individual molecules is quite irregular. At a given instant, some of the molecules are moving in one direction and some in another. They strike the sides of the vessel at all angles. It may be supposed, however, that the average effect is the same as though one third of the molecules were always moving in a direction perpendicular to a particular wall of the cubical vessel. This is equivalent to resolving the direction of the motion of each molecule into its three rectangular components.

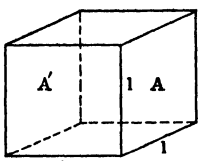


FIG. 13

Let us consider only the collisions of the molecules which strike the face, A. Each molecule moving back and forth between A

and A' will travel $2\,l$ cm. between successive collisions with A. Since the velocity of the molecule is u, the number of collisions with A per second is $u/2\,l$. The momentum of the molecule is defined as the product of the mass and the velocity and is equal to mu. At each impact of the molecule with A, the velocity of the molecule changes from $+\,u$ to $-\,u$, so that the change in momentum is $2\,mu$. There are $u/2\,l$ collisions per second. Hence, each molecule undergoes a change in momentum per second equal to mu^2/l. The total change in momentum per second at the surface of A is equal to $n/3 \cdot mu^2/l$. This represents the force, F, exerted on the face, A, by all of the molecules striking it in one second. The pressure, P, is equal to the force per unit area.

$$P = \frac{F}{l^2} = \frac{1}{l^2} \cdot \frac{n}{3} \cdot \frac{mu^2}{l} = \frac{n}{3} \cdot \frac{mu^2}{l^3}.$$

The volume of the vessel is l^3. Hence,

$$P = \frac{n}{3} \cdot \frac{mu^2}{V},$$

or

$$PV = \tfrac{1}{3}\, nmu^2.$$

Although this fundamental equation of the kinetic theory has been derived for a cubical vessel, it holds for any vessel. The equation would apply rigidly only to gases in which there is no attraction between the molecules; but it is applicable as a close approximation to actual gases at ordinary pressures. The kinetic energy of each molecule is equal to $\frac{1}{2}\, mu^2$; and the total kinetic energy of all n molecules in a gas sample is equal to $\frac{1}{2}\, nmu^2$. At fixed temperature, the total kinetic energy of the molecules in a gas sample is constant. Therefore, the product PV is equal to a constant. Since this is *Boyle's law*, it is clear that the deduction from the kinetic theory is in strict accord with the behavior of the gas.

The average kinetic energies of the molecules of all gases are identical at the same temperature. The change in the kinetic energies of the gas molecules is directly proportional to changes in the absolute temperature. The fundamental kinetic equation may be written in the form

$$PV = \tfrac{2}{3} \cdot \tfrac{1}{2}\, nmu^2.$$

That is, the product of the pressure and volume of a given mass of a gas is proportional to the total kinetic energy of its molecules. A change in the temperature causes the same change in this product for any gas. If the volume is constant, the pressure changes; and if the pressure is constant, the volume changes. This deduction is identical with *Charles' law.*

Confirmation of Avogadro's hypothesis may be obtained from the kinetic equation. If equal volumes of two gases are taken under the same pressure,

$$PV = \tfrac{1}{3}\, n_1 m_1 u_1^2 = \tfrac{1}{3}\, n_2 m_2 u_2^2.$$

In these equations, the subscripts are used to signify the two gases. If the two gases are also at the same temperature, the average kinetic energy of a molecule in one gas is equal to the average kinetic energy of a molecule in the other, or

$$\tfrac{1}{2}\, m_1 u_1^2 = \tfrac{1}{2}\, m_2 u_2^2.$$

If the first of these equations is divided by the second, it follows that

$$n_1 = n_2.$$

That is, under the same conditions of temperature and pressure, equal volumes of different gases contain the same number of molecules.

Deviations from the Gas Laws. *An ideal or perfect gas* would be a gas for which the pressure and volume relations are in strict accord with the gas laws. Exact measurements show that none of the actual gases conform exactly to these laws. According to Boyle's law, the product of the pressure and volume of a given mass of a gas should be constant at fixed temperature. With increasing pressure, the product for most gases first decreases, passes through a minimum, and then increases, as shown by the curves for carbon dioxide and oxygen in Fig. 14. The compressibility of gases is usually greater than accounted for by the gas laws up to some specific pressure and then becomes less as higher pressures are reached. This fact indicates two causes of deviation from the gas laws. One of these is usually more significant at the lower pressures; and the other, opposite in effect, at higher pressures. Under very low pressures, gases are very dilute forms of matter, the molecules are far apart, and the forces of attraction are slight. When the molecules are crowded closer together,

the attractive forces of the molecules for each other become increasingly significant and lead to a greater contraction in the volume than accounted for by Boyle's law. This effect is greater for gases which are easily liquefied than for those which are not. The forces of attraction of the helium and hydrogen molecules are so slight at 0° that no added contraction with increased pressure is observed.

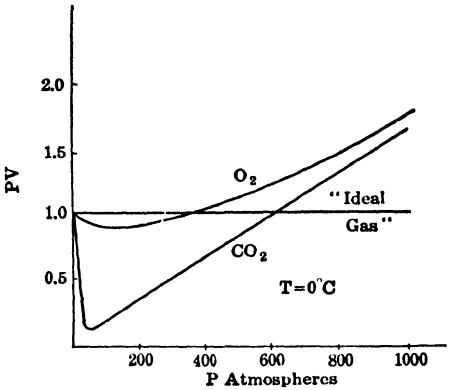


FIG. 14. — Deviations from Boyle's Law.

A second deviation from the gas laws is due to the volume of the molecules themselves. At low pressures, this volume of the molecules is insignificantly small relative to the entire volume of the gas. But, as the pressure increases and the molecules are crowded closer and closer together, their own volumes become an increasingly great fraction of the total volume. Hence, the deviation due to the volume of the molecules is more significant at higher pressures and for gases which exhibit extremely slight molecular attraction.

In 1879, van der Waals proposed the introduction of factors to take these two effects into account quantitatively. The attraction of the molecules increases the effect of pressure and this effect varies inversely with the square of the volume. Hence, the factor a/V^2, in which a is the constant of molecular attraction, is added to the pressure. Budde had previously introduced a correction, b, to represent the volume of the molecules. Using these factors, the general gas law equation takes the form known as van der Waals' equation:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

The factors, a and b, are empirical constants which differ in magnitude for different gases. In its modified form, the equation represents the behavior of actual gases in a more nearly accurate manner.

The Molar Volume of Gases. According to Avogadro's hypothesis, equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. Moles of all substances also contain the same number of molecules. Therefore, one mole of all gases must occupy the same volume under the same conditions of temperature and pressure. One mole of oxygen is equal to 32 g. This weight of oxygen occupies approximately, 22.41 liters at 0° and one atmosphere. *The molar volume* of a gas is 22.41 liters, the volume occupied by one mole of any gas measured under standard conditions of temperature and pressure.

The volume of any specified weight of a gas may be easily calculated. Thus, 5 g. of chlorine amount to 5/70.92 of one mole of chlorine; and the volume under standard conditions is equal to (5/70.92) × 22.41 liters, or 1.58 liters. Similarly, the weight in any volume of a pure gas may be calculated. Ten liters of chlorine at standard temperature and pressure contain (10/22.41) × 70.92 g., or 31.7 g. of chlorine. To compare the relative density of any gas with that of air, the weight of 22.4 liters of air may be calculated on the assumption that air is four-fifths nitrogen and one-fifth oxygen by volume. Hence, 22.41 liters of air contain 0.8 mole of nitrogen and 0.2 mole of oxygen and weigh 28.8 g. under standard conditions. To find the relative density of carbon dioxide and air, the weight of carbon dioxide in one mole is calculated from the atomic weights to be 44 g. Carbon dioxide is 44/28.8, or approximately 1.5, times as dense as air.

The Molecular Weights of Gases. The molecular weight of a substance is the weight of one molecule of the substance in units so chosen that the weight of the oxygen atom is 16. The experimental determination of molecular weights involves measuring the weight of one mole. The weight of one mole of any gas is found simply by determining the weight in 22.41 liters under standard conditions of temperature and pressure. It is found by experiment that 200 ml. of a gas weigh 0.52 g. under standard conditions. One mole of the gas is equal to 0.52 × 5 × 22.41 = 58.24 g.; and the molecular weight of the substance is 58.24.

The Molecular Weights of Volatile Substances. If the substance is not a gas under ordinary conditions, but can be volatilized without decomposition, the measurement of the vol-

ume of some weighed amount of the substance is made at a temperature and pressure at which it is a gas. The volume which it would occupy under standard conditions, if it were a gas, and the molecular weight are then calculated in the usual manner. It must be noted, however, that it is the apparent molecular weight of the substance in the gaseous condition which is calculated, and it is assumed that no change in the molecular state of the substance occurs during its evaporation.

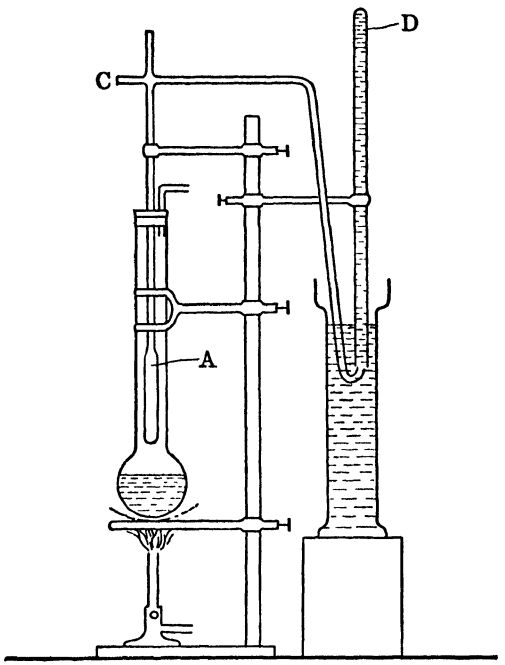


FIG. 15. — Victor Meyer Apparatus.

One of the methods of determining the molecular weight of a volatile substance is the *Victor Meyer method.* The apparatus, Fig. 15, for determining the molecular weight by this method consists of a tube *A* about one meter in length and 6 cm. in diameter, provided with a side tube to permit the collection of evolved gases. This tube is surrounded by a jacket through which steam or some other suitable vapor may be passed in order to vaporize the substance whose molecular weight is to be determined. When the apparatus has come to constant temperature, the inverted tube *D*, filled with water, is placed over the end of the delivery tube, and a small bulb which contains the accurately weighed sample of the substance is caused to drop into the apparatus from the side arm *C*. The bulb breaks when it strikes the bottom of the tube and its contents vaporize, forcing out from the delivery tube a volume of air equal to that of the vapor formed. The displaced air is measured and the temperature and pressure under which the measurements were made are noted.

To illustrate the calculation of the molecular weight from the

data, suppose that a sample of a substance weighing 0.155 g. is vaporized, and that the displaced air, collected over water, occupies 49.4 ml. at 20° and an atmospheric pressure of 757.5 mm.

Corrected pressure = 757.5 − 17.5 = 740 mm.

$$\text{Volume (0° and 760 mm.)} = 49.4 \times \frac{273}{293} \times \frac{740}{760} = 44.8 \text{ ml.}$$

44.8 ml. weigh 0.155 g.

$$\text{22.41 liters weigh 0.155 g.} \times \frac{22{,}400}{44.8} = 77.5 \text{ g.}$$

One mole of the substance is 77.5 g. and the molecular weight is found experimentally to be 77.5.

Molecular weight determinations are not usually made with a high degree of accuracy; but the results are accurate enough to establish the true formula of the substance on the basis of the analytical data, and the accurate molecular weight is obtained from the formula and the atomic weights. Suppose that the substance for which the molecular weight has just been calculated is a hydrocarbon containing 7.75% of hydrogen and 92.25% of carbon. The formula is derived in the following manner:

7.25 g. ÷ 1.008 g. = 7.69 gram atoms of hydrogen.
92.25 g. ÷ 12 g. = 7.69 gram atoms of carbon.

The atomic ratio is 1 : 1, and the empirical formula is CH. The molecular weight corresponding to this formula is 13. It is known, however, that the molecular weight of the compound is approximately 77.5. Hence, it is obvious that the true formula of the compound is $(CH)_6$, or C_6H_6, and the correct molecular weight is 78.

THE LIQUID STATE

A given mass of a liquid has a definite volume but no definite shape. Liquids may be compressed, and they expand with rise in temperature; but the changes in volume are very small compared to those observed for matter in the gaseous state. There are no general laws which describe the relation of the volume of a liquid to the temperature and pressure, for the compressibility and expansibility are specific properties of the substance. Liquids which are soluble in each other gradually diffuse to produce a solution when they are placed in separate layers in a vessel; but

the rates of diffusion are very slow. Under ordinary pressures, the density of a liquid is much greater than that of the substance in the gaseous state.

These properties indicate that the molecules are much closer together in liquids than in gases. One mole of water in the liquid state at its boiling point occupies a volume of approximately 18 ml.; but its volume in the gaseous state at the same temperature and pressure is approximately 31,000 ml. The molecules of liquids move rapidly, the rate of motion depending on the absolute temperature, but the mean free path of the molecules is small. The forces of attraction which the molecules exert upon each other are relatively great.

The liquid state is intermediate between the gaseous and solid states, and the properties of liquids show similarities to those of both gases and solids. Liquids undergo transitions into each of the other phases, and the temperatures at which these transitions occur are characteristic of the substance.

Surface Tension. The volume occupied by a given mass of a liquid is determined by the volumes of the molecules and the forces of attraction which hold them together. Beneath the surface of a liquid, a particular molecule is subject to attraction by all of the molecules around it. These forces are balanced in such a manner that the attraction is approximately equal in all directions. At the surface of the liquid, the forces of attraction are not uniform in all directions, because of the molecular discontinuity of the liquid phase. Consequently, the surface molecules are subject to a force which pulls them inward toward the center of the liquid, thus decreasing the number of molecules in the surface and causing a contraction in the surface area. Since a liquid surface contracts spontaneously until it has become as small as possible for the volume of the liquid, work must be done in order to extend the surface. A mathematical device is commonly used to simplify calculations relating to the equilibrium of surfaces. This device consists in substituting for the surface energy a hypothetical tension, called the *surface tension*, acting in all directions in the plane of the surface. The surface tension is usually regarded as the contractive force of the surface, expressed in dynes, and measured along unit edge of the surface. It is this force which causes liquids to form spherical drops when falling

freely under the influence of gravity, and to rise in capillary tubes if they wet the surface of the wall of the tube. The surface tension of a liquid is affected by the presence of other substances dissolved in it, and by surface contact with some other liquid in which it is not soluble.

Viscosity. The resistance shown by one portion of a liquid to flow over another portion is called the *viscosity*. Its reciprocal, the tendency of the liquid to flow, is the *fluidity*. The viscosity of liquids varies greatly and is a property of the specific substance. Some materials, such as gasoline, have low viscosity, while others, such as tar, have high viscosity. The viscosity of a given liquid decreases with rise in temperature. The viscosity of gases is extremely low.

Vapor Pressure. At fixed temperature, the average kinetic energy of all of the molecules in any liquid is the same; but in each liquid, some of the molecules have greater kinetic energy than this average value. These molecules may break away from neighboring molecules and escape into the gaseous state. Consequently, at the surface of a liquid, there is a continual escape of molecules into the space above the liquid. This process is known as *evaporation*, and gaseous molecules formed by the evaporation of a liquid constitute its *vapor*. Some of these molecules return to the liquid, and the rate at which this occurs depends on their concentration. This process, opposite to evaporation, is the *condensation of the vapor*. If the space above the liquid is closed so that none of the molecules may permanently leave the vicinity of the liquid, the concentration of molecules in the gaseous state gradually increases, thus causing an increased rate of condensation. The final result is that the rates of these two changes become the same. When this condition is attained, Fig. 16, the system is in a state of *dynamic equilibrium*, and the two changes of opposite effect continue at exactly the same rate. The space above the liquid is now saturated, that is, it contains the concentration of the vapor which is necessary for equilibrium. ***The pressure due to the vapor which is in equilibrium with the liquid phase of the same substance is the vapor pressure***

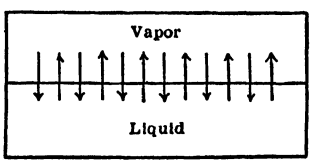


FIG. 16

of the liquid at that temperature. The vapor pressure increases with rise in temperature.

The vapor pressure of a liquid may be measured directly by introducing some of it into the space above the mercury in a barometer tube and measuring the depression of the mercury column which results. At 20°, the vapor pressure of water is equal to 17.5 mm., Fig. 17. The vapor pressure of different liquids at the same temperature differs. Thus, ether, which evaporates more rapidly than water, has the higher vapor pressure at the same temperature.

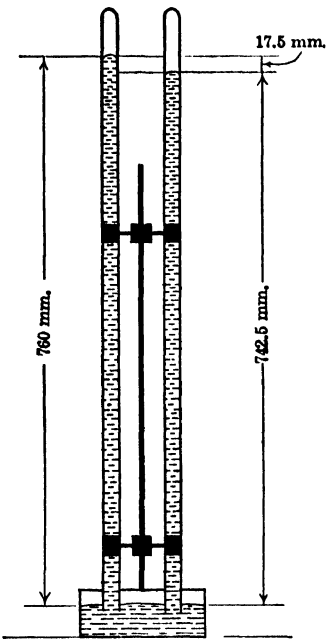


FIG. 17

The Boiling Point of a Liquid. The vapor pressure of a liquid increases with rise in temperature, because the rate of evaporation increases, and a greater concentration of gas molecules is required to establish equilibrium. The effect of changes in temperature on the vapor pressures of a few liquids is shown in Fig. 18. When the vessel is open to air, the maximum vapor pressure is equal to the atmospheric pressure, because all of the air in contact with the liquid is then displaced by the vapor of the liquid. The continued application of heat leads to no further rise in temperature and no increase in the vapor pressure after it has become equal to that of the atmosphere, but the rate of evaporation is increased and the liquid boils. The temperature necessary to boil a liquid depends on the pressure of the atmosphere in contact with it; but, for a particular substance, the boil-

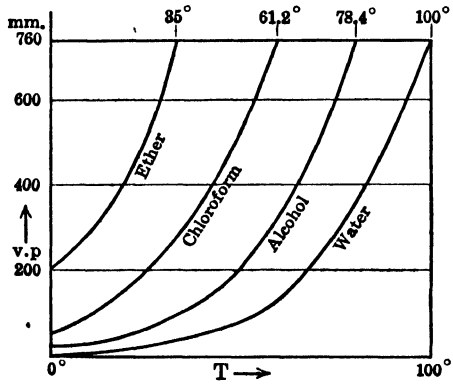


FIG. 18. — Vapor Pressure Curves.

ing temperature is definite at each pressure. ***The normal boiling point of a liquid is the temperature at which its vapor pressure is equal to one standard atmosphere, 760 mm.*** The normal boiling point of water is 100°, but it boils at 90° when the pressure is 526 mm.

During the boiling of a pure liquid at constant pressure, the temperature remains constant. The energy absorbed is expended in overcoming the attraction of the molecules for each other to such an extent that they become free to move as gas molecules. The number of calories of heat required to convert one gram of a liquid at its boiling point to vapor at the same temperature is the *heat of vaporization of the substance.* The heat of vaporization of water is 540 calories.

The Critical Temperature of a Substance. If a liquid is heated in a closed vessel, vapor pressures higher than one atmosphere may be obtained. For each liquid, however, there is a specific temperature above which equilibrium between the liquid and vapor cannot exist because the liquid phase ceases to exist. The highest temperature at which the liquid and gaseous phases of a substance can exist together in equilibrium is called the *critical temperature.* The pressure of the gas at the critical temperature is the *critical pressure.* The vapor pressure of water increases more and more rapidly as the temperature is raised. At 100°, the vapor pressure of water is one atmosphere; at 200°, 15.34 atmospheres; at 300°, 84.78 atmospheres; and at 374°, the critical temperature, 217.72 atmospheres, the highest vapor pressure which water can show. The vapor pressure curve of water from 0° to the critical temperature is represented in Fig. 19. On the scale shown, the pressures at temperatures below 100° are not distinguishable. For this portion of the curve, reference may be made to Fig. 18, in which the pressure unit is one millimeter of mercury instead of one atmosphere. The vapor pressure curve

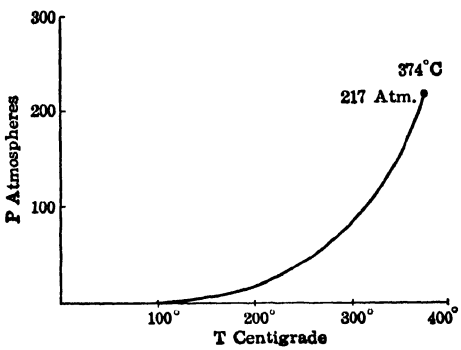


FIG. 19. — Vapor Pressure Curve of Water.

terminates abruptly at the critical temperature. Above this temperature only the gas phase is present.

As the temperature of a liquid rises, the kinetic energy of the molecules becomes greater and the effect of molecular attraction less significant than at lower temperatures. The force of molecular attraction is increased by crowding the molecules close together. At the critical temperature, the molecules of the gas possess the maximum amount of kinetic energy which still permits them to be forced into the liquid state by crowding them together under high pressure. At any temperature above the critical temperature, the kinetic energy of the molecules is so great that the forces of molecular attraction cannot be made great enough to cause liquefaction, no matter how great the pressure applied.

Liquefaction of Gases. The liquefaction of a gas requires establishing conditions at which the actual pressure of the vapor is greater than the saturated vapor pressure. To restore equilibrium in such a system, it is necessary for the concentration of the vapor to decrease so as to reduce the actual pressure of the vapor to that permitted by equilibrium, and liquefaction takes place. The liquefaction of a gas may be brought about by lowering the temperature so as to decrease the vapor pressure, or by increasing the actual pressure by compression, or by both cooling and compressing the gas.

When a gaseous substance is cooled sufficiently, it begins to liquefy at a temperature which is equal to its boiling point under the existing pressure, unless it is one of those substances which go directly from the gaseous into the solid state. Heat is evolved during the liquefaction of the gas. The amount of this heat of condensation is numerically equal to the heat of vaporization. The application of pressure raises the temperature at which liquefaction occurs; but each gas must be cooled at least to its critical temperature.

In 1823, Faraday commenced a series of experiments by which he succeeded in liquefying many of the gases known at the time. His method consisted in preparing the gas from solid substances in one limb of a strong, bent glass tube, which was sealed at both ends. The other end was placed in a cooling mixture, Fig. 20. The gas generated by heating the substance in the tube was found to develop enough pressure to cause liquefaction in the cold

end of the tube. There are a number of gases which cannot be liquefied by this method, because it is not practicable to obtain the necessary low temperatures and high pressures.

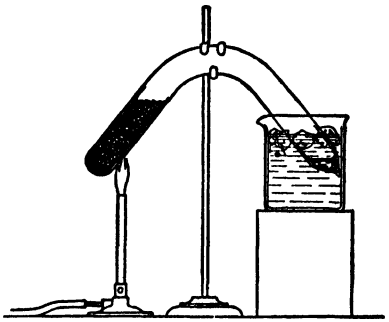


FIG. 20

Liquefaction of Gases of Low Critical Temperatures. When gases are suddenly compressed, the forces of molecular attraction are increased as the particles are crowded closer together. This tends to increase the rate of molecular motion and to cause the rise in temperature commonly observed during the compression of gases. If a highly compressed gas is allowed to expand, its molecules do work at the expense of their own kinetic energy in order to overcome the attraction of the molecules for each other. In this manner, the expansion of a gas produces a cooling effect. The temperature change in a gas when it expands without doing external work is known as the *Joule-Thomson effect.* The cooling effect is greater, the higher the pressure and the lower the temperature of the compressed gas, because the attractive forces of the molecules are greater under these conditions than at ordinary pressures and temperatures. This principle is applied in the liquefaction of gases of low critical temperatures. The compressed gas is cooled to the temperature of the gas which has just expanded. This cool, compressed gas is then allowed to expand, thus becoming still cooler. These effects are applied progressively until liquefaction takes place, when the pressure is sharply reduced.

If the compressed gas is at a temperature at which the forces of molecular attraction are insignificantly small, the Joule-Thomson effect is not applicable and the progressive cooling is not observed. Hydrogen and helium at ordinary temperatures are gases of this nature. Consequently, it is necessary to cool these highly compressed gases to very low temperatures at the start in order to produce the cooling effect by their expansion. This initial cooling may be caused by the use of liquid air.

The Liquefaction of Air. The principle discussed in the preceding paragraph is applied in the Linde apparatus, devised in

1895, for the liquefaction of air. Air, which has been dried and purified to remove carbon dioxide, is compressed under a pressure of approximately two hundred atmospheres and the heat of compression is removed by cooling with water. The compressed air then passes into the inner tube of a heat interchanger, Fig. 21, made of two concentric copper tubes closely coiled and packed in a heat-insulating material. The compressed air escapes through a needle valve at the lower end of the inner tube of the interchanger and the pressure abruptly drops to one atmosphere. The expansion of the air lowers the temperature, and this cooled air passes out through the outer tube of the coil so as to cool the incoming compressed air. As the process continues, the temperature becomes progressively lower, until a portion of the air liquefies when it passes through the needle valve, and the liquid collects in the receiver.

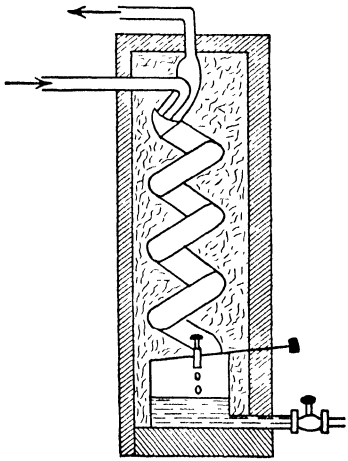


FIG. 21. — Heat Interchanger.

Containers for liquid air, known as Dewar flasks, Fig. 22, are double-walled glass vessels. The space between the walls of the flask is evacuated to prevent the conduction of heat to the contents of the flask. The inner surface of the outer flask may also be silvered to prevent the absorption of radiant heat from outside of the flask. Flasks made on this principle are familiar as thermos bottles.

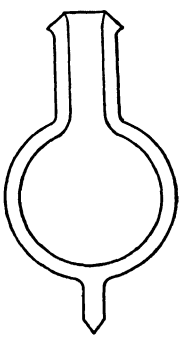


FIG. 22. — Dewar Flask.

The liquefaction of air is now of great industrial importance. When liquid air boils, different components predominate in the fractions obtained at different temperatures. By a suitable arrangement of the apparatus, it is possible to fractionate air so as to obtain several of its components in high enough concentration for industrial use. Commercial oxygen, nitrogen, argon, and neon are obtained by the liquefaction and fractionation of air. Liquid

air also has important scientific uses as a refrigerant for securing low temperatures.

Refrigerating Machines. An extensive application of the liquefaction of gases is in refrigeration. For use in refrigerating machines, a gas must have suitable freezing and boiling points, a high critical temperature, and a large heat of vaporization.

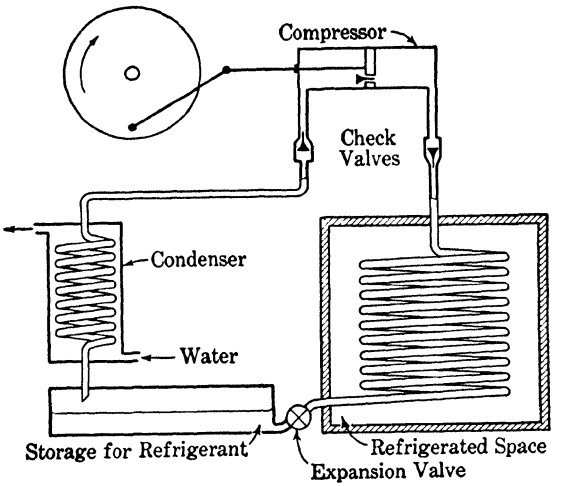


FIG. 23. — Compression Refrigerating Machine. (From "Chemistry in Refrigeration," by F. G. Keyes, in *Chemistry in Industry*, the Chemical Foundation, Inc.)

Ammonia, sulfur dioxide, methyl chloride, and difluorodichloromethane, CCl_2F_2, have the appropriate properties. There are two types of machines in common household use, the compression machines and the absorption machines. *In the compression machine*, Fig. 23, the pressure required to liquefy the gas in the condensing unit is developed by means of a motor-driven pump. The condenser unit may be water cooled or air cooled. The liquid then passes through an expansion valve into a coil in the space to be refrigerated. During the evaporation of the liquid, heat is absorbed. The cycle is repeated as required and is controlled by an automatic device which brings the compressor into operation when the liquid refrigerant in storage is reduced to a certain level.

In the absorption machine, Fig. 24, the gas is absorbed in a suitable material during the evaporation of the refrigerant and is

subsequently expelled from this material by heat in order to build up the pressure necessary for its liquefaction. Calcium chloride absorbs relatively large volumes of ammonia to form an addition compound. The pressure of ammonia gas in equilibrium with this product at room temperature is low, but increases rapidly with rise in temperature. Consequently, the

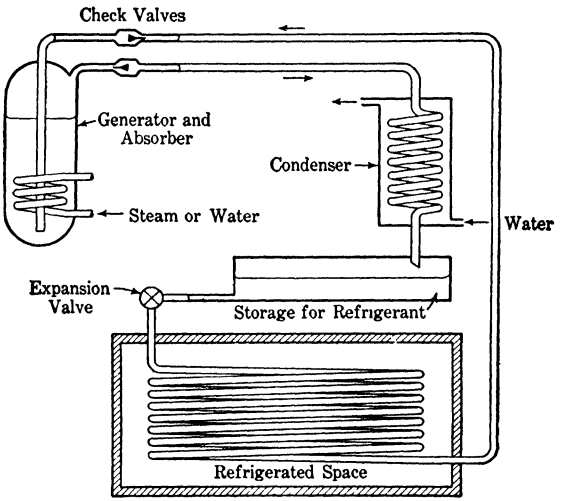


FIG. 24. — Absorption Refrigerating Machine. (From "Chemistry in Refrigeration," by F. G. Keyes, in *Chemistry in Industry*, the Chemical Foundation, Inc.)

calcium chloride-ammonia system may be applied in the absorption type of refrigerating machine. Ammonia is expelled from the absorbent by heat, and a high enough pressure to cause its liquefaction in the water-cooled condenser is developed. When most of the ammonia has liquefied and collected in storage, the heating is discontinued and the absorbent is cooled. The liquid passes through a valve into coils where the pressure is low, and rapidly evaporates, the gas being again absorbed in the absorbent. In this way a brine around the coil is cooled, and the cold brine refrigerates the space during the condensation stage of the cycle in which liquid ammonia is again formed. The whole process is operated automatically.

THE SOLID STATE

A sample of a solid has definite volume. The particles of which solids are composed are close together, and the forces existing

between them are great enough to give varying degrees of mechanical strength and rigidity. In crystalline solids, the motion of the particle is a vibration about a fixed position. An orderly arrangement of the particles determines the structure of the crystal.

The Melting Point of a Solid. A crystalline solid melts at a definite temperature which is characteristic of the substance. So long as the liquid and solid phases of the substance are present together in intimate mixture, the temperature is constant. ***The temperature at which the solid and liquid phases of a substance are in equilibrium under an external pressure of one atmosphere is the melting point of the solid.*** When heat is absorbed by a mixture such as this, the equilibrium is disturbed and the relative amount of the liquid phase increases. The number of calories of heat required to liquefy one gram of a solid at its melting point is *the heat of fusion.* The heat of fusion of water is 80 calories.

The changes which take place during the freezing of a solid are opposite to those which occur during its melting. Complete solidification occurs at a specific temperature in the presence of the solid phase. It is often possible to cool a liquid to some temperature below its freezing point; but equilibrium is established at the freezing point when a supercooled liquid is stirred or seeded with a small crystal of the solid phase.

Many crystalline substances exhibit appreciable vapor pressure at ordinary temperatures, and the vapor pressure of the solid increases with rise in temperature. The highest vapor pressure which a pure solid may show is at the melting point. The lowest vapor pressure which a liquid may show when in contact with some of the solid phase is at the freezing point. Since the melting point of the solid and the freezing point of the liquid are identical temperatures, and the two phases are in equilibrium, the melting point of a substance is the temperature at which the solid and liquid phases have the same vapor pressure, under a total external pressure of one atmosphere. The relation of the vapor pressure to the temperature is shown for water by the curves in Fig. 25. The curve, *AB*, shows the effect of changes in temperature on the vapor pressure of ice. The vapor pressure of the solid is zero at the absolute zero of temperature; but it becomes negligibly small for most solids at temperatures which are much higher. The curve, *BD*, not drawn to scale, represents the vapor pressure

of liquid water. This curve may be extended with increased pressures and temperatures to the critical temperature. The point, *B*, at which these curves intersect, represents the freezing point of water, 0°, at which the solid and liquid phases are in equilibrium and each has a vapor pressure of 4.5 mm. The curve, *BE*, the extension of the regular curve, *BD*, for liquid water to temperatures below 0°, represents the vapor pressures of supercooled liquid water. The vapor pressure of this unstable phase is greater than that of ice, the stable phase, at the same temperature.

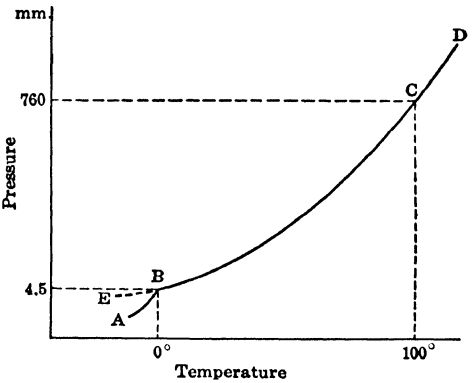


FIG. 25. — Vapor Pressure Curve of Water.

Sublimation. Solids, such as iodine, which have high vapor pressures at ordinary temperatures, may evaporate without melting. This phenomenon is called sublimation. When the vapors of such solids are cooled, they condense directly to the crystalline state without the formation of the intervening liquid. Iodine may be melted if the vapor is kept in contact with the solid so as to give a partial pressure of the gas equal to at least 100 mm. The vapor pressure curve of iodine is shown in Fig. 26. Solid carbon dioxide, "dry ice," has a vapor pressure greater than one atmosphere at any temperature above − 78.5°. Hence, this substance can be kept in the liquid state only under high pressure. At 20°, the vapor pressure of carbon dioxide is 56.5 atmospheres. The vapor pressure curve for carbon dioxide is shown in Fig. 27. The pressures are in atmospheres and the temperatures in degrees absolute. The solid substance has a vapor pressure of one atmosphere at a temperature of −78.5°, 194.5° A. It melts under a

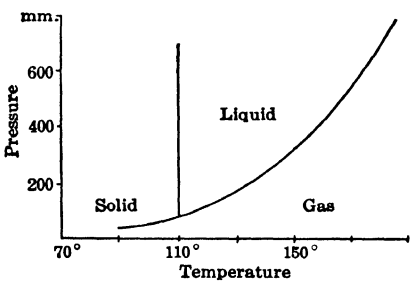


FIG. 26. — Vapor Pressure Curve of Iodine.

pressure of 5.3 atmospheres at − 56°, 217° A. The substance has no true melting point and the solid sublimes when it is exposed at a pressure of one atmosphere. If liquid carbon dioxide is poured from a cylinder, it evaporates so rapidly as it emerges that a large portion of the oxide is cooled to the solid state, forming carbon dioxide snow.

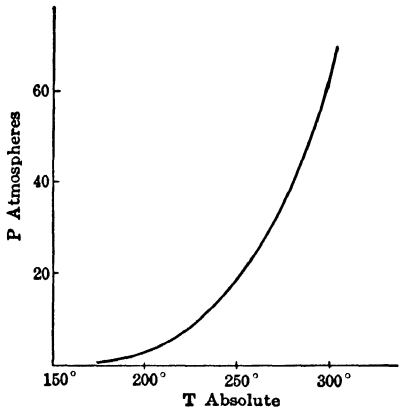


FIG. 27. — Vapor Pressure Curve of Carbon Dioxide.

Crystal Structure of Solids. A crystal has a definite geometrical form and is bounded by plane faces. The size and external shape of a crystal of a given substance may vary, depending on the conditions under which crystallization has occurred; but the angle between two corresponding faces of a crystal of a substance is the same at a specific temperature. The geometrical form of a crystal is determined by the arrangement of the particles throughout the entire crystal. It is not possible to determine the relative positions of these particles by examination of the crystal under ordinary light, because the light waves are not affected perceptibly by such minute particles. The wave lengths of X-rays are so much shorter than those of ordinary light that they are influenced by these small particles. Investigations of these effects by Laue, W. H. Bragg, W. L. Bragg, and many others have provided techniques for determining the relative positions of the particles in a crystal.

The position of the particles in the crystal determines the framework, known as the *crystal lattice*, on which the crystal is built. The smallest unit of this lattice which represents the relative positions of all of the particles is known as the *unit cell*. The structure and the size of the unit cell are characteristic properties of each crystalline substance. There are a large number of crystal forms which may be classified into six general types. In the *cubic system*, the three axes are of the same length and intersect at right angles. Consequently, this is the simplest of the systems; but there are three space lattices in this system, Fig. 28. In the

simple cubic lattice, one structural unit is at each corner of the cube. In the face-centered cubic lattice, one unit is at each

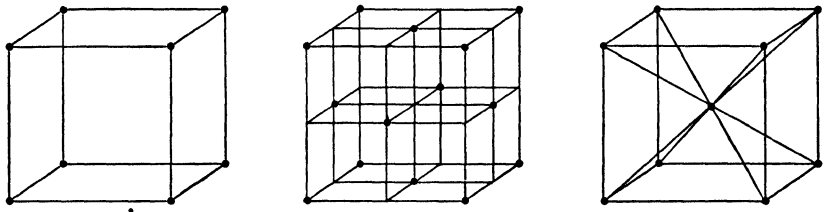


FIG. 28

corner and one in the center of each face of the cube. In the body-centered cubic lattice, one unit is at each corner and one in the center of the cube.

The unit cell of the sodium chloride crystal is represented by Fig. 29. The structural particles of this crystal are positively charged sodium ions and negatively charged chloride ions. *Ions are atoms or groups of atoms which bear an electric charge.* In the figure, sodium ions are shown by the black circles and chloride ions by the white circles. In this crystal, specific sodium and chloride ions do not "belong to each other," but each chloride ion is shared by six sodium ions, as shown in the figure by the chloride ion at the center of the unit cell. In a similar manner, each sodium ion in the complete crystal is shared by six chloride ions. The large crystal of this salt is built up by a repetition of this structure, so that the ratio of the two ions in the crystal is one sodium ion to one chloride ion, but no molecules of the salt are present. In cesium chloride, two cubic lattices interpenetrate so that each cube of eight chloride ions has a cesium ion at its center and each cube of

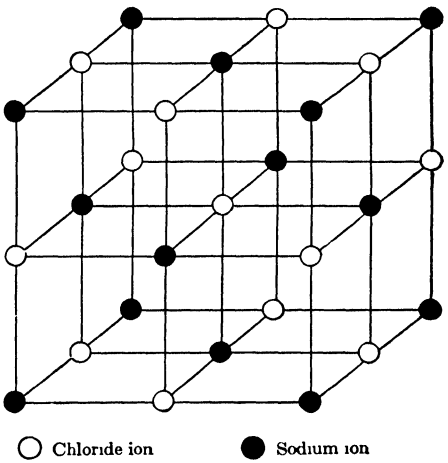


FIG. 29

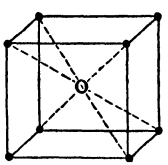


FIG. 30

eight cesium ions has a chloride ion at its center, Fig. 30. In other crystal systems, the axes differ in length and in the angles at which they intersect. Hence, a large number of space lattices are possible.

The structural units which occupy the positions in the space lattice may be ions, atoms, or molecules. In salts, the structural units are positively and negatively charged ions which are held in position by the forces of electrical attraction. In elementary metals, the atom is the unit, as in metallic sodium which is characterized by the body-centered cubic lattice. In solid carbon dioxide, the crystal lattice is the face-centered cube, with molecules of carbon dioxide as the units.

Amorphous Solids. Amorphous solids are noncrystalline. Some of these materials exhibit the strength and hardness ascribed to crystalline substances; but, when they are heated, they gradually soften until they will flow readily. Amorphous solids do not have the specific melting points and heats of fusion which characterize a change in state. The attractive forces of the structural units of such materials are exerted equally in all directions and result in a random arrangement. Amorphous solids are considered structurally to be liquids having very high viscosity. They are known as *supercooled liquids.* Many substances which appear to be amorphous, such as finely divided powders, are really crystalline in structure; but the particles are so minute that the crystalline structure is not apparent.

Polymorphism. Allotropy. There are many chemical substances which may exist in more than one form. Examples are calcite and aragonite crystals of calcium carbonate; body-centered and simple cubic crystals of ammonium chloride; and the different forms of elementary substances, such as diamond and graphite, red and white phosphorus, oxygen and ozone, and rhombic and monoclinic sulfur. This property of existing in more than one form is known as *polymorphism.* A special case is that of the elementary substances, to which the name *allotropy* is given. The different forms of the element are called allotropes. The difference between the allotropic forms of a substance is due either to the fact that the same structural units may be arranged in more than one crystal lattice, or that the atoms may be combined to form different molecules. The particular form which a sub-

stance assumes is determined by the physical conditions. Under identical conditions, a specific substance always crystallizes in the same form. The allotropic form which can exist indefinitely under particular conditions is stable. Graphite, in which the carbon atoms are arranged in a space lattice in hexagonal rings, is the stable form of carbon under ordinary conditions of temperature and pressure. If an allotrope shows no tendency to change form even though theoretically it should be unstable, it is metastable. The diamond, having the same structural unit as graphite, but arranged in a space lattice with tetragonal grouping is metastable. Allotropic forms which continually undergo change are unstable. White phosphorus continually changes to the red variety, but there is no specific transition temperature. Monoclinic sulfur is unstable at temperatures below 96° and slowly changes into the rhombic allotrope, but above 96° monoclinic sulfur is stable, and this definite temperature is a transition point. The crystallization of calcium carbonate from hot solution yields aragonite, which belongs to the rhombic system; while crystallization from cold solutions yields calcite in the hexagonal system. These forms are not convertible one into another under ordinary conditions. Aragonite is more soluble than calcite and is the metastable form of this substance.

A particular allotrope is associated with a definite amount of energy. During the change from one form to another, energy is either absorbed or liberated. The formation of one mole of ozone from oxygen is accompanied by the absorption of 34,500 calories of heat. Hence, ozone is the more active allotrope. Similarly, white phosphorus is much more active than the red modification. The stable form of the substance always contains less energy than a metastable or unstable form. When the vapor of a substance condenses, or a solid crystallizes from solution or from the fused substance, the least stable form is the first product. The condensation of phosphorus vapor yields white phosphorus; the crystallization of calcium carbonate from the hot solution yields aragonite; and the solidification of fused sulfur yields monoclinic crystals. If the form first produced is unstable, it then changes into the stable modification.

Isomorphism. Solid Solutions. There are many instances in which two substances crystallize in practically the same crys-

talline form. The property is known as *isomorphism.* In such instances a structural unit of one of the compounds may replace a similar unit of the other in the crystal. If aqueous solutions of chrome alum, $KCr(SO_4)_2(H_2O)_{12}$, and potassium alum, $KAl(SO_4)_2(H_2O)_{12}$, are mixed and allowed to crystallize, the crystals are found to contain both chromium and aluminum ions in addition to potassium and sulfate ions and the water of hydration. Furthermore, the proportions of chromic and aluminum ions in the crystals may be varied at will by changing the proportions in the solution. Mixed crystals such as these are known as *solid solutions.* The space lattice of the crystal contains both kinds of interchangeable ions at appropriate points.

EXERCISES

1. What three properties are characteristic of all gases?
2. State the assumptions of the kinetic theory and give evidence to support each of these assumptions.
3. Show how the kinetic theory may be employed to account for the following: gas pressure; the relation of the volume to the temperature and pressure of a gas sample; the partial pressures of mixed gases; the absolute zero of temperature; the transition between the liquid and gaseous states; the transition between the liquid and solid states.
4. What do deviations from the gas laws signify? What is meant by a "perfect gas"?
5. Correct to standard conditions the volumes of the gases measured under the conditions listed below:

	Volume	Temperature	Pressure
(*a*)	25.1 ml.	15°	770 mm.
(*b*)	38.7 ml.	20°	750 mm.
(*c*)	36.0 ml.	0°	740 mm.
(*d*)	100.0 ml.	− 13°	750 mm.
(*e*)	75.0 ml.	17°	765 mm.

6. Calculate:
   (*a*) The volume occupied by 5 moles of hydrogen chloride at 20° and 740 mm.
   (*b*) The volume occupied by 2 moles of carbon dioxide at 30° and 765 mm.
   (*c*) The volume occupied over water by 4 g. of oxygen at 23° and 755 mm.
   (*d*) The volume of the oxygen collected over water at 23° and 755 mm. produced by the heating of 12.25 g. of potassium chlorate.
7. What is meant by the molar volume of a gas? Show its relation to the standard of atomic and molecular weights.
8. How are the molecular weights of gases and easily volatilized substances determined?

9. Calculate the weight under standard conditions of one liter of chlorine; 600 ml. of nitrogen; 100 ml. of oxygen; 250 ml. of hydrogen; and 2 ml. of ammonia.
10. Two substances have the composition: nitrogen, 30.43%, and oxygen, 69.57%. It is found, however, that under standard conditions 200 ml. of one weigh 0.41 g., and 125 ml. of the other weigh 0.512 g. Derive the true formula of each.
11. Describe differences in properties between substances in the liquid and gaseous states and account for these differences in terms of the kinetic theory.
12. Define the following terms: vapor pressure; boiling point; heat of vaporization; critical temperature; freezing point; sublimation.
13. Mention differences between amorphous and crystalline solids.
14. To what is the crystalline form of a substance due? What is meant by the space lattice of a crystal? the unit cell?
15. Name three structural units of which crystals are composed and give examples of each.
16. What is meant by allotropy? isomorphism? solid solution?

SUPPLEMENTARY READINGS

Dampier-Whetham, *A History of Science*, pp. 248–253.

Findlay, *The Spirit of Chemistry*, Chapters VII and VIII.

Jaffe, *Crucibles*, Section IX.

Getman and Daniels, *Outlines of Theoretical Chemistry* (John Wiley and Sons, 1937), Chapters II, III, and IV.

Hildebrand, *Principles of Chemistry* (The Macmillan Company, 1940), Chapter III.

Meldrum and Gucker, *Introduction to Theoretical Chemistry* (American Book Company, 1936), Chapter III.

Stillwell, "Crystal Chemistry," *J. Chem. Education* **10,** 590, 637 (1933); **11,** 159 (1934); **13,** 415, 469, 521, 566 (1936); **14,** 34, 131 (1937).

CHAPTER IV

OXYGEN. HYDROGEN. EQUATIONS. CALCULATIONS

This chapter is intended primarily as a review of several types of simple reactions and of the equations by which they are represented. The reacting quantities of substances are also calculated on the basis of the equations. The two elementary substances, oxygen and hydrogen, and their compounds, water and hydrogen peroxide, are also briefly discussed. Since most of this material has already been covered by the student in his previous work, it will not be discussed in great detail here. For a more detailed account, including the historical development of the subject, the student is referred to some of the readings suggested at the end of the chapter.

Decomposition Reactions. Reactions in which complex substances are broken down to form two or more simpler products are decomposition reactions. The conditions which are necessary to cause decomposition vary, depending on the nature of the substances. Some substances, such as the high explosives, decompose with great violence when they are detonated, in some instances only slight mechanical shock being required to cause detonation. Many substances may be decomposed by heat, while others will withstand high temperatures. The oxides of several of the metals may be decomposed at temperatures easily obtained in the flame of the Bunsen burner. It was observed by Priestley, 1774, and by Lavoisier, 1777, that mercuric oxide decomposes when it is heated, with the formation of mercury and oxygen. Borch, 1678, observed the decomposition of potassium nitrate, producing oxygen. A large number of substances may be decomposed by the passage of an electric current through the material in the melted state or in aqueous solution.

Equations. Writing an equation demands first that the fact which is to be represented be known, or deduced as a particular case of a general type of behavior which is understood. The

formulas of the substances are then written through the application of the oxidation numbers of the elements and radicals involved, those of the initial substances to the left, and of the products to the right of the reaction sign. Coefficients are next introduced to balance the equation by showing the correct proportions. The decomposition of mercuric oxide yields mercury and oxygen. Since the formula of oxygen is O_2, two moles of mercuric oxide decompose for each mole of oxygen produced and two gram atoms of mercury are liberated.

$$2\ HgO \longrightarrow 2\ Hg + O_2.$$

Similarly, the decomposition of potassium nitrate yields potassium nitrite and oxygen.

$$2\ KNO_3 \longrightarrow 2\ KNO_2 + O_2.$$

The Laboratory Method for the Preparation of Oxygen. There are several decomposition reactions which may be employed in the laboratory as a source of oxygen; but the usual method is based on the thermal decomposition of potassium chlorate to produce oxygen and potassium chloride.

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2.$$

In practice, a mixture of potassium chlorate and manganese dioxide is heated and the gas is collected over water, Fig. 31. The manganese dioxide serves as a catalyst in this reaction. A

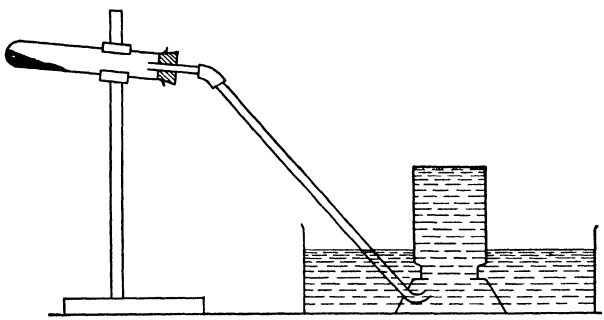


FIG. 31

catalyst is a substance which alters the rate of a reaction without undergoing permanent change during the reaction. On account of the accelerating effect produced by the presence of manganese dioxide, the thermal decomposition of potassium chlorate attains

suitable velocity for the laboratory production of oxygen at a lower temperature than required in the absence of the catalyst.

Displacement Reactions. Reactions in which atoms of an elementary substance replace an equivalent number of atoms of another element in a compound are displacement reactions. The displacing element must be more active under the conditions of the experiment than the element which is driven out of combination. The metals differ in activity; and in the accompanying list, a few of the metals are listed in the order of decreasing activity. Under proper experimental conditions, each metal will displace from suitable compounds those which follow it in the list. Thus, copper displaces silver from silver nitrate and copper nitrate is formed.

Activity of the Metals.
Potassium
Calcium
Sodium
Magnesium
Aluminum
Zinc
Iron
Tin
Lead
Hydrogen
Antimony
Bismuth
Copper
Silver
Gold

$$Cu + 2\,AgNO_3 \longrightarrow 2\,Ag + Cu(NO_3)_2.$$

Metals which are above hydrogen in activity displace hydrogen from some of the acids, such as hydrochloric and dilute sulfuric acids. Aluminum reacts with hydrochloric acid, producing hydrogen and aluminum chloride.

$$2\,Al + 6\,HCl \longrightarrow 3\,H_2 + 2\,AlCl_3.$$

Dilute nitric acid does not ordinarily react with metals to yield hydrogen.

The Laboratory Preparation of Hydrogen. The reaction of zinc with dilute sulfuric acid is usually employed in the laboratory method for the preparation of hydrogen and the gas is collected over water, Fig. 32.

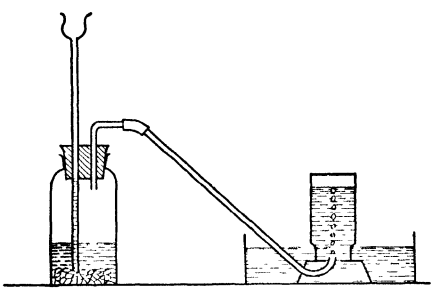


FIG. 32

$$Zn + H_2SO_4 \longrightarrow H_2 + ZnSO_4.$$

A small amount of copper sulfate is also introduced into the generator. Zinc displaces copper from the salt.

$$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4.$$

In the presence of a metal of low activity, zinc reacts more readily with sulfuric acid than in its absence. The surface of pure zinc becomes coated with a thin film of gaseous hydrogen when the

pure metal is placed in a dilute sulfuric acid solution. Under these conditions, the reaction goes so slowly that no evidence of reaction can be seen. When copper is present in contact with the zinc, the liberation of the hydrogen occurs at the surface of the inactive copper; and a fresh surface of the active zinc is constantly exposed to the acid.

The Direct Union of Elements. Many of the elements unite directly with each other with the formation of binary compounds, compounds which contain only two elements. In such reactions, atoms of the elements are held together in the compounds in a ratio determined by the oxidation numbers of the elements. In some instances, the products are molecular, in others, ionic. The nature of the changes which occur during these reactions will be discussed in Chapter VII. Binary compounds are characteristically named through the use of the suffix, *-ide*, attached to a significant part of the name of one of the elements, usually the non-metallic element. Thus, binary compounds of oxygen are oxides; of chlorine, chlorides; and of sulfur, sulfides.

Hydrogen unites actively with many of the non-metallic elements. It also combines with some of the metals; but the metal hydrides are not stable in solution. Reacting with the halogens, the hydrogen halides are formed. Hydrogen unites with sulfur to form hydrogen sulfide and with nitrogen to form hydrogen nitride, commonly called ammonia.

$$H_2 + Cl_2 \longrightarrow 2\,HCl.$$
$$H_2 + S \longrightarrow H_2S.$$
$$3\,H_2 + N_2 \longrightarrow 2\,NH_3.$$

Oxygen unites with most of the elementary substances. It does not unite with the inert gases, with the noble metals, nor with the halogens. With some of the metals, such as sodium, the peroxide is the stable product; and an unstable peroxide may be an intermediate product in many of these reactions. Calcium yields calcium oxide when it unites with oxygen; and phosphorus yields phosphorus pentoxide.

$$O_2 + 2\,Na \longrightarrow Na_2O_2.$$
$$O_2 + 2\,Ca \longrightarrow 2\,CaO.$$
$$5\,O_2 + 4\,P \longrightarrow 2\,P_2O_5.$$

The Reactions of the Oxides with Water. A number of the oxides unite with water to form *hydroxides.* An hydroxide is a compound containing an element in combination with one or more hydroxide groups. In all of these reactions of the oxides with water, an atom of oxygen in the oxide takes on one atom of hydrogen from the water molecule and two hydroxide groups result. Thus, the simple oxide of sodium unites with water to form sodium hydroxide; and phosphorus trioxide yields phosphorus hydroxide.

$$Na_2O + H_2O \longrightarrow 2\ NaOH.$$
$$P_2O_3 + 3\ H_2O \longrightarrow 2\ P(OH)_3.$$

In some of the hydroxides, not all of the oxygen atoms of the oxide are converted into hydroxide groups. This is usually the result for the elements in high oxidation states.

$$SO_2 + H_2O \longrightarrow SO(OH)_2.$$
$$SO_3 + H_2O \longrightarrow SO_2(OH)_2.$$

Some of the hydroxides produced by these reactions are basic and others are acidic. *The soluble basic hydroxides* characteristically cause certain indicators to assume specific colors: methyl orange, yellow; litmus, blue; phenolphthalein, red. The basic hydroxides react with acids and with acidic oxides. *Acidic hydroxides, acids,* also give characteristic colors with certain indicators: methyl orange, red; and litmus, red. Acids produce no color with phenolphthalein. Acids react with the metal oxides and hydroxides. The oxides and hydroxides which react with acids are called basic oxides and basic hydroxides. The elements which yield basic oxides and hydroxides are the *metals* The oxides which react with basic substances are acidic oxides and the corresponding hydroxides are acids. The elements which yield acidic oxides and hydroxides are the *non-metals.*

It is customary to write the formulas of the acidic hydroxides in a different manner from those of the basic hydroxides. The characteristic reactions of the acids are due to the replaceable hydrogen atoms in the molecule; and the formulas are written so as to emphasize the acidic nature of the substance. The hydroxide of phosphorus is acidic and its formula is usually written H_3PO_3. Similarly, the hydroxides of sulfur are acidic and their formulas are written H_2SO_3 and H_2SO_4, respectively. The acid

or basic character of the hydroxide depends on the relative strength of the attractive forces of the hydrogen and oxygen atoms for each other compared to the attraction of oxygen to the rest of the molecule, not on structural differences in the molecules themselves.

In order to write equations for the reactions of the oxides with water, one must know the formulas of the products or be able to derive these formulas from the oxidation numbers of the radicals which are formed. The relationships in the case of the metal hydroxides are simple, since the oxidation number of the hydroxide radical is 1 —. The relationships in the case of the acidic hydroxides are not so simple; and it is necessary to commit to memory the formula of the acid, or the formula and oxidation number of the radical, formed by the reaction of each of the acidic oxides. In Appendix V, the relation of some of the common non-metal oxides to the acids and salts is shown.

Nomenclature of Acids and Salts. The acids and salts are closely related to each other in composition. As noted above, the properties of the acids are associated with the replaceable atoms of hydrogen in their molecules. The *salts* contain metallic radicals in the place of the hydrogen atoms of the acids. In the naming of these compounds, this relation is emphasized.

The common oxyacid in which the non-metal has a high oxidation state is named by adding the suffix, *-ic*, to a significant part of the name of the non-metal. In the names of the salts, the suffix, *-ate*, is used for the salts of the *-ic* acids. Nitric acid is represented by the formula HNO_3, and sodium nitrate by the formula $NaNO_3$. The name of the acid containing the non-metal in its next lower oxidation state contains the suffix, *-ous*, and the salt, *-ite*. Nitrous acid has the formula HNO_2, and sodium nitrite $NaNO_2$. An acid containing the non-metal in a higher oxidation state than in the common oxyacid is named through the use of the prefix, *per-;* and an acid in which the non-metal is in a lower oxidation state than that of the *-ous* acid is named through the use of the prefix, *hypo-*. A binary acid, containing only hydrogen and a non-metal is a *hydroacid.* The significance of these names is illustrated by listing the acids of chlorine: hydrochloric acid, HCl; hypochlorous acid, HClO; chlorous acid, $HClO_2$; chloric acid, $HClO_3$; and perchloric acid, $HClO_4$.

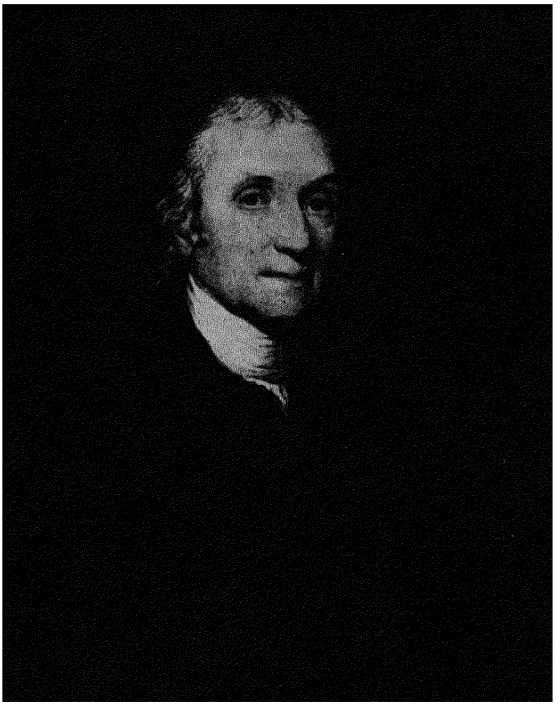
If a specific non-metal oxide may undergo more than one stage of hydration, the acid showing the ordinary high degree of hydration is called the *orthoacid.* The acid containing one mole of water less, per mole of acid, is the *metaacid.* An intermediate stage, often formed by the thermal decomposition of the orthoacid is called the *pyroacid.* Illustrating these names, orthophosphoric acid has the formula H_3PO_4; metaphosphoric acid HPO_3; and pyrophosphoric acid $H_4P_2O_7$. The prefix, *ortho-*, is often omitted, this acid being designated simply, phosphoric acid.

In the names of the salts of metals in the lower of two valence states, the suffix, *-ous*, is used; and in the higher state, *-ic.* Ferrous chloride has the formula $FeCl_2$; and ferric chloride $FeCl_3$. The prefixes, *mono-*, *di-*, *tri-*, etc., are more commonly used in naming compounds of non-metals containing only two elements, so as to indicate differences in the numbers of the atoms of one of these non-metals in the molecules of the different compounds: carbon monoxide, CO; carbon dioxide, CO_2; phosphorus trichloride, PCl_3; carbon tetrachloride, CCl_4; and phosphorus pentachloride, PCl_5.

The Reaction of the Metal Oxides with Acids. Water is a product of all of these reactions; and the proportions of the oxide and acid are, therefore, such that the ratio is two atoms of hydrogen to one atom of oxygen. The other product, a salt, contains the metal of the oxide and the non-metal radical of the acid. Magnesium oxide reacts with hydrochloric, nitric, sulfuric, and phosphoric acids.

$$MgO + 2\,HCl \longrightarrow H_2O + MgCl_2.$$
$$MgO + 2\,HNO_3 \longrightarrow H_2O + Mg(NO_3)_2.$$
$$MgO + H_2SO_4 \longrightarrow H_2O + MgSO_4.$$
$$3\,MgO + 2\,H_3PO_4 \longrightarrow 3\,H_2O + Mg_3(PO_4)_2.$$

The Reaction of Acidic Oxides with Metal Hydroxides. This is also a very general reaction and the products are water and salts. It is obvious that the salt formed in a particular reaction contains the metal of the hydroxide; and it should be equally obvious that the non-metal radical is the one corresponding to the acidic oxide, as shown in the formula of the acid which it yields when it reacts with water. Thus, carbon dioxide, sulfur trioxide,



JOSEPH PRIESTLEY (1733–1804)

Priestley first planned to be a clergyman, but was not very successful as a preacher because of an impediment in speech, and he gradually became more and more interested in chemical experiments. As a result of his sympathy for the cause of the French Revolutionists he became unpopular with some of his fellow-citizens. His attendance at a dinner held in 1791 to celebrate the fall of the Bastile so infuriated the people that they wrecked his house in Birmingham and burned the chapel in which he preached. He came to America in 1794 and lived at Northumberland, Pennsylvania.

He had great ability to carry out experiments and to make observations but did not always reason clearly. Although he discovered oxygen, Priestley missed the real significance of his discovery. To the last he held to the idea that combustion was due to "phlogiston" emerging from the burning substance, and thought the gas which he had discovered was the component of the air which combines with this phlogiston when it is set free during combustion.

and phosphorus pentoxide react with sodium hydroxide to form water and the carbonate, sulfate, and phosphate, respectively.

$$CO_2 + 2\ NaOH \longrightarrow H_2O + Na_2CO_3.$$
$$SO_3 + 2\ NaOH \longrightarrow H_2O + Na_2SO_4.$$
$$P_2O_5 + 6\ NaOH \longrightarrow 3\ H_2O + 2\ Na_3PO_4.$$

The Occurrence and Industrial Preparation of Oxygen. Approximately one half of the weight of the matter in the outer layer of the solid earth, together with the water on the surface of the earth and the atmosphere about it, is oxygen. The most abundant of its compounds are silicates of varying degrees of complexity; but large amounts of carbonates, sulfates, phosphates, and other salts and oxides also occur. Oxygen occurs in the elementary, *free*, condition in air, of which it comprises nearly one fifth by volume, approximately one fourth by weight. Nearly 89% of water is oxygen and this element is a constituent of a large proportion of the animal and vegetable matter.

The most important industrial source of oxygen is the air. Air is liquefied, as described in the preceding chapter, producing a solution which is chiefly nitrogen and oxygen. When this liquid boils, nitrogen, having the lower boiling point, − 195.8°, escapes more rapidly than oxygen, whose boiling point is − 183°. By a suitable arrangement of the apparatus, most of the nitrogen may be boiled out without the loss of much of the oxygen; and then the oxygen, of 96–99% purity, emerging from the liquid, is compressed into steel cylinders under a pressure of approximately 1000 pounds per square inch.

Oxygen is also prepared industrially by the *electrolysis of water*, *i.e.*, the decomposition of water which accompanies the passage of a direct current of electricity through it; but this process is more costly than the liquid air process, and cannot compete with it unless there is also a ready market for the hydrogen produced.

Properties and Reactions of Oxygen. At ordinary temperatures and pressures oxygen is a colorless, odorless, and tasteless gas. One liter of the gas at 0° and 760 mm. weighs 1.429 g., so that it is approximately 1.1 times as dense as air. The gas is slightly soluble in water, 3 volumes of oxygen in 100 of water at 20° and 760 mm., 4.9 volumes at 0° and 760 mm. The critical temperature of oxygen is − 118.8° and the critical pressure is

approximately 49.7 atmospheres. The liquid is pale blue in color, and has a boiling point of − 183° and a freezing point of − 218.7°. Liquid and solid oxygen are highly magnetic.

The reactions of oxygen with other elements have been discussed. It also reacts with a number of compounds. Most of the binary compounds composed of elements which are combustible will themselves react with oxygen. Thus, methane and hydrogen sulfide are combustible.

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O.$$
$$2\ H_2S + 3\ O_2 \longrightarrow 2\ SO_2 + 2\ H_2O.$$

There are also many oxy-compounds which can take up additional oxygen. Carbon monoxide burns to form carbon dioxide.

$$2\ CO + O_2 \longrightarrow 2\ CO_2.$$

Many of the reactions of oxygen which take place rapidly at high temperatures occur very slowly or not at all at room temperature. All of the common fuels must be heated to start the combustion, which then proceeds rapidly at high temperature. Some substances react rapidly with oxygen at ordinary temperatures, evolving a large amount of heat. Such substances become heated to high temperatures if they are also poor conductors of heat and are in a place where there is not sufficient circulation to carry away the heated air. As the temperature rises, the rate of reaction is progressively increased. These effects may lead to the ignition of the substance. This is *spontaneous combustion.* Oil-soaked cloths packed away in a cupboard often cause disastrous fires as the result of spontaneous combustion. The ignition of some organic materials, such as damp hay, is the result of bacterial action which generates heat and leads to the formation of spontaneously combustible products. The combustion of these products heats the organic material to its kindling temperature.

Ozone. Ozone is an allotrope of oxygen, with a molecular constitution shown by the formula O_3. The conversion of oxygen into ozone is accompanied by the absorption of 34,500 calories of heat per mole. Energy for this conversion may be supplied by ultraviolet light or by a silent electrical discharge. In the latter method, cold, dry oxygen is passed between highly charged

plates separated by an insulator, Fig. 33. The reaction producing ozone is reversible and the per cent of the gas in the oxygen emerging from the ozonizer is small.

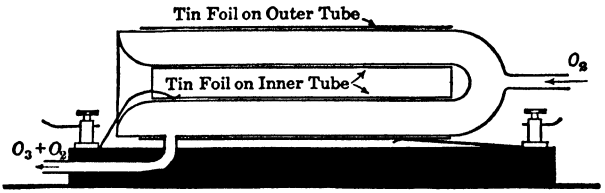


FIG. 33

At ordinary temperatures, the decomposition of ozone into oxygen occurs slowly. Ozone has the characteristic pungent odor often noticed in the vicinity of electrical machines. The gas may be condensed to a blue liquid which boils at $-$ 111.1° and freezes at $-$ 251.4°. Ozone is composed of the same atoms as molecular oxygen and its reactions are of the same general varieties as those of oxygen. Since it contains more internal energy, it reacts more vigorously than oxygen. Ozone combines with silver at ordinary temperatures, and liberates iodine from solutions of potassium iodide.

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

Ozone destroys certain microörganisms and is used to some extent in the sterilization of water. It is also used as a deodorant in the air in crowded auditoriums, and for the bleaching of paper pulp, flour, and some fabrics.

Industrial Uses of Oxygen. The reactions of oxygen in combustion and respiration are important as sources of energy. Ordinarily, the oxygen of the air is sufficiently concentrated; but oxygen itself is desired under certain conditions. The most extensive use of commercial oxygen is for the production of high temperatures in oxy-gas flames, such as the oxy-acetylene torch for cutting and welding metals.

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 624{,}000\text{ cal.}$$

The heat of combustion of acetylene, *i.e.*, the number of calories of heat evolved per mole, is large; and the reaction occurs rapidly in a relatively small space in the oxy-acetylene flame. Temperatures up to 3000° may be obtained in this flame. The oxy-

hydrogen blowpipe, Fig. 34, is also used, though it does not produce as high a temperature as the oxy-acetylene flame.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O + 113\,120 \text{ cal.}$$

The temperature of this flame is approximately 2500°. Pure oxygen is used in the treatment of patients suffering from severe cases of pneumonia or from asphyxiation. Oxygen is administered

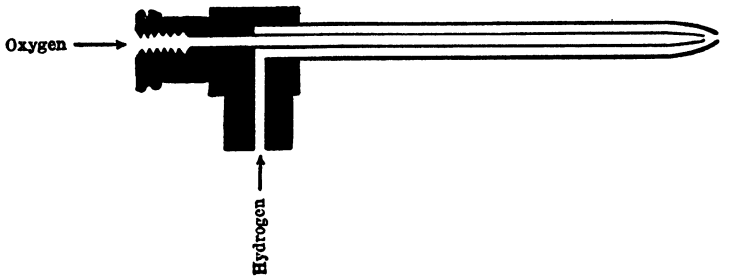


FIG. 34. — Oxy-Hydrogen Blowpipe.

along with the anaesthetics for anaesthetizing patients for surgical operations. When oxygen is used for respiration, it is usually mixed with carbon dioxide to give a mixture which contains 5.5% of carbon dioxide, the approximate percentage of this gas normally in the air in the lungs. This serves as an aid in the regulation of the respiratory function. Oxygen is used to maintain the proportions necessary for respiration in submarines and in airplanes at high altitudes.

Occurrence and Industrial Preparation of Hydrogen. Approximately one per cent of the matter in the outer part of the earth and its atmosphere is hydrogen. This percentage seems small, in view of the large amount of water and other hydrogen compounds on the surface of the earth, until it is recalled that the atomic weight of hydrogen is much smaller than that of the other elements. It has been estimated that hydrogen would account for about 16%, and stand next in order after oxygen, if the composition were expressed in relative numbers of atoms. The most abundant of the hydrogen compounds is water, which contains approximately 11% of this element. Hydrogen is a constituent of organic matter. Soft coal, natural gas, and petroleum are composed largely of hydrogen compounds. All acids

and metal hydroxides contain hydrogen. Free hydrogen does not occur to an appreciable extent.

The industrial preparation of hydrogen is based on the decomposition of its naturally occurring compounds. There are three common methods of preparing commercial hydrogen: the reaction of carbon with water; the electrolysis of water; and the destructive distillation of coal. *In the water-gas method* for the preparation of hydrogen, steam is passed over coke at a temperature of 1000°, producing carbon monoxide and hydrogen. The reaction is accompanied by the absorption of energy.

$$C + H_2O \longrightarrow CO + H_2 - 28{,}300 \text{ cal.}$$

When this gas mixture with an excess of steam is passed over a catalyst consisting of iron oxide with small proportions of the oxides of nickel and chromium, at a temperature of 500°, a second reaction occurs, yielding carbon dioxide and hydrogen.

$$CO + H_2O \longrightarrow CO_2 + H_2 + 9800 \text{ cal.}$$

These reactions show that carbon monoxide is the more stable product at temperatures above 500°, but that carbon dioxide is the more stable product below 500°. The carbon dioxide is largely removed by dissolving it in water under pressure, and the remainder is removed by reaction with sodium hydroxide or calcium hydroxide.

$$2\,NaOH + CO_2 \longrightarrow H_2O + Na_2CO_3.$$

The gas still contains a small percentage of carbon monoxide. This may be removed by preferential oxidation, by introducing the proper amount of oxygen to oxidize only the carbon monoxide and passing the mixture over a second oxide catalyst. The carbon dioxide formed in this step is removed as just indicated.

The electrolysis of water containing dissolved sodium hydroxide, to provide a conducting solution, yields hydrogen at the cathode and oxygen at the anode. Hydrogen is a by-product of the production of sodium hydroxide and chlorine by the electrolysis of solutions of sodium chloride.

Destructive distillation is a process in which a substance is strongly heated in the absence of air so that it decomposes with the volatilization of products of lower boiling points. *The destruc-*

tive distillation of soft coal produces coal gas and leaves a residue of coke. Approximately 50% of the gas is hydrogen. The other components of the mixture may be removed by liquefaction, leaving gaseous hydrogen.

Properties and Reactions of Hydrogen. The gas is colorless, odorless, and tasteless, and is very slightly soluble in water. It has the least density of all of the substances. At 0° and 760 mm., one liter of hydrogen weighs 0.0899 g. Hydrogen diffuses more rapidly than any of the other gases. This may be shown by placing a jar of hydrogen over a porous bulb containing air at atmospheric pressure, arranged as shown in Fig. 35. Molecules of hydrogen pass through the pores into the jar so much faster than molecules of nitrogen and oxygen emerge that a pressure is created and a jet of water is forced out of the side tube. Relatively large volumes of hydrogen are absorbed by some of the metals. Finely divided iron absorbs approximately 20 times its volume, and palladium approximately 800 times its volume of hydrogen at 20° and a pressure of the gas equal to one atmosphere. The critical temperature of hydrogen is − 240° and the critical pressure, 12.8 atmospheres. The liquid has a boiling point of − 252.7° and a freezing point of − 259.2°.

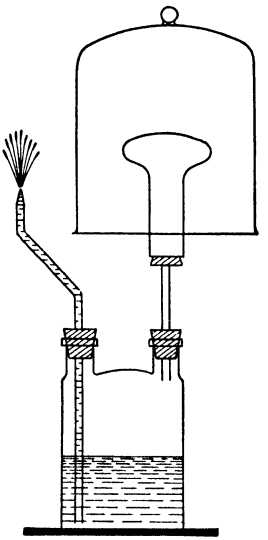


FIG. 35

The reactions of hydrogen with non-metallic elements have been discussed in a preceding paragraph. *The oxides* of a number of the elements react with hydrogen at elevated temperatures, yielding the metal and water.

$$CuO + H_2 \longrightarrow Cu + H_2O.$$

Under high pressure and in the presence of a zinc catalyst, hydrogen reacts with carbon monoxide to form methanol, methyl alcohol.

$$CO + 2\,H_2 \longrightarrow CH_3OH.$$

Hydrogen combines directly with some of the hydrocarbons and their derivatives, in a reaction known as *hydrogenation.* In the

presence of platinum as a catalyst, hydrogen combines with ethylene to form ethane.

$$C_2H_4 + H_2 \longrightarrow C_2H_6.$$

Compounds which, like ethylene, may undergo addition reactions are called unsaturated compounds.

Deuterium. In 1931, Urey, Murphy, and Brickwedde announced the discovery of a variety of hydrogen with an atomic weight almost double that of ordinary hydrogen. This heavy hydrogen is now known as *deuterium.* When sodium hydroxide solution is electrolyzed between nickel electrodes, the hydrogen set free at the cathode contains a much smaller proportion of deuterium than the water; and, consequently, deuterium-containing molecules of water accumulate. The physical properties of deuterium differ from those of hydrogen. The density of the gas is almost double that of hydrogen; the boiling point of the liquid is − 249.5° and the freezing point is − 254.3°. The chemical reactions of the two atoms are almost identical. Two varieties of atoms which have the same chemical properties, but different atomic weights, are called *isotopes.* Hydrogen and deuterium are isotopes.

Industrial Uses of Hydrogen. On account of its low density, hydrogen has been used extensively in balloons and dirigibles. Its combustibility is a serious objection to its use for this purpose; and a number of disastrous explosions and fires, resulting in the total destruction of the airship and the loss of the lives of most of those on board, have resulted from this cause. Helium, which has about 90% of the buoyant effect of hydrogen, is preferable for such uses, but the lack of available supplies of the gas in large quantity has prevented its extensive use.

In addition to its use in the oxy-hydrogen blowpipe, the gas is used in an atomic hydrogen blowpipe, developed by Langmuir about 1927. Gaseous hydrogen is composed of diatomic molecules which decompose into single atoms with the absorption of a large amount of heat when the gas is blown through a very hot electric arc. In contact with metal surfaces, the atoms reassociate rapidly and heat equal to approximately 103,000 calories per mole is evolved.

$$H_2 \rightleftharpoons 2\,H - 103{,}700 \text{ cal.}$$

Temperatures estimated to be between 4000° and 5000° may be obtained. Since the product of the reaction is gaseous hydrogen, an atmosphere of a reducing gas may be maintained at the surface of the metal and this serves to prevent the combustion of metals being welded.

Large amounts of hydrogen are used in the production of synthetic ammonia and synthetic methanol. An important industrial use of hydrogen is the hydrogenation of vegetable and animal oils to produce fats. In the process hydrogen combines with unsaturated compounds in the oil to produce saturated compounds which have higher melting points. The hydrogenation of cottonseed oil is carried out at 200°, in the presence of finely divided nickel as a catalyst, with the gas at a pressure of approximately 5 atmospheres. The products of the hydrogenation of such oils are used as edible fats, in soap making, and for various other purposes. Catalytic hydrogenation makes it possible to increase the yield of gasoline during the distillation and cracking of petroleum, and to produce liquid fuels from low-grade coal.

Occurrence and Properties of Water. In addition to its occurrence in the familiar liquid, gaseous, and solid states, large amounts of water are held in combination by mineral substances as water of hydration. Animal and vegetable matter contain relatively large proportions of water.

The physical properties of liquid water are highly important because it is the most familiar and important of the liquids. The melting and boiling points of water have been selected arbitrarily as two fixed points on the centigrade scale of temperatures. The heat capacity of water, the amount of heat necessary to raise the temperature of one gram of water one degree at 14.5°, is arbitrarily set as one unit of heat, one calorie. Since the heat capacity of water is the basis of the heat unit, the specific heat of a substance is the ratio of the heat capacity of that substance to water. The heat capacity of water is much higher than that of most common substances of which the soil and rocks are composed. Therefore, large bodies of water exert a moderating influence on atmospheric temperatures in the vicinity. The density of a substance is equal to the weight of unit volume. The weight of one milliliter of water at 4° is equal to one gram. The heat of fusion of water is 80 calories. It is due to the absorption of heat in melting that

ice is so extensively used as a refrigerant. The density of ice is lower than that of liquid water at the freezing point, and ice forms at the surface of a body of water. If the contraction in volume of water continued in a regular manner during its cooling and solidification, ice would sink to the bottom and bodies of water would become completely frozen during prolonged cold weather. The heat of vaporization of water is 540 calories. Consequently, steam possesses a great deal more energy than liquid water at the same temperature and this additional energy may in part be converted into useful work.

Deuterium Oxide. The oxide of the heavy isotope of hydrogen, deuterium oxide, is also known as *heavy water*. At 25°, this substance has a density of 1.1 g. per milliliter. Its boiling point is 101.4°, and its heat of vaporization is approximately 260 calories per mole greater than that of ordinary water. The melting point of the solid is 3.8°. The chemical properties are the same as those of water modified to only a small extent by the greater molecular weight.

Composition of Water. The composition of water *by weight* may be determined most accurately by synthesizing the compound, *i.e.*, preparing the compound from the elementary constituents. The principle involved may be illustrated by the following simplified experiment for measuring the proportions of hydrogen and oxygen in water. An accurately weighed sample of copper oxide contained in the boat, *B*, Fig. 36, is placed in the

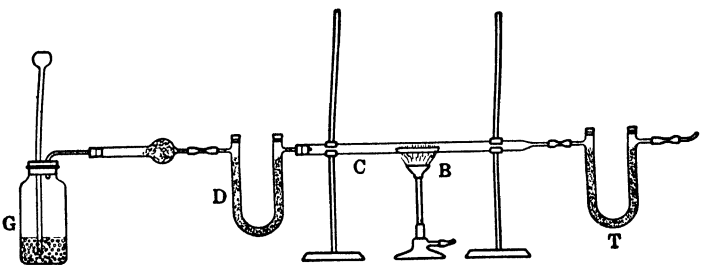


FIG. 36

combustion tube, *C*, where it may be heated in a current of hydrogen. Hydrogen from the cylinder, or generator, *G*, is dried by passage through the calcium chloride tube, *D*. The absorption tube, *T*, also contains calcium chloride; and the weight of this tube and its contents is determined. When the copper oxide is heated in the current of hydrogen, water is formed and is swept

along into the calcium chloride tube by the current of hydrogen. In this tube, the water is absorbed and the excess of hydrogen is allowed to escape. At the conclusion of the experiment, both the boat and the absorption tube are weighed again. The loss in weight of the boat and its contents represents the weight of oxygen. The gain in weight of the calcium chloride tube is the weight of water formed. The difference in weight between the water and the oxygen is the weight of hydrogen which enters into the reaction. Using many refinements to increase the accuracy of the results, Dumas obtained as the average of a number of closely agreeing measurements the ratio, 1.002 parts by weight of hydrogen to 8 parts by weight of oxygen. Using a different method in which he weighed the hydrogen, oxygen, and water directly, Morley obtained the average ratio of 1.0076 parts by weight of hydrogen to 8 of oxygen.

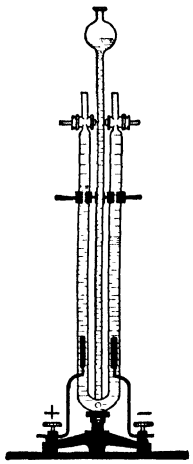


FIG. 37. — Electrolysis of Water.

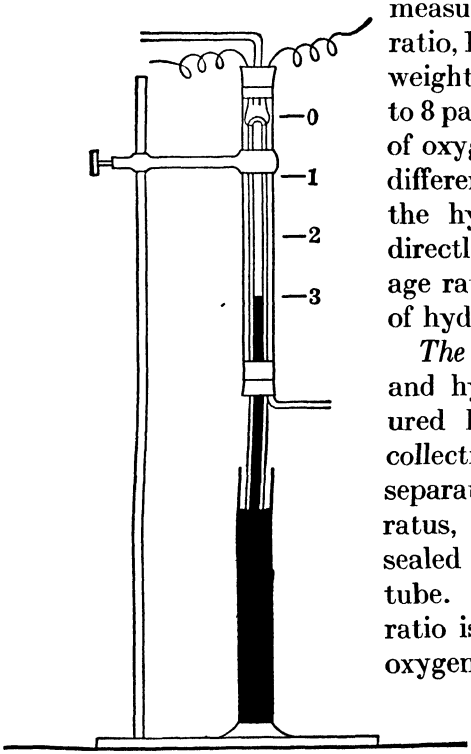


FIG. 38

The volume ratio in which oxygen and hydrogen unite may be measured by electrolyzing water, and collecting the gases produced in separate containers. In the apparatus, Fig. 37, the electrodes are sealed in the opposite limbs of the tube. It is found that the volume ratio is two of hydrogen to one of oxygen. To determine the ratio of the volumes of these gases to that of the water formed, it is necessary to make measurements under conditions of temperature and pressure at which water also is in the gaseous state. In the apparatus, Fig. 38, hydrogen and oxygen

are collected in a volume ratio of two to one over mercury in a barometer tube, maintained at a temperature of 100°. Reaction is caused by a spark and the pressure is readjusted to its former value. It is found that the volume of gaseous water is two thirds that of the mixed gases, or equal to the volume of the hydrogen and double that of the oxygen.

Reactions of Water. Relatively large amounts of energy are evolved in the union of hydrogen and oxygen, and water is stable toward heat. At 2000°, it is decomposed into the elementary gases to the extent of only 1.8%. The reaction of water with the active metals yields hydrogen and the hydroxide of the metal. Many metals of lower activity, which do not react with water at ordinary temperatures, do react when they are strongly heated in contact with water. When steam is passed through a tube containing finely divided zinc or iron which is strongly heated, hydrogen and the oxide of the metal are formed.

$$Zn + H_2O \longrightarrow ZnO + H_2.$$

The reactions of water with the oxides of the metals have been illustrated previously. There are a number of compounds which react more or less extensively with water in a reaction known as hydrolysis. *Hydrolysis* is a reaction in which water is one of the reactants and an acid or a base, or both acid and base, are formed. Calcium hydride, CaH_2, reacts with water to produce calcium hydroxide and hydrogen.

$$CaH_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + 2\,H_2.$$

Calcium carbide, sometimes called calcium acetylide, CaC_2, reacts in a similar manner, yielding calcium hydroxide and acetylene.

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2.$$

The products of these reactions do not interact with each other. There are, however, many salts which hydrolyze, forming both a basic and an acidic product. These products interact with each other in a reaction which is opposite in effect to the reaction of hydrolysis. Consequently, the hydrolysis of salts is usually incomplete. A number of factors determining the extent of reactions of hydrolysis remain to be considered so that this topic will be discussed more fully in Chapter XIV.

Hydrated Compounds. Many compounds combine with water to form products known as *hydrates.* If copper sulfate is dissolved in water and the solution is allowed to evaporate, a mass of irregular blue crystals, blue vitriol, is obtained. When the dry crystals are analyzed, it is found that the water and copper sulfate are in the definite proportions of five moles of water to one of copper sulfate. Examination of the internal structure of the crystals by X-ray methods shows that the water is present in the form of molecular particles held in combination by the other crystal units. The formula of the hydrated copper sulfate is written $CuSO_4(H_2O)_5$.

Hydrated compounds differ greatly in their stability. If the hydrate is stable, only a low pressure of water vapor in the air in contact with the crystal is required to prevent decomposition. Unstable hydrates give up their water of hydration so rapidly that a large pressure of water vapor is necessary to prevent decomposition. The hexahydrate of strontium chloride, $SrCl_2(H_2O)_6$, decomposes to form the dihydrate, $SrCl_2(H_2O)_2$, as the first dehydration product. The change is reversible and a definite pressure of water vapor is required to maintain equilibrium, as in the evaporation of pure water.

$$SrCl_2(H_2O)_6 \rightleftharpoons SrCl_2(H_2O)_2 + 4\,H_2O.$$

At 20°, the pressure of water vapor in equilibrium with the hexahydrate is 5.65 mm. Suppose that the hydrate is exposed to air on a day when the relative humidity is 30 and the temperature is 20°. The pressure of water vapor in the air is 30% of 17.5 mm., 5.25 mm. Consequently, the hydrate decomposes to produce the dihydrate. If, however, the relative humidity is 40, the pressure of water vapor in the air is 40% of 17.5 mm., or 7 mm. Under these conditions the hexahydrate does not decompose; and, if already partially dehydrated, it will become fully hydrated again. The spontaneous dehydration of a hydrate is known as *efflorescence.* Whether a hydrate decomposes or not depends on the pressure of water vapor required for equilibrium at the particular temperature, and the pressure of the water vapor actually in the air. Anhydrous salts contain no water of hydration. If such substances yield hydrates having very low equilibrium pressures of water vapor, they may be used for drying gases.

Natural Waters. Rain results from the condensation of water vapor in the air and is very nearly pure water, containing only small proportions of dust and dissolved gases. However, as water flows over the surface of the earth and seeps down through the soil, soluble substances are leached out and finely divided solids may be carried along in suspension. As a result, water in streams and lakes, fed either by surface water or by springs, contains impurities held partly in solution and partly in suspension. The suspended matter may consist of mineral substances such as sand and clay, or of organic matter such as living microörganisms or dead animal and vegetable matter. The dissolved matter may be dissolved gases, solids, or liquids.

When the velocity of flowing water decreases, suspended solids tend gradually to settle, forming a deposit of sand or mud, unless the particles are exceedingly finely divided; but dissolved solids are carried along by the water until eventually they reach the ocean. Such dissolved matter does not evaporate with water from the surface of ocean water, and the concentration of mineral matter in sea water very slowly increases. Sea water contains approximately 3.6% of mineral matter held in solution.

Water Supplies. As the density of population increases and industrial developments become more extensive, the problem of securing an adequate supply of water becomes more urgent. The suitability of water for different uses depends on the nature of the impurities in the natural water supply. For use in steam boilers, water should be free from substances which cause the formation of a scale in the boiler and the corrosion of the boiler tubes. For use in the laundry, substances which react with soap are objectionable. For use as drinking water, it is necessary that it be free from all impurities which render it dangerous; and it is desirable that it be free also from substances which impart disagreeable odor and taste. The water from springs and wells, protected from contamination by surface drainage, is no longer sufficient to meet the demands, except in rural sections of the country. One can be sure of the safety of surface streams for drinking water only in sparsely settled regions, remote from human habitation. Near many of our cities we find enormous reservoirs constructed in suitable water courses. Large areas of surrounding land on the water sheds from which such reservoirs

receive their supply are fenced off to prevent, in so far as it is possible to do so, the danger of contamination of the water.

Water Treatment and Purification. The purification of water involves different methods of treatment, depending on the impurities which are present and the uses for which the water is intended. Suspended matter may be removed by allowing it to settle out and by filtration; but dissolved substances are not removed in this way. The presence of dissolved salts of calcium and magnesium is particularly objectionable in water to be used in steam boilers. Water containing these substances is known as hard water. The treatment of water to remove such impurities will be considered later.

In the case of drinking water, disease germs are the most dangerous form of impurity. These minute organisms are largely present attached to particles of suspended matter; but perfectly clear water may also contain such microörganisms. Many epidemics of disease have been traced to the contamination of the water supply by sewage. This is particularly true in the case of typhoid fever and cholera. Since it may not be possible entirely to prevent

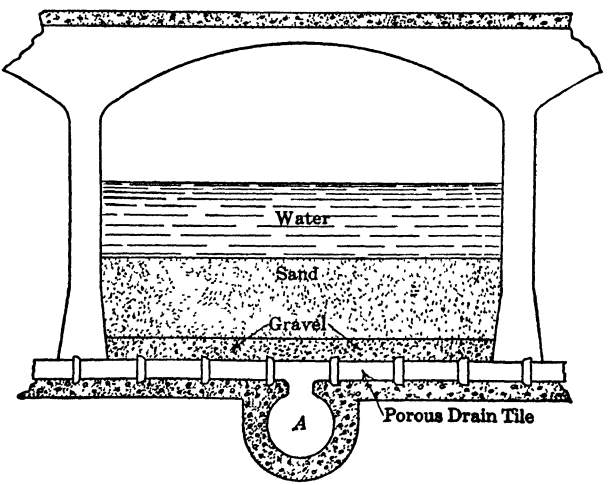


FIG. 39. — Filter Bed.

the entrance of sewage into streams from which city water supplies are secured, it is necessary to treat the water so as to insure the removal of excessive numbers of dangerous living organisms in order to secure a safe supply of water. This treatment usually

involves the clarification of water, followed by the use of disinfectants. The most general method of clarifying water consists in filtering it through beds of sand, Fig. 39. In most cases, substances such as alum and lime or ferrous sulfate and lime are added in the proper amount. These substances react to produce gelatinous precipitates which cause the coagulation of the suspended matter in the water. The coagulated solids may be allowed to settle, or may be removed by filtration through a thin sand filter in a rapid process. This coagulation treatment causes the removal of nearly all of the living organisms in the water. In order to insure a water supply entirely free from disease germs, however, the filtered water is disinfected by the use of chlorine. Ozone is used to some extent for this purpose, and ultraviolet rays have also been found effective. Nevertheless, the use of chlorine is the common method. The significance in modern civilization of the purification of water cannot be overestimated. The health of the community is safeguarded, and a saving of millions of dollars annually is accomplished by the chemical control of water supplies.

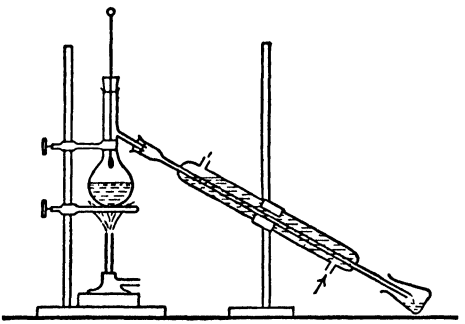


FIG. 40. — Distillation.

The presence of the impurities found in natural water is objectionable also when the water is to be used as a solvent in chemical processes. Suspended matter is first removed by filtration or settling, and the water is then distilled. In this operation, water is boiled and the steam is condensed so that it flows into a clean vessel. A laboratory apparatus for carrying out a simple distillation is shown in Fig. 40. Impurities which are not volatile at the temperature of boiling water are left in the distilling flask. The water may be subjected to chemical treatment to remove certain volatile compounds and organic matter by distilling it from alkaline potassium permanganate solution. Water slowly attacks glass, and does not remain pure when it is kept in glass vessels. Tin is frequently used for making the condenser tubes and receivers for distilled water, since it is not appreciably attacked by water.

Hydrogen Peroxide. This substance contains the same two elements as water but the atomic proportions are different, as shown by the formula, H_2O_2. The substance is a weak acid containing two replaceable hydrogen atoms per molecule. The metal peroxides are salts of this acid. The peroxide radical contains two atoms of oxygen and has an oxidation state of 2 −.

Preparation of Hydrogen Peroxide. Hydrogen peroxide is prepared by the reaction of barium peroxide with sulfuric acid, barium sulfate being precipitated and separated by filtration.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2.$$

Hydrogen peroxide is also prepared by the electrolysis of sulfuric acid of 1.35–1.45 specific gravity. The principal reaction at the anode, the positive electrode, when a high potential is used is the formation of peroxydisulfuric acid, $H_2S_2O_8$. This substance reacts with water, forming hydrogen peroxide and sulfuric acid.

$$H_2S_2O_8 + 2\,H_2O \longrightarrow 2\,H_2SO_4 + H_2O_2.$$

Both methods are used commercially.

Properties and Reactions of Hydrogen Peroxide. Hydrogen peroxide is unstable, but decomposes only slowly in dilute solutions in the dark. By evaporation under reduced pressure, it may be concentrated to a 30% solution, or higher. The usual pharmaceutical solution contains approximately 3% of hydrogen peroxide. The rate of decomposition is retarded by the presence of acetanilide, and is accelerated by the presence of finely divided metals, manganese dioxide, ferrous sulfate, saliva, and blood serum.

The decomposition of hydrogen peroxide yields water and oxygen in an exothermic reaction.

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2 + 46{,}200 \text{ cal.}$$

Consequently, it exhibits reactions which are similar to those of oxygen; but, like ozone, it is more active than oxygen, because it contains a larger amount of energy. It reacts with potassium iodide to liberate iodine.

$$2\,KI + H_2O_2 \longrightarrow 2\,KOH + I_2.$$

Since starch gives a blue coloration with free iodine, a test for hydrogen peroxide may be based on this reaction, if it is known

that ozone, chlorine, and other substances which also liberate iodine from potassium iodide are not present. The most important use of hydrogen peroxide is as a germicidal and antiseptic solution. It is also used as a bleaching agent for hair, silk, and feathers.

Oxidation and Reduction. Many of the reactions discussed in preceding pages in this chapter involve changes in the oxidation states of some of the atoms and radicals. Changes of this nature occur in all decomposition and displacement reactions and in the direct union of the elementary substances. Reactions in which such changes occur are known as oxidation-reduction reactions. A provisional definition of the processes of oxidation and reduction will be given now; but a more exact definition may be given only after the study of the electronic nature of such changes. An *oxidation* is a change in which the valence, or oxidation state, of an element is raised; and a *reduction* is a change in which it is lowered. Since the two changes occur simultaneously, the reaction is an oxidation-reduction. The increase in the oxidation state of one element is compensated by an equivalent reduction in the oxidation state of another element. During the decomposition of potassium chlorate, oxygen is oxidized to the free state and chlorine is reduced to the chloride state. When zinc displaces hydrogen, zinc is oxidized and hydrogen is reduced. The combination of hydrogen with chlorine involves the oxidation of hydrogen and the reduction of chlorine. Substances which cause oxidation are *oxidizing agents.* Oxygen, ozone, and hydrogen peroxide are oxidizing agents; and their most important uses are based on this property. Substances which are easily oxidized are *reducing agents.* Hydrogen and the metals are reducing agents.

Calculation of the Reacting Quantities of Substances. The equations which represent reactions show the proportions in which the substances react. In equations the proportions are expressed in moles and gram atoms. To calculate the quantities expressed in other units it is merely necessary to convert the proportions stated in moles into the units demanded in the problem, and then perform the very simple arithmetical operations required. The reacting proportions may be expressed in ordinary units of weight; and, if gaseous, they may be stated in volumes

also. The solutions of problems to illustrate these simple types will now be given.

Suppose the problem requires the calculation of the weight of oxygen that can be obtained from 10 g. of potassium chlorate. The equation is:

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2.$$

2 moles of potassium chlorate yield 3 moles of oxygen.
1 mole of potassium chlorate yields $1\frac{1}{2}$ moles of oxygen.

The unit of measurement required in this problem is the gram.

122.56 g. of potassium chlorate yield 48 g. of oxygen.
10 g. of potassium chlorate = 10/122.56 = 0.0816 mole of potassium chlorate.
10 g. of potassium chlorate yield $0.0816 \times 48 = 3.917$ g. of oxygen.

If the reaction involves gaseous substances, the volumes of the gases involved may be calculated from the equation. Suppose that the problem is to calculate the volume of oxygen required for the complete combustion of 5 liters of acetylene.

$$2\ C_2H_2 + 5\ O_2 \longrightarrow 4\ CO_2 + 2\ H_2O.$$

2 moles of acetylene require 5 moles of oxygen.
1 mole of acetylene requires $2\frac{1}{2}$ moles of oxygen.

But equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. Hence, 5 liters of acetylene require $5 \times 2\frac{1}{2}$ liters = 12.5 liters of oxygen.

A third type is that in which the volume of a gas is calculated from the weight of a solid involved in a reaction. The volume of dry hydrogen, measured under standard conditions of temperature and pressure, produced by the reaction of 5 g. of zinc with sulfuric acid is to be calculated.

$$Zn + H_2SO_4 \longrightarrow H_2 + ZnSO_4.$$

1 gram atom of zinc yields 1 mole of hydrogen.
5 g. of zinc = 5/65.38, or 0.0765 gram atom.
1 mole of hydrogen at standard conditions occupies 22.4 liters.
5 g. of zinc yield 0.0765×22.4 liters = 1.614 liters of hydrogen.

If conditions other than standard are involved, one has merely to apply the gas laws for the conversion of this volume to the new conditions. Other problems of these types are included in the list of problems at the end of the book.

EXERCISES

1. In terms of the atomic-molecular theory, what changes occur during the following types of reactions: decomposition; displacement; direct union of elements?
2. Write equations to illustrate several reactions of each type.
3. What changes in valence accompany reactions of the types just illustrated? For each type, select an example and specify the valence changes which occur.
4. In terms of valence, state the meaning of oxidation-reduction.
5. What two classes of products result from the union of oxides with water? How are the differences explained?
6. Represent by equations reactions of oxides with water, with acids, and with metal hydroxides.
7. Describe the laboratory preparation of oxygen and of hydrogen.
8. How is oxygen prepared industrially? Discuss the industrial importance of oxygen.
9. Discuss the industrial preparation and importance of hydrogen.
10. What are hydrates? Discuss the relation of the anhydrous material to the hydrate.
11. Compare the composition of water and hydrogen peroxide. State the law illustrated and account for the fact in terms of the atomic theory.
12. How do you account for the fact that oxygen, ozone, and hydrogen peroxide show many common reactions, but that ozone and hydrogen peroxide are more active than oxygen?

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CHAPTER V

ATOMIC WEIGHTS. THE CLASSIFICATION OF THE ELEMENTS

Dalton's atomic theory emphasized the significance of the weights of the atoms as their distinguishing feature. Consequently, attempts to classify the elements on this basis were soon made. Early determinations of the atomic weights indicated that the weights of the atoms of all of the elements were multiples of that of hydrogen. In 1815, Prout, a British physician, advanced the suggestion that the atom of hydrogen might be the fundamental unit of which all atoms are composed. The more accurate determination of atomic weights by Berzelius and by Stas showed that many of the atomic weights are not multiples of the atomic weight of hydrogen, and the hypothesis of Prout was abandoned.

The Triads of Döbereiner. Similarities in the behavior of certain elements were observed and associated with the atomic weights of the elements. In 1829, Döbereiner pointed out that there are a number of elements which may be arranged in groups of three, so related to each other that the atomic weight and properties of one of the three are approximately the mean of those of the other two. This relationship may be illustrated by the three common halogens. The mean of the atomic weights of chlorine, 35.46, and iodine, 126.92, is 81.19; whereas the atomic weight of bromine is found to be 79.92. It will be recalled that bromine is intermediate between chlorine and iodine in both physical and chemical properties. The relations shown by such triads indicate the validity of the assumption that the properties of the elements are related to the atomic weights; but the triads did not serve as a basis for the classification of the elements. Insufficient data were available for a complete classification prior to 1860. A number of the elements had not been discovered and the relationships between equivalent weights, atomic weights, and molecular weights were not clearly understood.

The Determination of Atomic Weights. According to the atomic theory, the atom is the chemical unit of elements; and molecules of compounds contain integral numbers of atoms of the constituent elements. The number of molecules in one mole is the same as the number of atoms in one gram atom, because both are based on the same unit. Consequently, one mole of any compound contains at least one gram atom of each element in that compound; but, of course, one mole may contain some other integral number of gram atoms of each element. If a large number of compounds of some particular element are investigated, one or more of these is likely to contain only one gram atom per mole. *The gram atom of an element is the smallest weight of that element found in one mole of any of its compounds.*

The determination of atomic weights on the basis just given was proposed by Cannizzaro in 1860. He revived the hypothesis of Avogadro, which had been advanced nearly fifty years earlier, and showed that the molecular weights of gases and easily volatilized substances may be measured experimentally through the application of this principle. Such determinations have already been illustrated in the discussion of matter in the gaseous state. Methods are also available for the determination of the molecular weights of substances in solution. These will be discussed in Chapter IX.

In the experimental determination of the atomic weight of an element by this method, the first step is to find the weight of one

TABLE 2

COMPOSITION OF SOME COMPOUNDS OF CHLORINE

Compound	*Molecular Weight*	*Per Cent of Chlorine*	*Weight of Chlorine in 1 Mole*
Hydrochloric acid	36.2	97.3	35.2
Carbonyl chloride	99.6	71.8	71.5
Chloroform	119.0	89.1	107.0
Phosphorus trichloride	138.2	76.7	106.0
Phosphorus pentachloride	209.4	85.1	178.2
Methyl chloride	50.8	70.3	35.7
Carbon tetrachloride	154.8	92.2	142.7
Ethyl chloride	64.2	55.0	35.3
Sulfur monochloride	135.5	52.6	71.4
Aluminum chloride	133.1	79.8	106.2

mole of a large number of its available compounds. The next step is to calculate the weight of that element in one mole of each compound. These weights are equal to one gram atom or some integral number of gram atoms of the element. The smallest weight so found is taken to be the gram atom of the element. The data for a number of compounds of the element chlorine are listed in Table 2.

Inspection of the data shows that the average value of the gram atom found by this method is 35.4 g. Hence, the atomic weight is equal to approximately 35.4. The values obtained from different compounds do not all agree, and are not highly accurate, because the molar weights upon which they are based are not usually determined with a high degree of precision.

Approximate Atomic Weights from Specific Heats. According to the *Rule of Dulong and Petit*, which was stated in 1819, the product of the gram atomic weight of a solid element and its specific heat is approximately equal to a constant. That is, the atomic heat capacity, or the number of calories required to raise the temperature of one gram atom of solid elementary substances one degree, is approximately constant. At 20°, the average value is equal to 6.2, if one leaves out of consideration four elements for which the atomic heat capacities differ widely from the average: *viz.*, carbon, boron, silicon, and beryllium. This rule furnishes a basis for the determination of the approximate atomic weights of solid elements, and is particularly useful for those elements which form few volatile compounds. The specific heat of iron at 20° is 0.113. The approximate atomic weight of iron, calculated according to this rule, is equal to

$$6.2 \div 0.113 = 56.6.$$

Accurate Atomic Weights. It has been shown previously that the atomic weight of an element is a multiple of its equivalent weight, because the atomic weight is a measure of the weight of the atom while the equivalent weight takes into account also the numerical ratio in which the atoms unite. The number by which the equivalent weight is multiplied to obtain the atomic weight is the oxidation number of the element in the compound which was used in the determination of the equivalent weight. The equivalent weights of the elements may be determined with a high

degree of accuracy. The determination of the approximate atomic weight is necessary to show which multiple of the equivalent weight is the true atomic weight. Suppose that the smallest weight of sulfur in one mole of its compounds is found to fall between 31 g. and 33 g. It is known from this that the atomic weight of sulfur is approximately 32. Suppose also that the equivalent weight, determined as the average value of a large number of closely agreeing results based on conversion to sulfates, is found to be 5.3433. It is now clear that the accurate value of the atomic weight of sulfur is

$$5.3433 \times 6 = 32.0598, \text{ or } 32.06.$$

Six is the only multiple of the equivalent weight which gives an atomic weight near 32. Hence, the oxidation state of sulfur in sulfates is six.

Classification of the Elements Based on Atomic Weights. With more accurate atomic weights, progress was made in the attempts to classify the elements. In 1865, Newlands proposed his *law of octaves*, that each eighth element in the order of increasing atomic weights "is a kind of repetition of the first." He attempted to make a classification of all of the elements known at the time, arranging them in natural families and periods. His work was not well received, although it involved the fundamental principle that there is a repetition in the properties of the elements with increasing atomic weight. His chief error was due to failure to recognize that there might be other elements not yet discovered, for which blank places in the table should be provided.

The Periodic System of Mendeléef. The fundamental principle which Newlands had attempted to apply was stated by the Russian chemist, Mendeléef, as the **Periodic Law: The properties of the chemical elements are a periodic function of their atomic weights.** This principle was also recognized at about the same time by Lothar Meyer. When the elements are arranged in the order of their atomic weights, it may be observed that, at definite intervals in the list, there are elements which show repetitions in properties. The periodic function is not mathematically exact. The significance of a periodic function is shown in Fig. 41 in which the atomic volumes are plotted against the atomic weights, as was done by Lothar Meyer. It may be

observed that similar elements occupy corresponding positions in the different branches of the curve.

A complete classification of the elements known at that time was made independently by both Mendeléef and Meyer in 1869. Their success was due to recognition of the fact that some of the

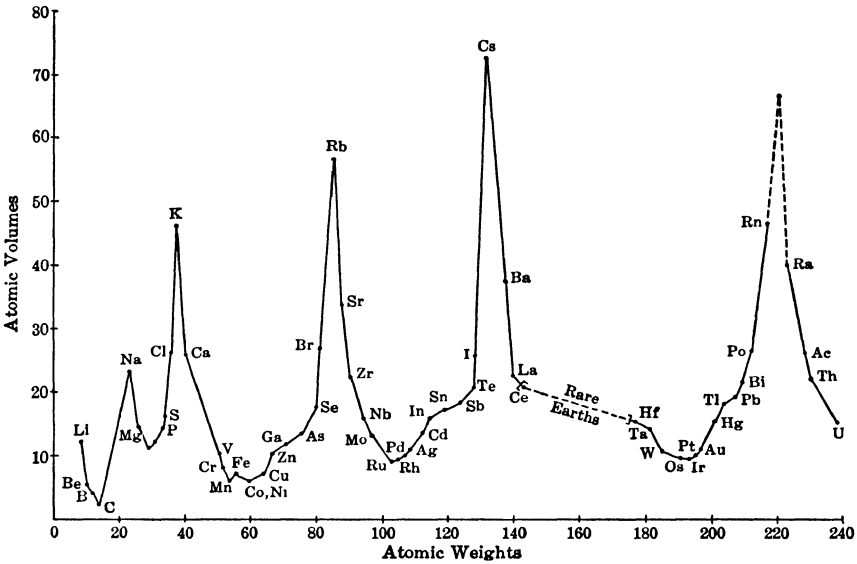

FIG. 41. — Periodic Curve of Atomic Volumes.

elements needed for a complete system had not then been discovered, that the atomic weights of some of the elements were in error, and that the repetition in properties occurs at a longer interval for the elements of the higher atomic weights than for those of the lower atomic weights. Consequently, in the arrangement of the elements in periods and families, blank places were left to represent the positions of elements whose existence was indicated even though they had not been discovered. It was necessary in several instances to invert the order of certain pairs of elements from that of their atomic weights in order to bring them into natural families according to their properties. The inert gases had not been discovered when Mendeléef first made his classification of the elements; and hydrogen was placed alone in the first period, because the regular progression of the elements indicated that it did not fit into any longer period. It was then

observed that the repetition in properties occurs with each eighth element from lithium to chlorine, thus providing two short periods of seven elements each. The next two periods are long periods in which the repetition in properties was observed with the eighteenth element. By making this change in the interval between successive similar elements, a complete classification was secured.

The Periodic Table. A number of forms of the periodic table have been proposed. Each classification is an empirical arrangement based on the atomic weights and properties of the elements, and the different forms serve to emphasize different specific relationships. With the discovery of the inert gases, it is now apparent that there is a second element, helium, in the first period with hydrogen. Each of the two short periods which follow contain eight elements; the fourth and fifth periods contain eighteen elements; and the sixth period contains thirty-two elements. The seventh period is incomplete. The most useful form of the periodic table is one which contains eighteen columns, so as to provide a space for each of the elements in the long periods. It is evident that the number of elements in each of the short periods is not great enough to furnish an element for each of these columns. In the first period of two elements, hydrogen is listed in the first column and helium in the last column, Table 3. In this table, the elements are represented by their symbols, and the atomic weights are written beneath the respective symbols. The elements of the second period are lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, and neon. The best correlation of the properties of the elements throughout the table is secured by placing lithium in the column with hydrogen, and beryllium in the second column. The remaining six elements of this period are entered in order in the last six columns, bringing neon in the column with helium. In a similar manner, the eight elements of the third period, sodium to argon, are arranged in the successive columns with the corresponding elements of the second period: *i.e.*, sodium and magnesium in the columns with lithium and beryllium, respectively; and aluminum, silicon, phosphorus, sulfur, chlorine, and argon in the columns with boron, carbon, nitrogen, oxygen, fluorine, and neon, respectively. Argon is the eighth member of this period even though the atomic weight of potassium follows next in order

TABLE 3

PERIODIC CLASSIFICATION OF THE ELEMENTS

Group →	*I*	*II*	*III-B*	*IV-B*	*V-B*	*VI-B*	*VII-B*	*VIII-B*			*I-B*	*II-B*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*
Period ↓																		
I 2 Elements	H 1.008																	He 4.003
II 8 Elements	Li 6.94	Be 9.02											B 10.82	C 12.01	N 14.008	O 16.000	F 19.00	Ne 20.18
III 8 Elements	Na 22.997	Mg 24.32	*Transition Elements*										Al 26.97	Si 28.06	P 30.98	S 32.06	Cl 35.46	A 39.94
IV 18 Elements	K 39.10	Ca 40.08	Sc 45.10	Ti 47.90	V 50.95	Cr 52.01	Mn 54.93	Fe 55.85	Co 58.94	Ni 58.69	Cu 63.57	Zn 65.38	Ga 69.72	Ge 72.60	As 74.91	Se 78.96	Br 79.92	Kr 83.7
V 18 Elements	Rb 85.48	Sr 87.63	Y 88.92	Zr 91.22	Cb 92.91	Mo 95.95	Ma —	Ru 101.7	Rh 102.91	Pd 106.7	Ag 107.88	Cd 112.41	In 114.76	Sn 118.7	Sb 121.76	Te 127.61	I 126.92	Xe 131.3
32 Elements VI	Cs 132.91	Ba 137.36	La* 138.92	Hf 178.6	Ta 180.88	W 183.92	Re 186.31	Os 190.2	Ir 193.1	Pt 195.23	Au 197.2	Hg 200.61	Tl 204.39	Pb 207.21	Bi 209.0	Po —	—	Rn 222
VII 6 Elements	—	Ra 226.05	Ac —	Th 232.12	Pa 231	U 238.07												

*Rare Earth Elements	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	140.1	140.9	144.3	—	150.4	152	156.9	159.2	162.5	163.5	167.2	169.4	173	175

after that of chlorine. It is evident that the properties of potassium do not permit placing it in the group with helium and neon, while argon does fit appropriately in this group and potassium is properly classified as the first member of the next period in the group with lithium and sodium. The columns now occupied may be numbered I to VIII, respectively, leaving at this point in the arrangement, ten columns without numbers between Groups II and III.

The eighteen elements, potassium to krypton, constitute the fourth period. The first two elements, potassium and calcium, are placed appropriately in Groups I and II; and the last six elements in this long period, gallium, germanium, arsenic, selenium, bromine, and krypton, are properly placed in the order of their atomic weights in Groups III to VIII, respectively. The ten elements, scandium to zinc, with atomic weights between those of calcium and gallium, are now listed in the successive ten columns thus far unoccupied. The elements of the fifth period, numbering eighteen and including the elements from rubidium to xenon, may now be distributed correctly in the order of their atomic weights, one in each of the eighteen groups, except that the order of iodine and tellurium is reversed in order to bring these elements into the proper groups. The sixth period contains thirty-two elements; but fifteen of these elements so strongly resemble each other and also scandium and yttrium that they may be placed together in the position of a single element in Group III–B. The six remaining elements, one of which has not been discovered, start the seventh and final period which is incomplete.

The ten columns which intervene between II and III are conveniently designated in serial order III–B to VIII–B, and I–B and II–B. These numbers are intended to indicate certain general relationships with the elements in Groups I–VIII, which will become more apparent after the study of atomic structures in the following chapter. The elements in these groups are known as "transition elements."

Another form of the periodic table, shown in Appendix XII, is used extensively. In this form the long periods bend back, placing two elements in each of the groups except the inert gas group. The elements of the B-group are shown in a separate column in each of these groups.

Applications of the Periodic System. The most important application of the periodic system is in the *systematic arrangement of the elements.* The grouping of the elements according to periodic functions brings into the same column elements which are similar to one another in both physical and chemical properties. An important similarity shown by the elements in each group is in their oxidation states. Many of the elements may exhibit more than one state of oxidation and only the regular group states may be correlated with the positions of the elements in the system. The maximum positive oxidation number of an element is usually the same as the group number, except for the elements in Group VIII. Although many irregularities are observed and the negative oxidation state is unimportant for many of the metallic elements, the negative oxidation number usually increases with the group number to a maximum of four, and then decreases one unit for each group to a value of one for the elements of Group VII. The elements in Group VIII are inert and do not ordinarily exhibit any chemical reactions; and the most common oxidation numbers for the elements in Group VIII–B are two and three positive.

Each of the Groups I–VII, commonly called the *main groups,* contains five or six elements; and the elements in these groups so closely resemble each other that the group relationships are a great aid in the study of the properties and reactions of the elements. Group relationships are not so prominent in the B-groups, frequently called the *subgroups,* but are helpful. Two important generalizations may be listed in dealing with the groups of elements. *The elements in a main group or family closely resemble one another in chemical properties.* As an illustration, the student is reminded that all of the halogens, Group VII, combine with hydrogen to form acids and with metals to form salts which are similar in many respects; and that the oxidation states of these elements are the same in compounds of the same type. The alkali metals of Group I are active metals which react vigorously with water to form basic hydroxides, and with many non-metals to form binary salts. All of these metals exhibit the same oxidation state. *The elements in each family differ in chemical activity, but a regular change in activity is noted in the family.* In families of metals which constitute main groups, the activity generally increases with atomic weight; while in families of non-metals, the

activity decreases with atomic weight. There is also a gradation in physical properties; the density in the same state, for example, commonly increases with the atomic weight. The melting points and boiling points of the non-metals in a family also increase; but there is usually a decrease in these properties for the active metals. Since a great deal of information may be correlated with the position of an element in the periodic table, it is important to know both the group and the period in which the common elements are placed.

In the table originally arranged by Mendeléef, blanks were left to represent elements which were believed to exist even though they were unknown at that time. *On the basis of the general relationships, it was possible to predict the properties of missing elements, and then to proceed in a systematic manner in the search for these elements.* In 1871, Mendeléef predicted the properties of three missing elements to which he gave the hypothetical names, eka-boron, eka-aluminum, and eka-silicon. Within fifteen years, each of these elements was discovered, scandium in 1879 by Nilson, gallium in 1875 by Boisbaudron, and germanium in 1886 by Winkler, and found to exhibit properties remarkably close to those which had been predicted. In Table 4 the properties predicted by Mendeléef are listed under the name "eka-silicon," and the experimentally determined properties under the name "germanium," which was given the element.

TABLE 4

	"Eka-silicon"	*Germanium*
Atomic weight	72	72.5
Specific gravity	5.5	5.47
Color	Dirty-gray	Grayish white
Oxide	Dioxide	GeO_2
Specific gravity of oxide	4.7	4.703
Chloride	Tetrachloride	$GeCl_4$
Boiling point of chloride	Below 100°	86°

In the past, discrepancies in the accepted values of the atomic weights of certain of the elements have become apparent from the relations of the system as a whole. In some cases, the properties of the element obviously placed it in a given group, while the value of the atomic weight as then accepted would have placed it in a

different group. *This has led to a redetermination of the atomic weights and to the correction of errors in the previous determinations.*

Defects in the Periodic System. Although the value of this system of classification is great, there are some respects in which it fails to be fully satisfactory. The relation of hydrogen to the groups is uncertain. Only one or two of the oxidation states of the elements in the groups can receive emphasis, while other states may be as important or more important, particularly in the B-groups. No relation between the activity of the elements in one group and in another group is apparent from the system. Fifteen elements, known as the *rare earths*, with atomic weights between those of barium and hafnium, do not fit into the scheme. These elements show characteristically the common positive valence of three, except that cerium also has a positive valence of four. They are so similar to each other in their chemical properties that their separation offers difficulties. These fifteen elements occupy the position of a single element in the Mendeléef system; and their properties do not permit distributing them in series throughout the other groups. The elements are rare and few of them have practical importance, so that the failure of the system to take them into account is commonly not important.

The periodic system of Mendeléef is based entirely on experimental observation and affords no explanation of the arrangement of the elements according to the scheme employed. Mendeléef had little sympathy with attempts to attach philosophical meaning to the periodic relationships, but insisted that the classification was strictly empirical in nature. The student, however, naturally wishes to know more than the empirical statement of the facts correlated in the periodic classification. He wishes to learn, as fully as may be, why the elements exhibit the gradual change in properties and activity, and why the periodic repetition in properties occurs. The interpretation of the periodicity of the elements was not possible until the composition and structure of the atoms of which they are composed had been fully established by the accumulation of a large amount of experimental data.

EXERCISES

1. What is the relation between the molecular weights of compounds and the atomic weights of the constituent elements? Explain.

2. What is the relation between the atomic weight and the equivalent weight of an element?
3. The smallest weight of a specific element in one mole of any of its compounds is found by experiment to average 11.7 g. An oxide of this element contains 72.727% of oxygen. Calculate the atomic weight of the element.
4. State fully the significance of the periodic law.
5. Sodium in Group I is an active metal, and chlorine in the same period in Group VII is an active non-metal. What properties would you expect to find in a study of the elements in this period between sodium and chlorine? Illustrate by considering the behavior of the hydroxides.
6. Carbon, the element of lowest atomic weight in the main family of Group IV, is non-metallic; and lead, the element of highest atomic weight, is metallic. Predict the properties of the hydroxides of the elements in this family.
7. Referring to the periodic table, estimate the probable atomic weight of the missing element in Group VII in the sixth period. From the properties of the group of which it is a member, predict the probable properties of this element.
8. How has the periodic system aided in the search for missing elements? in the correction of atomic weights?

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CHAPTER VI

ATOMIC STRUCTURES

The relationships expressed in the periodic law show that the properties of the chemical elements are related to successive increases in the weights of the atoms, and lend support to the notion that there are common units of matter of which the atoms of all of the elements are composed. We have seen that the suggestion of Prout, that the atom of hydrogen might be the common unit of all of the atoms, was abandoned because it appeared to be contradictory to the experimental facts. Although Prout's hypothesis was not accepted and was far beyond the experimental resources of the time, in modified form it agrees closely with modern ideas of the constitution of the atoms. It has now been found that a small number of fundamental particles, possibly only three, are required to serve as structural units of all atoms and to account for the differences between them.

The Electron. The nature of one of the minute structural particles, the electron, is best studied by investigating the effects which electrons produce during their existence as independent particles. These effects are produced during the passage of electricity through rarefied gases. The conductivity of electricity by gases at low pressures was discovered by Plücker in 1859. Gases under ordinary pressures are poor conductors of electricity; and an electrical discharge through air at ordinary pressures requires high voltage and takes the form of a spark. If the electrodes are sealed in a glass tube and the air is pumped out, it is found that a continuous flow of the current takes place at low pressures. When the pressure is approximately one thousandth of one atmosphere, beautiful color effects may be observed during the passage of the current through the gas. At a pressure of 0.01 mm., the luminous column disappears and a greenish light, originating in the walls of the tube, is observed. A familiar application of the color effects which accompany the passage of electricity through gases is the

use of tubes containing neon at low pressures for display signs. The mercury and sodium vapor lights are also familiar and have important applications. Another important application is in fluorescent lighting which is coming into increasingly great use for general illumination.

The nature of the radiation which causes the effects observed during the passage of electricity through rarefied gases was investigated by Hittorf, Crookes, Thomson, and many others. Rays originate at the cathode, the negative electrode, and travel in straight lines at right angles to its surface. These rays are known as *cathode rays*. They have low penetrating power so that they are stopped by opaque objects placed in their paths, casting a shadow on the wall of the tube, Fig. 42. They cause the emission of light in certain materials on which they fall. The emission of light caused by subjecting a substance to different kinds of radiation is called *fluorescence*. The rays may be brought to a focus by the use of a concave cathode; and metals which are placed at this focus become highly heated, showing that the rays carry energy. By using a thin metal foil as a portion of the wall of the tube at the end opposite the cathode, the rays may be allowed to pass out of the tube and fall on a photographic plate. The plate is darkened because of the chemical effects produced. The rays cause the formation of gas ions in air, so that they cause rapid loss of the charge on the leaves of a charged electroscope placed in the path of the rays, Fig. 43. A narrow beam of rays may be subjected to the action of an electrical field or a magnetic field. In such a field, the rays are deflected in a direction which shows that they consist of a stream of rapidly moving, negatively charged particles, Fig. 44. The particles which constitute the cathode rays are identical with the "natural unit of electricity," to which Stoney gave the

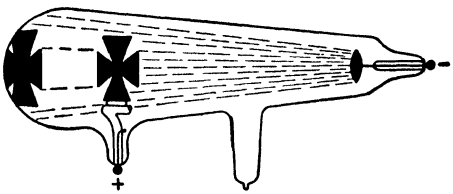


FIG. 42. — Cathode Rays.

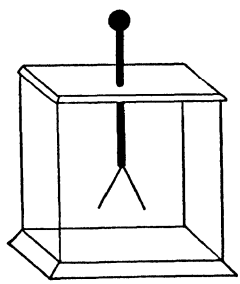


FIG. 43. — Electroscope.

name *electron* in 1891. The determination of the mass, charge, and velocity of the particles is important.

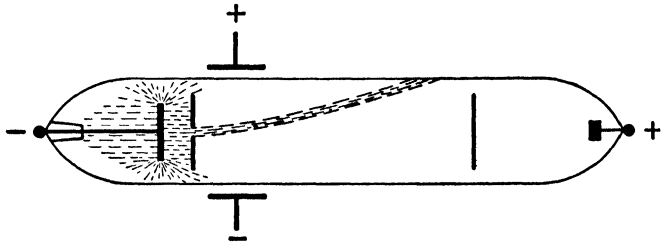


FIG. 44. — Cathode Rays.

Sir J. J. Thomson, in 1897, developed a method for the determination of *the velocity of the cathode particles, and the ratio of the charge to the mass.* The method is based on the deflection of the particles in electrostatic and magnetic fields. By means of a narrow slit in the metal screen, *D*, Fig. 45, a pencil of rays from the cathode, *C*, is allowed to pass on through the tube. The place which the rays strike may be located by the fluorescence which they produce on suitable materials coating the end of the tube. The rays may be subjected to the effects of magnetic and electrostatic fields, *M* and *E*, either separately or simultaneously. A charged particle moving through a magnetic field suffers deflection in a circular path which lies in a plane at right angles to the field. The force tending to cause deflection is determined by the strength of the field, *H*, the charge of the particle, *e*, and the velocity of the particle, *u*, and is equal to the product, *Heu*. Since the particle moves in a circular path, this force is balanced by the centrifugal force acting outward along its radius of curvature, *r*. The centrifugal force is equal to mu^2/r. The two forces are equal, because the relation between them determines the path along which the particle moves.

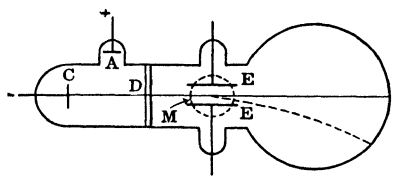


FIG. 45. — Diagram of Thomson's Cathode Ray Tube.

$$Heu = \frac{mu^2}{r}, \quad \text{or} \quad Hr = \frac{mu}{e}.$$

The strength of the field and the radius of curvature may be measured; and the ratio of the product of the mass and velocity

to the charge of the particle may be calculated. An electrical field is now applied so as exactly to counteract the effect of the magnetic field. The force in the electrical field depends on the strength of the field, X, and the charge of the particle.

That is, $$Heu = Xe, \quad \text{and} \quad u = \frac{X}{H}.$$

The strength of both fields may be measured and, thus, the velocity may be calculated. The velocity having been determined, the ratio of the charge to the mass may now be calculated also. The velocity of the particles varies, depending on the potential; but the average velocity during the discharge of electricity through rarefied gases is 2.8×10^9 centimeters per second. The ratio of the charge to the mass, however, is constant for all cathode rays, independent of the nature of the electrodes and of the residual gas in the tube. This ratio is also independent of the velocity unless it approaches that of light. At the higher velocities, the mass of the particle increases and this ratio diminishes. The ratio of the charge to the mass for the cathode ray is found to be 1845 times greater than that for the hydrogen ion. If the charge on the particle is of the same magnitude as that on the hydrogen ion, it is apparent that the mass of the particle is 1/1845 that of the hydrogen ion.

The next step requires the determination of the amount of the *unit charge* and its relation to the charge of the hydrogen ion. The amount of the unit charge has been measured most accurately by Millikan. By the use of an atomizer, minute drops of an oil are blown into the chamber, C, Fig. 46. These droplets slowly settle and eventually one passes through the opening, H, into the observation chamber, O, between the uncharged plates of a condenser. Here it is illuminated by a transverse beam of light, and its motion is observed through a short-focus telescope. The opening into the observation chamber is now closed and the air between the plates is ionized by the passage of X-rays. The rate of fall of the droplet under gravity alone, independent of any charge which it may bear, is measured and compared with the rate of fall when a charge of several thousand volts is placed on the plates of the condenser. When the plates are uncharged the rate of fall of the drop is proportional to its mass and the acceleration of gravity.

When the plates are charged, the droplet, which bears a charge in consequence of the capture of gas ions, is subjected to an additional force which alters the rate of fall; and the behavior of the droplet now depends on the combined effect of the forces of gravity and the electrical field. By the application of these principles, it was found possible to calculate not only the smallest

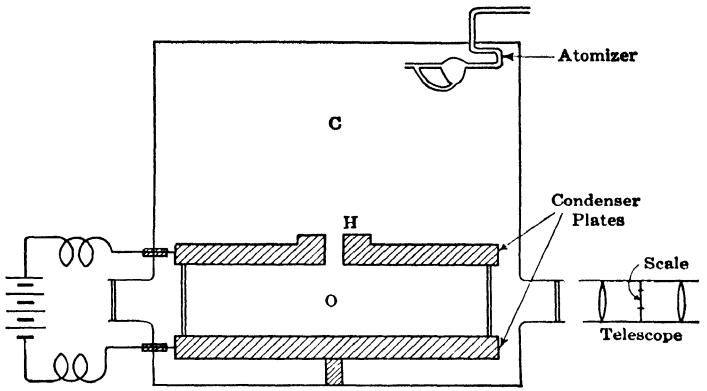


FIG. 46. — Diagram of Millikan's Apparatus for Measuring the Electron Charge.

charge borne by any of the droplets, but also the fact that all other charges, and changes in charge caused by the capture of ions, are multiples of the unit charge. The average value of the unit charge of electricity was found by Millikan to be 4.774×10^{-10} electrostatic units, or 1.59×10^{-19} coulombs, which is the same as the charge of the hydrogen ion.

Millikan's work established the fact that the amount of the charge of the electron is the same as that of any monovalent ion. It is, therefore, established that the mass of the electron is 1/1845 that of the hydrogen ion, since it has been shown that the ratio of the charge to the mass of the cathode ray particle is 1845 times that for the hydrogen ion. There are 6.064×10^{23} molecules in one mole of hydrogen. Hence, one molecule weighs

$$\frac{2.016}{6.064 \times 10^{23}} = 3.324 \times 10^{-24} \text{ g.},$$

and one atom weighs 1.662×10^{-24} g. The mass of the electron is

$$\frac{1.662 \times 10^{-24}}{1845} = 9 \times 10^{-28} \text{ g.}$$

This weight is equal to 0.00054 atomic weight units.

The Proton. In 1886, Goldstein discovered a different type of radiation during the discharge of electricity through rarefied gases at very low pressures and high potential differences. Using a perforated cathode, he observed bands of light in the region of the tube away from the anode, Fig. 47; and he attributed these to rays passing through the cathode in a direction opposite to that of the cathode rays. He called these rays *canal rays.* The nature of these rays was determined by Thomson through the use of methods essentially the same as those used in the investigation of the cathode rays. He found that these rays also consist of particles, but that the particles have masses of atomic magnitudes and move with much lower velocities than the electrons in the cathode rays. The charge borne by these particles is always positive, so that they are called *positive rays.* The magnitude of the charge is either the same as that of the electron or an integral multiple of this unit charge.

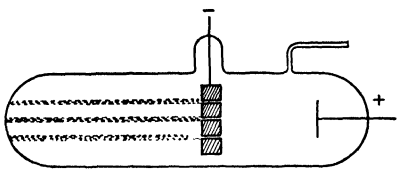


FIG. 47. — Canal Rays.

Positive rays are formed by the removal of one or more electrons from the atoms of the gases remaining in the tube, forming gas ions. *It thus appears that electrons are common constituents of the atoms of the chemical elements.* Methods have been developed which make it possible to analyze positive rays consisting of mixtures of particles of different masses, and to determine the relative masses of these particles. The masses of all of the positive ray particles are nearly multiples of that of hydrogen and are approximately integral numbers on the atomic weight scale. Since the mass of the positive ray formed from ordinary hydrogen is the smallest and all others are multiples of it, when energy relationships are taken into account, this particle is considered to be a second fundamental unit of matter. The name *proton* was suggested by Rutherford for this particle. In the free condition it has an atomic mass of 1.0076, practically equal to that of the hydrogen atom, and a positive electrical charge of one unit.

Röntgen Rays. X-Rays. In 1895, Röntgen discovered a third type of radiation originating in the cathode ray tubes. These rays are not deflected by an electrostatic charge or by a magnet. They have great penetrating power so that they readily

pass through the walls of a tube, affect a photographic plate, cause ionization in air, and produce fluorescence when they fall on materials such as zinc sulfide. These rays, known as the Röntgen or X-rays, originate when the rapidly moving electrons of the cathode rays strike a dense target, so that a portion of their energy is transformed into the rays. In the X-ray tube, Fig. 48, the cathode is so constructed that its rays converge and strike an oblique target, the anti-cathode, made of some dense metal such as tungsten. The X-rays consist of the same kind of radiation as ordinary light and are electromagnetic waves. They differ from ordinary light in that they have much shorter wave length, about one thousandth that of the shorter waves in ordinary light. The wave length of X-rays is of approximately the same magnitude as the distance between the atoms in a crystal. It has been found that crystals may serve as diffraction gratings for X-rays and thus make possible the calculation of the wave length, just as the wave length of light is calculated by the use of diffraction gratings. The radiation from an X-ray tube is usually complex; but certain specific wave lengths are characteristic of the substance of which the surface of the target or anti-cathode is composed. The property of penetrating many substances which are opaque to ordinary light is the basis of the familiar uses of X-rays. They penetrate substances of low density, such as paper and flesh, more readily than substances of high density, such as bones, teeth, and metals.

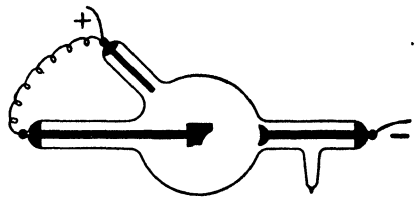


FIG. 48. — X-Ray Tube.

Radiations Produced by the Spontaneous Disintegration of Atoms. The radiations discussed in the preceding paragraphs originate during the passage of electricity through rarefied gases. However, soon after the discovery of X-rays, Becquerel, in 1896, made the first observation of penetrating radiations from chemical substances. The emission of these penetrating radiations by chemical substances is called *radioactivity;* and the elements which emit such radiations are called *radioactive elements.* Becquerel observed that uranium salts emit a radiation which affects the photographic plate, even when it is protected by a wrapping of black paper, and that this radiation causes the formation of gas

ions in air through which it passes, as is shown by the loss of the charge when a uranium salt is placed near the knob of a charged electroscope.

It was observed subsequently that the activity of the radiations from uranium compounds is proportional to the quantity of uranium which they contain. Uranium ores were found to exhibit an activity greater than could be accounted for by their uranium content. Madame Curie and her husband, Pierre Curie, discovered the fact that radioactivity is shown by pitchblende residues from which the uranium has been extracted; and they soon discovered a new radioactive element to which they gave the name, *polonium*. After long and painstaking work, they separated from uranium minerals a compound of an element which was found to be a million times more active than uranium. To this active element the name *radium* was given. The element itself was isolated in 1910 by Madame Curie.

Nature of the Radiations from Radioactive Substances. Three different types of radiation are emitted by the compounds of uranium and the other elements which are found associated with it. These radiations are analogous to those which are observed during the passage of electricity at high potential through rarefied gases.

Beta rays consist of a stream of electrons, particles which are identical with the cathode ray particles. These particles are discharged from uranium and radium minerals with a velocity approaching that of light. They have relatively high penetrating power.

Alpha rays are made up of positively charged particles with a mass equal to approximately four times that of the proton. These particles are identical with the atoms of helium except for their electric charges. When an alpha particle gains two electrons it becomes an electrically neutral atom of helium. The velocity of the alpha particle is approximately one tenth that of light; and these particles have relatively little penetrating power, being stopped by thin metal foil and by a layer of air a few centimeters thick. They have the property of causing fluorescence in many minerals, affecting a photographic plate, and causing the formation of gas ions in air.

Gamma rays, the most penetrating of the radiations, are able to pass through thick layers of metals. These rays do not suffer

deflection in a magnetic or an electrical field and are of the same nature as X-rays, but they have still shorter wave lengths. They probably originate as the result of the mutual destruction of the electron and the positron, a second particle of low mass which is discussed in a subsequent paragraph. In this change, both the electron and the positron disappear, being converted into gamma radiation.

Source of the Alpha and Beta Radiations. Soon after the discovery of radioactivity, the study of the nature of the radiations led Madame Curie to propose the generalization: ***Radioactivity is a property of the atoms of the radioactive elements.*** A particular variety of radioactive atom characteristically emits only one kind of particle; but a mixture of the atoms of two different radioactive elements may give out both varieties. Soddy demonstrated the fact that a pure uranium compound at first exhibits only one kind of radiation, but gradually begins again to show all three kinds. This means that a pure uranium compound contains only one variety of radioactive atom; but through some change which takes place spontaneously other radioactive atoms are produced. It was shown by McCoy that uranium ores always contain radium, and by Boltwood that they contain radon. From these observations, it appears that the emission of either an alpha particle or a beta particle causes the atom to change into another variety of atom, and that other radioactive substances are formed spontaneously from uranium.[1] In 1902, Rutherford and Soddy advanced the disintegration theory of radioactivity which is now universally accepted: ***The atoms of the radioactive elements are complex and they spontaneously disintegrate with the emission of alpha and beta particles and the formation of other complex atoms.*** The atoms of the radioactive substances contain such large amounts of energy that the spontaneous evolution of energy in the form of alpha and beta particles is necessary to maintain equilibrium. In a given period of time, only a definite fraction of the atoms in the sample of the radioactive element reach the condition of instability which causes them to disintegrate. The rates of disintegration of different radioactive elements differ greatly.

[1] The effect of alpha and beta particle emission on the properties of the atomic particles and other radioactive transformations are discussed in greater detail in Chapter XXXIII. The object at this point is to indicate the connection between the observed radiations and the complex structures of the atoms of the elements.

Decomposition of Atoms. There are two types of change affecting the constitution of atoms which have been discussed in preceding paragraphs. In one of these the change is not extreme, but consists, in some instances, in the removal of one or more electrons with the formation of positively charged residues of atoms, known as ions. In other instances, some small number of electrons may be added to the atom to form negatively charged ions. These changes may be brought about by the action of the different radiations and also by chemical reactions. This change is easily reversed; and the atom is restored to its former neutral state by adding the correct number of electrons, if it has suffered a loss, or taking away the excess, if it has experienced a gain. The other change, illustrated by spontaneous radioactive disintegrations, is more profound than that resulting in the formation of ions. This change also is caused by the loss of material particles. Since these transformations result in a complete change in the nature of the substances, it is evident that an alteration in the constitution of the atom is involved. In 1919, Rutherford and Chadwick caused the transmutation of elementary nitrogen by subjecting it to the action of alpha particles. More recently, a large number of atomic transformations have been effected through the use of several different projectiles for the atomic bombardment. Most changes of these types result in the formation of simpler atoms, though there are some instances in which the change involves the capture of the projectile with the formation of a more complex atom. Since atoms may be decomposed, it is necessary to conclude that they are complex.

Detection of Fast-Moving Charged Particles. One of the most effective methods of detecting these particles is based on the formation of gas ions. Experiments devised by C. T. R. Wilson have made it possible to observe the path of a single charged particle through a gas. Gas ions act as nuclei for the condensation of water vapor in a supersaturated space. The apparatus, Fig. 49, known as the "cloud chamber," is a cylindrical vessel containing dust-free air saturated with water vapor. It is provided with a light piston which can be suddenly lowered. The gas in the chamber, A, expands and is cooled, thus becoming supersaturated with water vapor. If a source of alpha particles is in the chamber and the amount of the expansion is properly adjusted, each gas

ion produced becomes a center for the condensation of a droplet of water; and a trail of these minute drops shows the path of the rapidly moving particle. By these experiments, the path of a

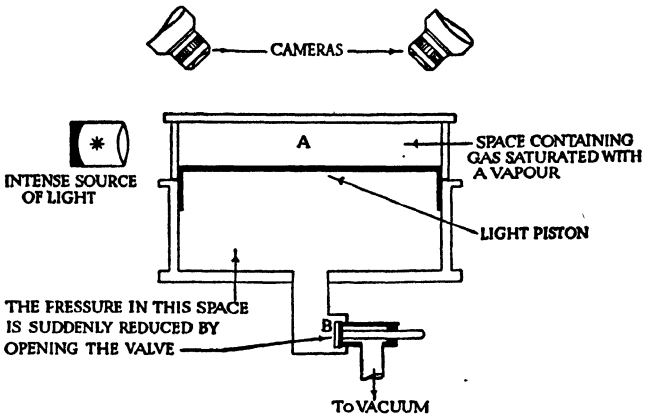


FIG. 49. — The Wilson Cloud Chamber. (From Rutherford, *The Newer Alchemy*.)

single atom was for the first time made visible. A photograph showing the tracks of alpha particles produced in this way is shown in Fig. 50. The tracks end abruptly where the velocity of the particle has become so low that it no longer produces ions.

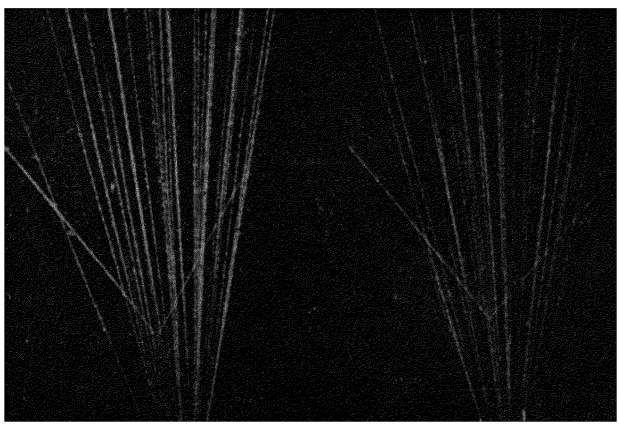


FIG. 50. — Tracks of Alpha Particles. The effect of a collision with a helium atom is also shown. (Professor P. M. S. Blackett, Cavendish Laboratory.)

The track produced by the beta ray is much less dense than that of the alpha ray because it produces fewer ions along the

way. The light beta particles are easily deflected from a straight-line course.

Moving particles having no electrical charge do not cause ionization and, consequently, leave no visible track.

The Neutron. The possibility of the existence of neutral particles as units of atomic structure was suggested by Rutherford in 1920. Since such particles would leave no track in the cloud chamber and would not affect a charged electroscope, the detection would be difficult. It was discovered by Bothe and Becker

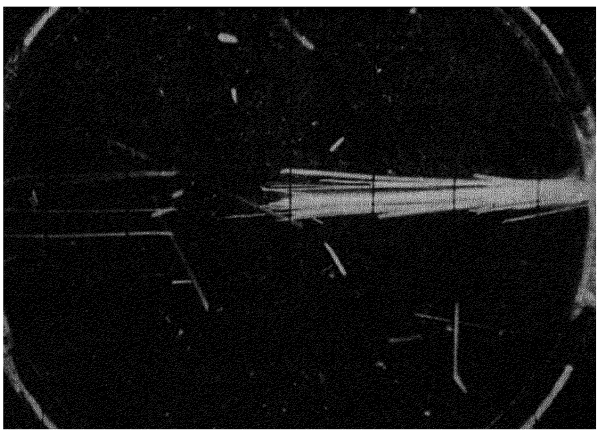


FIG. 51. — Atomic Disintegration Caused by Neutrons.

High speed protons and neutrons enter the cloud chamber from the left where they have been formed by bombardment of a carbon target with deuterons. An atomic disintegration caused by a neutron striking an atom of nitrogen is recorded in the lower right portion of the photograph. The longer branch of the curve is due to an alpha ray, the shorter to the recoil of the remainder of the atom. The heavy tracks from the right are due to α-rays from thorium C and C′. (Photographed by Dr. L. Ott, Yale University.)

that the bombardment of beryllium atoms by alpha particles gives rise to a very energetic type of radiation. It was next found by Madame Irène Curie Joliot and her husband, F. Joliot, that these rays cause the discharge of protons having high energy when they pass through certain hydrogen compounds. The energy relationships cannot be explained on the assumption that these rays are of the nature of gamma radiation. In 1932, Chadwick solved the relationships by assuming that a *neutral particle of the mass of the proton* is thrown out during the bombardment of

beryllium with alpha rays, and that this particle causes the decomposition of other atoms, giving rise to alpha and beta rays. This particle leaves no track as it passes through the cloud chamber; but it causes the formation of charged particles which do leave tracks when it strikes the center of a gas atom, Fig. 51. This neutral particle formed during atomic disintegration is called the *neutron.* It has an atomic mass of 1.0090.

The Positron. An additional particle, the positron, was discovered by Anderson in 1932. Its mass is equal to that of the electron and its charge is of the same magnitude but opposite sign. Consequently, the electron and positron are deflected in opposite directions in a magnetic field, Fig. 52. This particle appears to originate in energy changes which take place during the decomposition of some of the atoms.

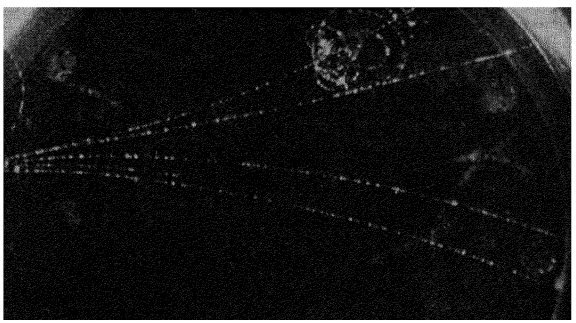


FIG. 52. — Tracks of Electrons and Positrons. (Professor Carl D. Anderson, California Institute of Technology.)

Fundamental Units of Structure. The existence of minute particles, negative, neutral, and positive, in the atoms of the elements is now considered to be established. In the preceding paragraphs, five minute particles which might serve as units of structure have been discussed: *viz.*, the electron, the positron, the proton, the neutron, and the alpha particle. Since the alpha particle has an atomic mass of four units and a positive charge of two units, it is not considered to be a fundamental unit of matter. Alpha particles may actually exist in atoms, but it is clear that they are themselves complex. At least three of the four remaining particles are necessary to account for the observed relationships. The three particles now commonly accepted as unit particles of

the structure of all of the atoms are *the electron, the proton, and the neutron.* It is possible that the neutron may consist of a proton-electron pair, and that the proton may be a neutron-positron pair. However, the mass, energy, and volume relationships do not indicate that this is the case, but that each of the three is a distinct unit. It is presumed that the positron is produced in consequence of the energy changes which occur within the atom and lead to positron emission.

The Nuclear Atom. In 1904, Thomson advanced the hypothesis that the atom of any element consists of a specific number of electrons in a sphere of uniform positive charge. There were found to be many facts for which this structure proved inadequate, and Rutherford proposed the nuclear atom in 1911. According to this hypothesis, *all of the positive electricity and nearly all of the mass of the atom are concentrated in a very small nucleus, and there are enough electrons outside of the nucleus to equal the positive charge of the nucleus.* This assumption is supported by a consideration of the deflection which alpha rays suffer when they pass through thin metal films. If a stream of alpha particles is directed against a thin metal film, a large proportion of these particles passes through the film without experiencing great change in direction; but others show large deflections from a straight line, Fig. 53. Consequently, the rays are scattered over a wide area after passing through the film. Deflections of the extent observed cannot be accounted for by assuming that the alpha-ray particles pass in close proximity to an electron or a proton, because the masses of these particles are too small. The great deflecting force may be accounted for by the assumption that *all of the protons are located in a very small nucleus.* The infrequency of these deflections shows that the nucleus is so small that many of the alpha particles may pass through the metal without coming close enough to an atomic nucleus to be affected.

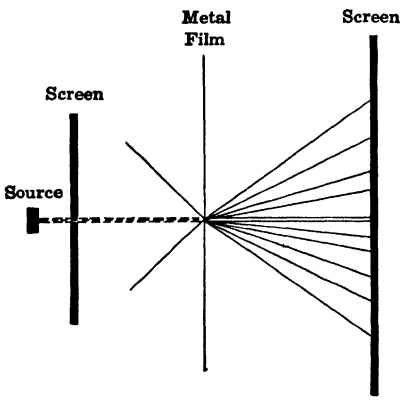


FIG. 53. — Alpha Ray Scattering.

The radius of the nucleus is calculated to be approximately a ten-thousandth that of the atom.

The examination of the fog tracks of alpha particles in the cloud chamber makes possible the estimation of the manner in which the atomic particles are distributed. The sizes of the atoms of the gases in the chamber are known, so that it is possible to calculate the number of atoms an alpha particle passes through in traveling an observed distance. It comes close enough to an electron to cause the formation of a gas ion in only a relatively small number of the atoms it actually passes through. The conclusion that *the electronic constituents of an atom are separated by distances which are great relative to their sizes* is confirmed by this observation; and there is much unoccupied space in an atom. The alpha particle sometimes suffers a sudden deflection from a straight line. This is due to its passage very close to the nucleus of an atom.

Atomic Numbers. Rutherford calculated the nuclear charges of a number of the atoms from the deflections of alpha particles passing through metal films, and concluded that the charge of the nucleus is equal to approximately one half of the atomic weight. A method for the exact determination of the nuclear charge was developed in 1913 by the British physicist, Moseley, who was killed at Gallipoli in 1915. The method is based on his discovery that the characteristic wave lengths of the X-rays are related in a simple manner. The use of a thin crystal to serve as a diffraction grating in determining the spectra of X-rays has been mentioned. Moseley found that characteristic X-rays of slightly different wave length result from the use, successively, of different elements on the surface of the target which the cathode rays strike. The characteristic spectrum of an element consists of one or more series of lines. The lines of shortest wave length, *i.e.*, of highest frequency, constitute the K-series, the only series exhibited by the elements of lowest atomic weight. Other series of lines appear successively in the spectra of the elements with increasing value of the atomic weight. The wave lengths of the lines for a particular series are shorter for the heavier elements than for those which are lighter. Moseley observed further that the relation of these wave lengths may be expressed in an arithmetical progression, Fig. 54; and that a number may be assigned to each of the ele-

ments, beginning with 1 for hydrogen and continuing regularly to 92 for uranium, which shows the position of the element in the series. These numbers are called the *atomic numbers.* Moseley

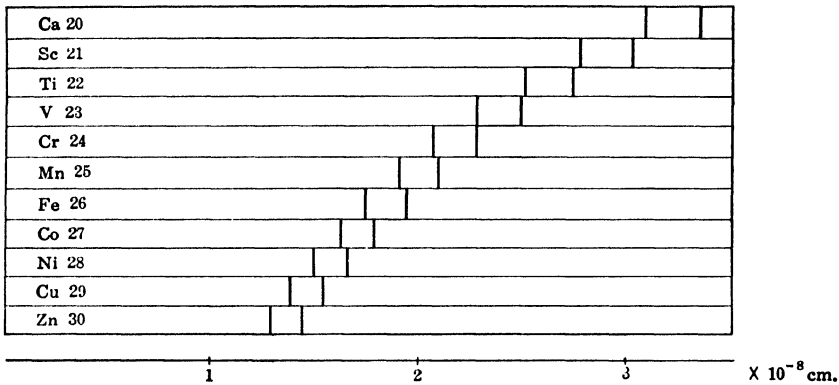


FIG. 54. — Wave-Lengths of K-Series X-Ray Lines (Moseley).

determined the atomic numbers of most of the elements in the list from aluminum to gold. It has been proved definitely by Chadwick that *the atomic numbers are equal to the charges of the nuclei of the respective atoms.*

The Nucleus of the Atom. According to the accepted theories dealing with atomic structure, the nucleus is the very small, compact, central part of the atom. It contains all of the protons and neutrons in the atom; and, consequently, its mass is determined by the sum of the numbers of these two particles in the atom. It has a positive charge represented by the atomic number and determined by the number of protons which it contains. The number of neutrons in a particular nucleus is equal to the difference between the mass and charge of the nucleus.

The fact that the weights of all of the atoms, which are almost identical with the weights of the nuclei, are not multiples of the weight of a single neutron and proton has been explained by Harkins as due to the "packing effect": *i.e.*, the loss of mass due to the energy change caused by the close packing of these particles in the atomic nuclei. The naturally occurring varieties of many of the elements are mixtures of two or more atomic particles containing the same number of protons, but different numbers of neutrons. Such particles have the same chemical properties but differ in mass. The atomic weight, determined by experiments

based on the equivalent weight, is an average value depending on the relative number of each of the particles of different mass present in the mixture. Hence, many of the atomic weights are not integral numbers.

The atomic nuclei vary greatly in their stability. Some, like those of the radioactive substances, are unstable, so that they spontaneously disintegrate with the formation of atoms of a different variety. Some of the nuclear changes, resulting in the transmutation of elements, are discussed in Chapter XXXIII. Most of the naturally occurring elements are not radioactive, showing that these atomic nuclei are relatively stable. The majority of the stable elements contain an approximately equal number of protons and neutrons per atom. This may be taken to indicate the existence in atomic nuclei of specific complex particles composed of neutrons and protons.

The Electrons in the Atom. The atom of an uncombined element is electrically neutral in its normal state, so that it evidently contains an equal number of electrons and protons. The radius of the electron is calculated to be only approximately a fifty-thousandth that of the atom. Hence, the distances between the nucleus and the electrons are enormous relative to their sizes.

The chemical reactions of the elements are correlated with the relationships of the electrons. The chemical properties of the elements differ and they react with each other, if they react at all, in definite atomic ratios, usually expressed by small integers. It therefore seems reasonable to conclude that the electrons in an atom do not all bear exactly the same relation to the nucleus, except in the helium atom. The periodic grouping of the elements supports the conclusion that there are structural similarities which are periodically repeated.

The Inert Elements. Among the ninety-two elements, all show varying degrees of activity except six. These, together with their atomic numbers, are shown in Table 5.

TABLE 5

INERT GASES

Helium	He	2	Krypton	Kr	36
Neon	Ne	10	Xenon	Xe	54
Argon	A	18	Radon	Rn	86

Since these elements are inert, it is evident that electrons in the numbers 2, 10, 18, 36, 54, and 86 impart chemical stability to the atom. Atoms of all other atomic numbers are active under appropriate experimental conditions. Hence, it is a reasonable assumption that certain "arrangements" of the electrons are responsible for the stability of the atom and that the arrangement involves the repetition of certain characteristic features.

Electron Distribution. Chemical evidence, based on the periodicity of the elements, supports the conclusion that the properties of the elements result from the distribution of their electrons into specific series or periods. These series of electrons are considered to be in different *energy levels*, an energy level being determined by the amount of energy required to remove an electron. According to this mechanical picture, the electrons of a particular energy level are moving in different kinds of paths about the nucleus; and all of these paths together may be considered as a *region or shell* occupied by the electrons. It is, therefore, customary to speak of classifying the electrons into shells at different energy levels. On this assumption, the first shell is complete with two electrons, and the second with eight. In the atom of hydrogen, there is a single electron at a particular energy level; and in helium there are two at the same level. Since helium is an inert gas, this structure is considered to be stable, *i.e.*, no more electrons may enter that level. The atoms of the next eight elements are assumed to contain successively from one to eight electrons in a second shell, at a lower energy level. The third electron shell is likewise complete with eight electrons, so long as it is the outermost shell, as in the inert gas, argon. It must be assumed, however, that further increases in the number of electrons in the third

TABLE 6

ELECTRON DISTRIBUTION IN THE INERT GASES

Element	*Atomic Number*	*First Shell*	*Second Shell*	*Third Shell*	*Fourth Shell*	*Fifth Shell*	*Sixth Shell*
Helium .	2	2					
Neon . .	10	2	8				
Argon . .	18	2	8	8			
Krypton .	36	2	8	18	8		
Xenon . .	54	2	8	18	18	8	
Radon . .	86	2	8	18	32	18	8

shell may result in building it up to a maximum of eighteen, after two additional electrons have come into the fourth shell. This accounts for the long period of elements between argon and krypton. Similar assumptions are made regarding subsequent energy levels. The maximum number of electrons at any energy level is that shown by the inert gases, Table 6.

The electron distribution in the atoms of the elements through the first long period is shown in Table 7.

TABLE 7

ELECTRON DISTRIBUTION IN THE ATOMS OF ELEMENTS 1–36

Element	*Atomic Number*	*First Shell*	*Second Shell*	*Third Shell*	*Fourth Shell*
H	1	1			
He	2	2			
Li	3	2	1		
Be	4	2	2		
B	5	2	3		
C	6	2	4		
N	7	2	5		
O	8	2	6		
F	9	2	7		
Ne	10	2	8		
Na	11	2	8	1	
Mg	12	2	8	2	
Al	13	2	8	3	
Si	14	2	8	4	
P	15	2	8	5	
S	16	2	8	6	
Cl	17	2	8	7	
A	18	2	8	8	
K	19	2	8	8	1
Ca	20	2	8	8	2
Sc	21	2	8	9	2
Ti	22	2	8	10	2
V	23	2	8	11	2
Cr	24	2	8	12	2
Mn	25	2	8	13	2
Fe	26	2	8	14	2
Co	27	2	8	15	2
Ni	28	2	8	16	2
Cu	29	2	8	18	1
Zn	30	2	8	18	2
Ga	31	2	8	18	3
Ge	32	2	8	18	4
As	33	2	8	18	5
Se	34	2	8	18	6
Br	35	2	8	18	7
Kr	36	2	8	18	8

The assumption that the electrons reside at different energy levels in the atoms is supported by a consideration of the X-ray spectra. The lines in the K-series are attributed to the group of two electrons in the helium structure. Lines in this series are shown by all of the following elements, indicating that this shell is common to the structures of all of the more complex atoms. A second series of lines, beginning with the element of atomic number 3, indicates the presence of electrons at a second energy level in the atom. These lines also are characteristically shown by all of the subsequent atoms. A third series begins with sodium, atomic number 11; and additional series, with more complex atoms.

A number of attempts have been made to picture the structure of the atoms by means of mechanical models. One of the best-known of these, advanced by Lewis in 1916 and subsequently modified and extended by Langmuir, assigns a definite geometrical structure to the atom, in which the electrons occupy definite positions. Although this model of a static atom was useful in the correlation of the chemical properties of many of the simpler atoms, it failed to account satisfactorily for a number of atomic phenomena.

Meanwhile, toward the end of the nineteenth century, a profound change had taken place in the fundamental methods of physical science. At this time, it became evident that the methods of Newtonian physics were inadequate for the treatment of the mechanics of particles of atomic size. The criticisms culminated in the formulation of the quantum theory by Planck in 1900. The theory assumes that in certain atomic processes energy can be emitted or absorbed only in discrete, finite amounts, or *quanta*. This idea of a discontinuity in the amounts of energy which are absorbed or emitted in radiation was applied by Bohr, 1913, to the structure of the atom. He postulated the existence of definite geometrical orbits for the electrons in their motion around the atom, each orbit corresponding to a definite energy content for the electron. Although this theory met with considerable success in explaining the behavior of the simpler atoms, arbitrary and unreasonable assumptions were necessary to secure agreement with the experimental observations in the more complicated atoms.

Following the recognition of the necessity of assigning some corpuscular or particle properties to radiation, it was shown by de Broglie, in 1924, that certain properties of electrons require a wave theory similar to that of ordinary electromagnetic waves. Attempts to reconcile this *wave-particle duality* led to the formulation by Schrödinger and Heisenberg of the wave mechanics. The significance of the theory from the present point of view is its abandonment of physical or mechanical models, and its adoption of mathematical equations for the expression of ideas. This represents a complete change in method from classical procedures. In the light of modern theory, it is not correct to ascribe any particular geometrical position or motion to particles of electron size. Modern theory, however, does confirm the partitioning of the electrons into energy regions; and it is in this sense that the term "electron shell" may be used.

The Direct Union of the Elements. During the reactions of the elements, the atoms tend to redistribute the electrons in their outer shells so as to acquire the electron distribution of the inert gases. There are three changes which an atom may undergo in approaching this state. *It may lose the electrons* in its outer shell, thus acquiring the stable configuration of the element at the beginning of the particular period. *It may gain enough electrons* to attain the stable grouping of the inert gas at the end of the period. *The atoms may share electrons*, so that each approaches the inert gas structure, but neither actually reaches it. The electrons in the outer shell of the atom are called the *valence electrons*, because chemical reactions involve changes affecting these electrons and their number determines the reacting ratio of the atoms.

When sodium, atomic number 11, reacts with chlorine, 17, the single valence electron of the sodium atom is transferred to the chlorine atom. Each particle now has the electron configuration of an inert gas. The electron relation in such reactions may be represented in a simple and useful manner according to a system proposed by Lewis. The symbol is allowed to represent all of the atom except the electrons in the valence shell. This part of the atom is usually called the *kernel.* Dots are now written to represent the valence electrons. The electron distribution in the sodium atom is 2, 8, 1; and in the chlorine atom, 2, 8, 7. In accord with this plan, the electronic symbol Na· represents the sodium

atom; and $:\ddot{\underset{\cdot\cdot}{Cl}}\cdot$ the chlorine atom. The equation representing the reaction of the sodium atom with the chlorine atom may be written

$$Na\cdot + :\ddot{\underset{\cdot\cdot}{Cl}}\cdot \longrightarrow (Na)^{+} + (:\ddot{\underset{\cdot\cdot}{Cl}}:)^{-}$$

During the change, the sodium atom acquires the electronic configuration of the neon atom by the loss of one electron; and the chlorine atom, that of the argon atom by the gain of one electron. Each of the particles now has an electrical charge. Due to the charges developed in this manner, the ions of sodium and chlorine attract each other and occupy fixed positions relative to each other when in the solid salt. Similarly, magnesium, 12, unites with sulfur, 16, each magnesium atom giving up two electrons which are taken in by the sulfur atom.

$$Mg: + \ddot{\underset{\cdot\cdot}{S}}: \longrightarrow (Mg)^{++} + (:\ddot{\underset{\cdot\cdot}{S}}:)^{--}$$

Molecules of some elementary gases such as hydrogen, chlorine, and fluorine contain two atoms. The union of the two atoms to produce the molecules of these gases is assumed to involve the sharing of electrons so that a pair of electrons is held jointly by both atoms. Such electrons are not transferred from one atom to another, but remain in the field of attraction of both atoms.

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}:$$

Pairs of electrons which are inherent structural parts of two atoms are known as *shared electrons.* The equation for the reaction of sodium with chlorine may now be written,

$$2\ Na\cdot + :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow 2\ (Na)^{+} + 2\ (:\ddot{\underset{\cdot\cdot}{Cl}}:)^{-}$$

It is not necessary that both of the atoms be alike in order to share electrons, and many reactions involve the sharing of electrons by dissimilar atoms. Hydrogen unites with chlorine to produce molecular hydrogen chloride. The electronic equation may be written,

$$H:H + :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow 2\ H:\ddot{\underset{\cdot\cdot}{Cl}}:$$

In some instances, both of the electrons in the electron pair originate from a single atom. In the reaction of sulfur with oxygen to form sulfur dioxide, it is supposed that both of the electrons in each of the shared pairs are from the sulfur atom.

$$:\ddot{S}: + :\ddot{O}:\ddot{O}: \longrightarrow :\ddot{O}:\ddot{S}:\ddot{O}:$$

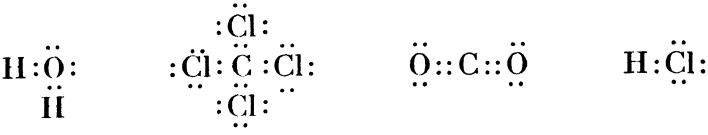
The direct union of two elementary substances involves either a transfer of electrons from one variety of atom to the other or the sharing of electrons by the atoms of the two elements.

Electronic Interpretation of Valence. The valence of an element is equal to the number of hydrogen atoms to which its atom is equivalent. Chemical reactions of the elements involve the electron as the unit and changes in valence result from electronic changes. Uncombined elements are considered to be in the zero valence state. Three types of bonds result from the electronic changes which occur during the union of elementary substances.

Electrovalence. The particle of sodium resulting from the loss of an electron has a positive electrical charge, because it now contains eleven protons but only ten electrons. Similarly, the chlorine atom is converted into an electrically negative particle by the gain of an electron, and the ion formed contains eighteen electrons but only seventeen protons. Valence due to the electrical charges borne by the ions is known as electrovalence. *Positive electrovalence* is due to the loss of electrons and is numerically equal to the number of electrons each atom of the element has lost. *Negative electrovalence* is equal to the number of electrons each atom of the element has gained. The maximum positive electrovalence which an atom may show is equal to the number of electrons in the valence shell, increased in some of the elements by one or more electrons from an incomplete and unstable inner shell. The maximum negative electrovalence is equal to the difference between the number of valence electrons and eight. This summary should not, however, be taken to mean that in all instances the elements may actually exhibit these valences. The elements containing only a small number of electrons per atom usually lose electrons in their reactions forming positive ions, and show no tendency to gain electrons forming negative ions. These are in general the metallic elements. Those elements having only one or two electrons less than the next higher inert gas readily gain additional electrons to form negative ions, a reaction which is characteristic of the active non-metals.

Covalence. Valence due to the sharing of electrons is known as covalence. In the ordinary covalent bond, each atom contributes one electron of the pair and no electric charge is developed. The

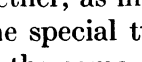
resulting particle is a molecule. One unit of covalency is due to a bond made up of one electron pair. The covalency of hydrogen and chlorine in hydrogen chloride is one. The covalency of oxygen is two and of carbon four in many of their compounds. In the following electronic formulas, the valence electrons of the elements are represented by dots, as an aid in visualizing the nature of the covalent bond.



H_2O CCl_4 CO_2 HCl

In some of the compounds formed by the sharing of electrons, the molecules are symmetrical and the electron pairs appear to be held with equal force by both atoms. Such molecules are *nonpolar*. Carbon tetrachloride and molecular chlorine exist in the form of nonpolar molecules. In other substances, the pairs constituting the electron bond may be considered to be closer to one of the atoms than to the other, so that one part of the molecule is negative toward the other part. Such molecules become oriented in an external electrical field. Each molecule behaves as a minute *dipole* and such molecules are *polar molecules*. Water, hydrogen chloride, and ammonia are familiar substances which exist as polar molecules. The degree of polarity of the molecule depends on the extent to which the positive and negative charges are separated within the molecule. Compounds which are composed of polar molecules differ in many of their properties from those which are nonpolar. The effects of polarity are particularly prominent when the molecules are close together, as in the liquid state.

Coördinate Valence. The special type of covalent bond with both of the electrons from the same atom is called a coördinate bond. The shared electrons in the molecule of sulfur dioxide are considered to be those of the sulfur atom.



The valence bond is of the coördinate type.

Oxidation Number. It has been observed previously that the name *oxidation* is given to that process in which the positive valence of an element increases. The relation of the electron to

valence now indicates that valence changes are electronic in nature. The loss of an electron causes an increase in the positive charge; and the gain of an electron causes a decrease in the positive charge. Hence, in electrovalent compounds it is evident that *oxidation* is the result of the loss of electrons, and *reduction* is the result of the gain of electrons. *Oxidation-reduction* is due to the transfer of electrons from one atom or ion to another. It is desirable to assume that all oxidation-reduction processes involve these same essential changes. In the covalent bond, however, the electrons of the bonding pair have not been transferred, but are shared. In order to simplify the relationships, arbitrary assumptions are made so that positive and negative numbers may be assigned to the atoms. In many molecules, the electron pair actually may be displaced toward one of the atoms; but it must be assumed that they are shared equally in the non-polar molecules. The numbers which represent the oxidation state, either the actual electrical charge or the numbers arbitrarily assigned, are called the *oxidation numbers*. In the compounds in which covalent bonds exist, the oxidation numbers are assigned from a consideration of the general behavior of the atoms involved. Thus, chlorine exhibits a strong tendency to gain electrons, and hydrogen to lose them. Hence, the oxidation number of the chlorine atom in most of its binary compounds, except those with oxygen, is called 1 −; and the oxidation number of hydrogen is 1 +, even though no transfer of electrons has taken place. Likewise, the oxidation number of oxygen is 2 − in most of its common compounds, except the peroxides. On the basis of such numbers as these, and the rule that the sum of the positive and negative oxidation numbers is equal to zero, a series of oxidation numbers is derived. Phosphorus trichloride, PCl_3, exists in the form of molecules in which the bonding is of the covalent type. Since the oxidation number of chlorine is 1 − and there are three atoms of chlorine in the molecule, the oxidation number of phosphorus in this compound is 3 +. A similar procedure is employed for the calculation of the oxidation numbers of the elements in more complex compounds. In potassium chlorate, $KClO_3$, the oxidation number of potassium is 1 +, and of each oxygen 2 −, or a total of 6 − for the three oxygen atoms. Therefore, the oxidation number of the chlorine in this compound is 5 + to

balance the excess equal to 5 −, the algebraic sum of the numbers for potassium and the three oxygen atoms.

From the examples already considered it is apparent that some of the elements may have more than one oxidation number. This is to be expected, since a given element may gain or lose electrons in one reaction and may share them in some other reaction. Thus, we have seen that sulfur may exhibit the oxidation numbers, 2 − and 4 +. The oxidation number 2 − may be an electrovalent bond as in metal sulfides; but it may also be due to a covalent bond in non-metal sulfides; and the number 4 + is assigned only in compounds which involve covalence. Not all of the valence electrons of an element are lost or shared under identical experimental conditions. Thus, the remaining electron pair possessed by the sulfur atom in sulfur dioxide enables it to combine with an additional atom of oxygen to form sulfur trioxide in which the oxidation number of sulfur is 6 +.

The Periodic Classification Based on Atomic Numbers. The arrangement of the elements in the order of their atomic numbers places them in the same order as the arrangement according to atomic weights, except that it corrects the discrepancies previously noted in the positions of argon and potassium; cobalt and nickel; and tellurium and iodine. Since the atomic numbers range from hydrogen 1 to uranium 92, there should be ninety-two naturally occurring elements. The chemical reactions of the elements depend on the number of planetary electrons and, consequently, on the atomic numbers. **The Periodic Law may be restated: The properties of the chemical elements are a periodic function of their atomic numbers.** The repetition in properties is due to a repetition of the essential features of the structure of the atoms of the elements, which determine the tendency of the atoms to gain, lose, or share electrons, and to the number of electrons involved in the reactions of the elements. The elements in a closely related family have the same number of valence electrons; and these electrons bear a similar relation to that part of the atom which lies beneath the valence shell. A form of the periodic system, based on atomic numbers, is shown in Table 8. With the exception of the inert gases of Group VIII, the group numbers indicate the number of valence electrons in the atoms of the elements in the main groups. The elements at

TABLE 8

PERIODIC CLASSIFICATION OF THE ELEMENTS BASED ON ATOMIC NUMBERS

Group / Period	I	II	III-B	IV-B	V-B	VI-B	VII-B	VIII-B			I-B	II-B	III B	IV B	V B	VI B	VII B	VIII
I 2 Elements	H 1																	He 2
II 8 Elements	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
III 8 Elements	Na 11	Mg 12	*Transition Elements*										Al 13	Si 14	P 15	S 16	Cl 17	A 18
IV 18 Elements	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
V 18 Elements	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	Ma 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
VI 32 Elements	Cs 55	Ba 56	57* 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85	Rn 86
VII 6 Elements	— 87	Ra 88	Ac 89	Th 90	Pa 91	U 92												

*The elements having atomic numbers 57–71 are: La, 57; Ce, 58; Pr, 59; Nd, 60, Il, 61, Sm, 62; Eu, 63; Gd, 64; Tb, 65; Dy, 66; Ho, 67; Er, 68; Tm, 69; Yb, 70; Lu, 71 These elements comprise the "Rare Earths." They contain the same number of valence electrons and their atoms differ in the number of electrons in the fourth shell.

the right of the table, to the right of the heavy line, are the nonmetals.

The difference in properties between the subgroups and the main groups may be attributed to the fact that some of the details of the structures of the atoms are different. In each main group, all of the elements possess the same number of valence electrons; and the structure beneath the valence shell, the kernel, contains stable electronic shells. Consequently, the differences in properties shown by the elements may be correlated with the energy shell in which the valence electrons are located and with the total number of complete electron shells between the valence shell and the nucleus. In each subgroup there are differences in a shell beneath the valence shell, Table 7, p. 119, and this shell is not usually complete. Consequently, electrons from the outer shell and also those in the incomplete inner shell of the atom affect the properties. In the first long period, the ten elements in which the number of electrons in the third shell builds up from eight to a final complete and stable structure of eighteen, with increases in the atomic number, constitute the transition elements. The rare earth elements are those in which the number of electrons in the fourth shell increases successively with the atomic number, from an intermediate shell of eighteen to a final maximum of thirty-two, after some electrons are already present in both the fifth and sixth shells.

Isotopes. It has already been observed that there are a number of elements which are composed of atoms having the same atomic number, but different atomic masses. Atoms of different mass but the same atomic number are called *isotopes. An element is a variety of matter composed of atoms having the same atomic number.* Aston has shown that it is possible to separate isotopes and to determine the relative masses of the individual particles. Such separations may be effected by converting the atoms into positive rays, or gas ions, and observing the deflections which they experience when they pass through a magnetic field. The extent of the deflection depends on the mass, velocity, and charge of the particle and the strength of the field. If a beam of positive rays is made up of charged atoms having the same charge and the same velocity, but different mass, the amount of the deflection of the particles differs. By the application of this principle, the separated

rays may be allowed to fall on a photographic plate, producing a spectrum, Fig. 55. From the amount of the deflection, it is possible to determine the masses of the atoms by reference to a standard.

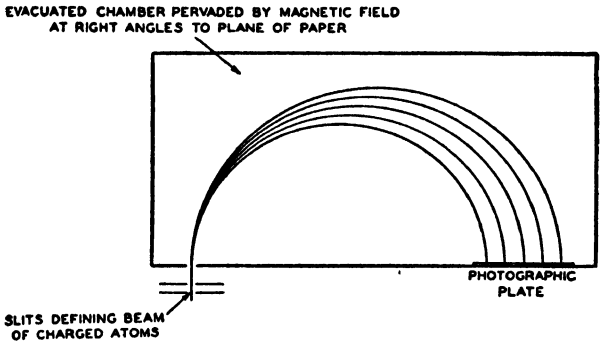


FIG. 55. — Illustrating the Separation of Isotopes. (From Darrow, *The Renaissance of Physics.*)

The apparatus is known as the *mass spectrograph.* By its use, accurate methods may be developed for the determination of the atomic weights. In the following table, Table 9, isotopes of some of the familiar elements are listed, the more abundant isotope being the first number written in each instance.

TABLE 9

STABLE ISOTOPES OF SOME OF THE COMMON ELEMENTS

Element	*Atomic Number*	*Atomic Weight*	*Isotopes*
H	1	1.0080	1, 2
C	6	12.01	12, 13
N	7	14.008	14, 15
Mg	12	24.32	24, 25, 26
Cl	17	35.457	35, 37
Fe	26	55.84	56, 54, 57, 58
Cu	29	63.57	63, 65
Br	35	79.916	79, 81
Ag	47	107.88	107, 109
Cd	48	112.41	114, 106, 108, 110, 111, 112, 116
Sn	50	118.70	120, 112, 114, 115, 116, 117, 118, 119, 122, 124
Te	52	127.61	128, 130, 120, 122, 123, 124, 125, 126
Pb	82	207.21	208, 207, 204, 206
U	92	238.07	238, 235

The different isotopes of an element have the same atomic number and, therefore, the same number of electrons. Thus, the isotopes of chlorine, atomic number 17, have seventeen protons in the nuclei of the atoms. Ordinary chlorine is a mixture of the two isotopes of atomic weights 35 and 37 in such proportions that the average is 35.46. The difference in the weights of these atoms is due to the fact that the atom of mass 35 contains seventeen protons and eighteen neutrons, while the atom of mass 37 contains seventeen protons and twenty neutrons. Deuterium consists of atoms whose nuclei contain one proton and one neutron, giving an atomic number of 1; but the atom of the ordinary abundant isotope, hydrogen, contains a single proton and also has an atomic number of 1.

The work of Aston and of others in determining the weights of the atoms in isotopic mixtures at last furnished confirmation of the essential assumptions in the hypothesis of Prout.

EXERCISES

1. Name and state the nature of five minute particles which might be assumed to be the fundamental units of atomic structure.
2. Indicate the evidence which leads to the assumption of the existence and nature of each of these particles.
3. Which three of these particles are accepted as the actual unit particles of structure? Show how these three are sufficient to account for the structure of the atoms.
4. Give evidence that these particles are present in the atoms of radioactive substances, of ordinary substances.
5. Give evidence to support the assumption of the nuclear atom.
6. What is meant by the atomic number of an element? How may you account for the difference in the atomic weight and atomic number of an element?
7. What justification is there for the assumption that the electrons are relatively remote from the nucleus?
8. What is the significance of an electron shell? What evidence is there that the electrons are distributed in shells?
9. What electronic changes take place during the direct union of the elementary substances?
10. What three types of valence result from the electronic changes which accompany the direct union of elements? Define and give an example of each type.
11. Represent the products of the following reactions by electronic formulas:
    (*a*) The union of lithium with fluorine and of potassium with bromine;
    (*b*) The union of calcium with chlorine and of aluminum with sulfur;
    (*c*) The union of phosphorus and of silicon with oxygen.

12. Give a definition of oxidation-reduction in terms of electronic changes.
13. What is meant by the oxidation number of an element? How is it estimated in an electrovalent compound and in a covalent compound?
14. Derive the oxidation number of each element in the compounds: As_2O_5; NH_4Cl; HNO_3; $KMnO_4$; $K_2Cr_2O_7$.
15. What is meant by an ionic compound, a nonpolar molecule, and a polar molecule?
16. Show how the assumptions dealing with the structures of the atoms account for the following:
    (*a*) The periodic repetition in the properties of the elements;
    (*b*) The changes in the properties of the elements in a period;
    (*c*) The similarities shown by the elements in a family;
    (*d*) The differences in the activities of the elements in a family;
    (*e*) The inverted order of tellurium and iodine;
    (*f*) The existence of isotopes;
    (*g*) The divisibility of atoms;
    (*h*) The constancy of the reacting proportions of the elements.

SUPPLEMENTARY READINGS

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CHAPTER VII

THE ALKALI METALS AND THE HALOGENS

The properties and the reactions of the chemical elements may be successfully correlated with their positions in the periodic system, and may be interpreted and explained in terms of electronic relationships. The alkali metals are in Group I and the halogens in Group VII of the periodic table. Atoms of the alkali metals contain one electron more than the preceding inert gas and atoms of the halogens one less than the following inert gas in each period. Consequently, the alkali metals and the halogens differ widely in their properties and reactions, so greatly indeed that they exhibit opposite types of behavior in many of their reactions. They thus supplement each other in furnishing material which illustrates the application of important principles developed in the chapters dealing with the periodic system and electronic relationships. Moreover, the relationships in these two families of elements are simpler in most respects than in elements which are further removed structurally from the inert gases.

THE ALKALI METALS

The elements, *lithium*, *sodium*, *potassium*, *rubidium*, and *cesium*, are a closely related group of metals. There should be another element, number 87, in this family. Although evidence of its existence in certain minerals has been reported, neither the element nor any of its compounds has been isolated. These elements are called the *alkali metals*, because their hydroxides are highly soluble, strongly basic substances known as alkalies. The atoms of these elements contain one valence electron, which is given up actively in chemical reactions. Hence, these elements always exhibit an oxidation state of 1 + in their compounds, and the bond is commonly electrovalent.

Occurrence of the Alkali Metals. These metals occur naturally in compounds. The average relative amounts of sodium

and potassium present in the igneous rocks in a ten-mile crust of the solid earth are estimated to be 2.85% and 2.60%, respectively. The percentage of the other alkali metals is very small. Sea water contains approximately 2.8% of sodium chloride and slightly less than 0.1% of potassium chloride. Consequently, both of these salts are present in the deposits formed by the evaporation of sea water. The carbonates, sulfates, and nitrates of both metals are also found in the soil and in waters and salt deposits in different parts of the world. The sodium salts of each class occur to the greater extent. Compounds of sodium and potassium are present in plants, the potassium compounds being more abundant in land plants, and the sodium compounds in sea plants. The metals occur extensively in their silicates, potassium feldspar, $KAlSi_3O_8$, being a component of granite. Lithium is found in complex phosphates and silicates, and cesium in a complex silicate. Very small percentages of rubidium and cesium chlorides occur in some natural waters and salt deposits.

Preparation of the Metals. Sodium is the only one of the alkali metals which has extensive commercial applications. It was first prepared in 1807 by Davy through the electrolysis of the hydroxide. An industrial method for the production of sodium by the electrolysis of the fused hydroxide was developed by Castner in 1890, and this was the only method in use for a number of years. However, sodium hydroxide is itself a manufactured product and both hydrogen and sodium are liberated at the negative electrode, the cathode, during the process. Hence, the current efficiency is much lower than could be secured by the electrolysis of some compound liberating only sodium at the cathode. A process using the cheap, naturally occurring sodium chloride is now an important source of sodium.

In the *Downs cell* for the production of sodium by the electrolysis of the fused chloride, Fig. 56, the container is made of iron lined with firebrick. The graphite anode projects into the cell from the bottom; and the cathode is in the form of an iron cylinder around the end of the anode. An iron gauze diaphragm, separating the anode and cathode compartments of the cell, is connected to a dome in which chlorine collects. Sodium is liberated at the cathode, fills the riser pipe, and flows out into the receiver. The fused sodium chloride is introduced from time to time through

a hole in the cover of the cell. Chlorine, produced at the anode as a by-product, is stored in cylinders for industrial use. The temperature at which the cell operates, about 600°, is maintained by the passage of the current.

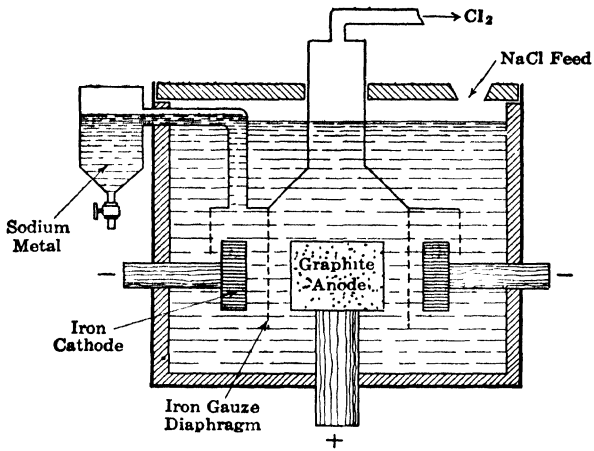


FIG. 56. — Diagram of a Downs Cell.

The other metals in the family may be prepared by the same general procedure, the electrolysis of the fused hydroxide or of the fused chloride. The metals may be prepared also through the reduction of suitable compounds by heating them with calcium or magnesium. Although these two metals are less active than some of the alkali metals, the greater volatility of the alkali metals makes the reaction possible.

Properties of the Alkali Metals. These metals are soft and have relatively low melting points and boiling points. They also have low density, lithium, sodium, and potassium being less dense than water. The metals are good conductors of electricity, a property associated with the fact that, in the solid state, they do not hold the valence electron firmly, so that electrons may pass along freely from atom to atom when a difference in potential is applied. The untarnished surfaces of these metals exhibit silvery luster, but they rapidly tarnish and become non-lustrous. The metals are stored out of contact with air, as beneath an oil. When they are stored in this way, they usually do not appear to be lustrous. A few of the properties of the members of this group are listed in Table 10.

TABLE 10

PROPERTIES OF THE ALKALI METALS

	Lithium	*Sodium*	*Potassium*	*Rubidium*	*Cesium*
Atomic Weight	6.94	23.00	39.1	85.48	132.91
Atomic Number . . .	3	11	19	37	55
Isotopes . .	6, 7	23	39, 40, 41	85, 87	133
Electron Distribution	2, 1	2, 8, 1	2, 8, 8, 1	2, 8, 18, 8, 1	2, 8, 18, 18, 8, 1
Melting Point	179°	97.5°	63.5°	39.0°	28.4°
Boiling Point	1372°	892°	774°	679°	690°
Density, g. per ml. 20°	0.53	0.97	0.86	1.53	1.90

Reactions of the Alkali Metals. Since the atoms of these metals contain a single valence electron, they are chemically active and exhibit the same variety of reactions. They react vigorously with the halogens, electrons being transferred from the atoms of the alkali metals to the atoms of the halogens. The electronic equation showing the reaction of potassium with chlorine may be written,

$$2\,K\cdot + :\ddot{Cl}:\ddot{Cl}: \longrightarrow 2\,(K)^+ + 2\,(:\ddot{Cl}:)^-$$

These particles are electrically charged and the simple equation may be written,

$$2\,K + Cl_2 \longrightarrow 2\,K^+ + 2\,Cl^-.$$

The alkali metals also react with many of the other non-metals.

$$2\,Na + S \longrightarrow 2\,Na^+ + S^{--}.$$

In reactions with oxygen, lithium yields the simple oxide; but sodium yields the peroxide, and potassium, rubidium, and cesium yield a dioxide which is really a salt containing the perhydroxyl ion, O_2^-.

$$4\,Li + O_2 \longrightarrow 2\,Li_2O.$$
$$2\,Na + O_2 \longrightarrow Na_2O_2.$$
$$K + O_2 \longrightarrow KO_2.$$

Combining with hydrogen, these metals produce unstable hydrides in which the oxidation number of hydrogen is 1 −.

The alkali metals react with water, producing gaseous hydrogen and the hydroxide of the metal in solution. With potassium,

rubidium, and cesium, the heat of the reaction is so great that the metals ignite when they are placed on water.

$$2\,Na + 2\,H_2O \longrightarrow H_2 + 2\,NaOH.$$

They also react violently with the common acids, such as hydrochloric and acetic acids, liberating hydrogen.

In most of the reactions of the alkali metals, the elements of high atomic number are more active than those of low atomic number, although lithium, the first member of the family, shows irregular behavior in this respect. The activities of the metals depend on the ease with which they give up valence electrons. In the reactions of the metals with water the hydration of the ions takes place in addition to the displacement of hydrogen and the formation of the electrovalent ion.

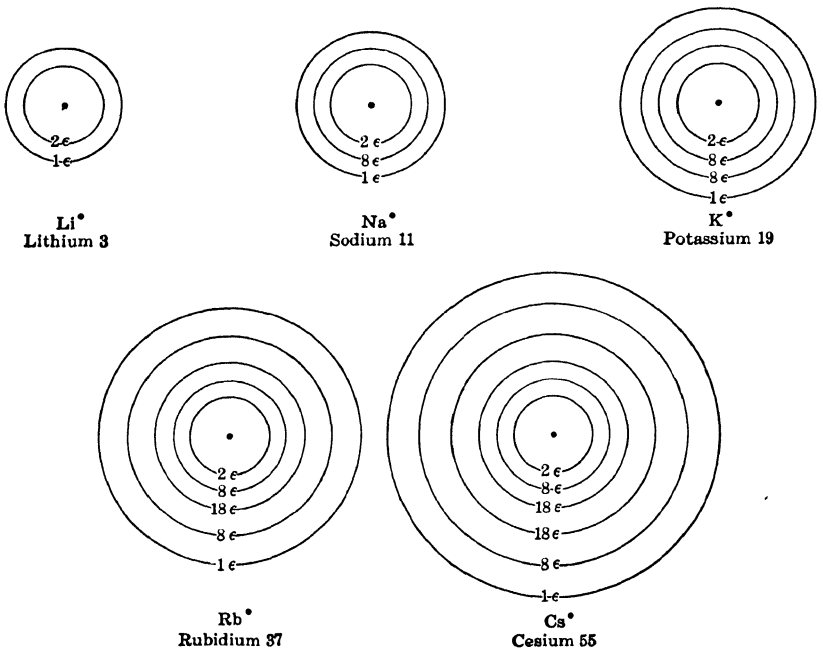


FIG. 57. — Diagrams of the Atoms of the Alkali Metals.

The greater activity in the loss of electrons shown by the larger and more complex atoms may be understood by the consideration of the diagrams in Fig. 57. The small circle at the center represents the nucleus of the atom, and the other circles the electron shells. The two electrons in the inner shell are bound more

strongly to the nucleus than the other electrons because they are inside the shells of all of the remaining electrons in the more complex atoms, and are in the field of the nuclear charge. Those in the second shell are not bound so strongly because they are partially screened from the nuclear charge by the intervening shell of two electrons. Similarly, the electrons in a third shell are bound less strongly to the atoms than those in the second shell. The valence electron in the atom of each alkali metal is held less firmly than in the preceding atom, arranged in the order of their atomic numbers.

Uses of the Alkali Metals. The most important uses of sodium are in the preparation of sodium peroxide and of sodium cyanide, and as a reducing agent in the production of certain organic chemicals. Sodium forms an amalgam with mercury and the formation of this amalgam evolves heat. The amalgam is often used in preference to the free metal as a reducing agent, because its reactions are more readily controlled than those of the metal itself. An alloy of lead and sodium is used in the production of lead tetraethyl. The other metals of this group do not have extensive uses.

The emission of electrons by the atoms of the metals has been discussed. The atoms of the alkali metals are activated by light so that they give up electrons more actively than in the dark; and, on account of this property, sodium and lithium, and cesium to some extent, are used in photoelectric cells. The surface of an electrode in a cell from which air has been removed as completely as possible is coated with a thin film of the metal. The gap between the electrodes is made just great enough to prevent the flow of electrons, when the cell is connected in a circuit at the proper voltage and is protected from light. Therefore, the current cannot flow through the circuit. When light strikes the coated electrode, the metal is activated and electrons now flow across the gap, thus completing the circuit. By the proper arrangement of the connections of the circuit and the use of relays, many important applications of this principle may be made.

An important but limited use of sodium is in the sodium vapor lights which are becoming increasingly familiar for highway illumination. The lamps are made with an elongated inner bulb

containing the electrodes. In this bulb a small amount of sodium is placed and the bulb is filled with argon under low pressure. An outer glass cylinder serves to minimize the loss of heat. The current is first conducted by the argon gas and enough heat is developed to vaporize the sodium. Sodium vapor then conducts the current and emits the yellow glow which is very efficient for general illumination.

Compounds of the Alkali Metals. Since the alkali metals are active metals, they yield compounds with most of the nonmetallic elements. In their familiar and important compounds, these metals exhibit the electrovalence 1 +.

The Oxides. The only oxide of the metals of this group which has extensive commercial uses is sodium peroxide. This substance is prepared by heating metallic sodium at a temperature of 300° in a current of air which is free from carbon dioxide and water vapor. Sodium peroxide is a salt of hydrogen peroxide. The peroxide radical has an oxidation number of 2 −; and the bonding of the oxygen atoms is of the covalent type. This compound reacts with water to produce hydrogen peroxide and sodium hydroxide, a reaction of hydrolysis.

$$Na_2O_2 + 2\,H_2O \longrightarrow H_2O_2 + 2\,NaOH.$$

If only a small proportion of water is used, the hydrogen peroxide decomposes as fast as formed and oxygen is evolved.

$$2\,Na_2O_2 + 2\,H_2O \longrightarrow O_2 + 4\,NaOH.$$

Because of these reactions, sodium peroxide is used as a source of hydrogen peroxide and, to a limited extent, of oxygen.

The Hydroxides. The hydroxides of these metals are soluble, highly reactive, basic hydroxides. Their most important reactions are characteristic of this entire class of compounds: *viz.*, with acids; with acidic oxides; and with solutions of salts of other metals which yield insoluble hydroxides. These reactions are illustrated by the following equations:

$$NaOH + HCl \longrightarrow H_2O + NaCl.$$
$$2\,NaOH + SO_3 \longrightarrow H_2O + Na_2SO_4.$$
$$3\,NaOH + FeCl_3 \longrightarrow Fe(OH)_3 + 3\,NaCl.$$

A more detailed description of the hydroxides of sodium and potassium appears in Chapter XVI, with the discussion of the other basic hydroxides.

Salts. The compounds of the alkali metals with non-metals and non-metallic radicals are salts. Many of these salts have important laboratory and commercial uses. In the crystalline state, the salts exist in characteristic space lattices with charged ions as the structural units. Thus, the halides of all of the alkali metals except cesium are in the simple cubic lattice, and the halides of cesium in the body-centered cubic lattice. When the crystals are melted or dissolved in water, free electrically charged particles result. These are more or less affected by the presence of other nearby particles. The discussion of some of the more important salts is given in later chapters in which the salts are classified according to the negative ions which they contain.

THE HALOGENS

This closely related group of elements contains *fluorine*, *chlorine*, *bromine*, *iodine*, and *number 85*, which has not yet been isolated from its natural minerals, though a radioactive isotope has been reported as the result of nuclear transformations. The binary compounds of these elements with metals are salts; and the name *halogen*, "salt former," is based on the property indicated. The atoms of these elements contain seven valence electrons, so that they gain electrons with a high degree of activity, and exhibit an electrovalence of 1 −. The atoms may also share electrons to form covalent bonds. The oxidation state of the elements is determined by the number of electrons involved in the transference or sharing process.

Occurrence of the Halogens. The activity of the halogens is so great that they do not occur in the uncombined state among natural substances. *Chlorine*, the most abundant, occurs to the extent of only approximately 0.2% in the outer part of the earth. The halogens occur primarily as halides. In addition to sodium chloride, *chlorides* of several of the other metals occur in sea water and in salt deposits; but sodium chloride is the source of most of the chlorine and of its manufactured compounds. *Bromides* also are found in sea water and in salt beds, and both serve as sources of the element. The percentage of *iodides* in sea water is so small that the salt beds and brines are not usually a practicable source of the element, unless special conditions have led to the concentration of its compounds. The salt brines obtained from certain

oil wells in California and Louisiana contain a high enough concentration of iodides to serve as a source of the element. Some varieties of marine plants contain iodine compounds, and small percentages of sodium iodide remain in the residue when these plants are charred. Thyroxine, a compound secreted in the thyroid gland of animals, contains iodine. *Sodium iodate*, $NaIO_3$, is found in small percentages in the sodium nitrate deposits in Chile. Fluorides do not occur in the salt beds. The most important naturally occurring compound of fluorine is the mineral *fluorspar*, *calcium fluoride*, CaF_2; and the element also occurs in the mineral, *cryolite*, Na_3AlF_6.

Preparation of the Halogens. The oxidation state of the halogens in their binary compounds is 1 −. Hence, the preparation of the elements from their binary salts requires the removal of the electron which imparts the negative charge, a reaction called oxidation.

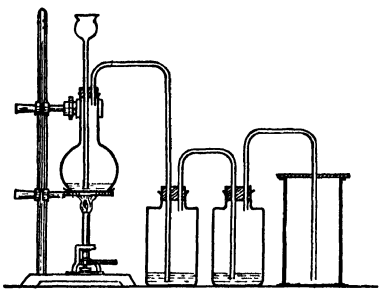


FIG. 58. — Laboratory Preparation of Chlorine.

The Laboratory Preparation. *Chlorine* was first prepared by Scheele in 1774, by warming hydrochloric acid with manganese dioxide. This reaction is still the basis of the laboratory method. The apparatus is shown in Fig. 58. Chlorine may be collected by the upward displacement of air. In this reaction, the oxidation number of manganese is decreased from 4 + to 2 +, a change which is compensated by an increase in the oxidation number of chlorine from 1 − to 0. Hence, one mole of chlorine is produced for each mole of manganous chloride that is formed.

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

Other oxidizing agents might be used instead of manganese dioxide, and other chlorides instead of hydrochloric acid. An acid, however, is required as one of the reactants. If sodium chloride is used as the direct source of chlorine, sulfuric acid is also introduced.

$$2\,NaCl + MnO_2 + 3\,H_2SO_4 \longrightarrow 2\,NaHSO_4 + MnSO_4 + Cl_2 + 2\,H_2O.$$

Bromine was discovered by Balard in 1826, and *iodine* by Courtois in 1811. These elements are liberated from their compounds by a reaction of the same nature as that used for chlorine. A mixture of the salt, manganese dioxide, and sulfuric acid is heated and the halogen is evolved. Bromine is condensed to the liquid and iodine to the solid.

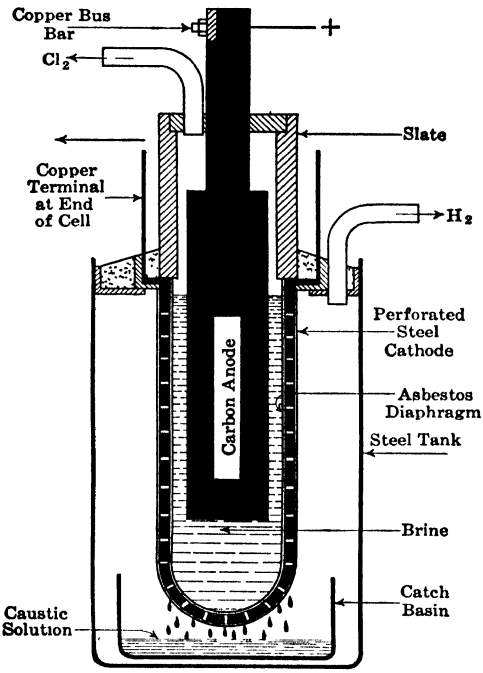


FIG. 59. — Nelson Cell.

Industrial Preparation. The industrial preparation of *chlorine* is accomplished by the electrolysis of sodium chloride. The products are sodium and chlorine when the fused salt is electrolyzed, sodium hydroxide, hydrogen, and chlorine when the salt is in aqueous solution. Chlorine reacts with sodium hydroxide so that it is necessary to use a special type of cell in which the products do not come in contact with each other. A number of different cells have been invented for this purpose, but all of them operate on this same principle. *The Nelson cell*, Fig. 59, will serve to illustrate the procedure. The anodes are graphite rods projecting down into the cell, and the cathode is a perforated steel plate. A layer of asbestos cloth at the inner surface of the cathode serves as a porous diaphragm to divide the cell into two compartments and prevent the mixing of the substances formed at the electrodes. This diaphragm, nevertheless, permits the passage of dissolved substances under the influence of the electric current. The brine solution is kept at a constant level in the anode compartment by means of an automatic feed device. Chlorine, liberated at the anode, passes from the cell through an outlet at the top of the anode compartment and is dried, liquefied, and stored under

pressure in steel cylinders. Hydrogen and sodium hydroxide are formed at the cathode, and the hydrogen escapes from the cell through an outlet from the outer compartment. The solution containing sodium hydroxide drips out through the perforated steel cathode into a catch basin. Sodium hydroxide, separated from the undissolved salt, is a valuable co-product of this operation.

Bromine is obtained in the United States from two main sources: the brine from the salt wells in Michigan, and sea water at a plant near Wilmington, North Carolina. Although bromine can be prepared by electrolysis, it is commonly liberated by the reaction of chlorine with bromides, the chlorine being produced by electrolysis as discussed in the preceding paragraph.

$$Cl_2 + 2\ NaBr \longrightarrow Br_2 + 2\ NaCl.$$

The bromine may be blown out of the solution by warm air. A portion of the bromine is condensed directly to the liquid state, and the remainder is absorbed in sodium carbonate solution with the formation of sodium bromide and sodium bromate. From this product, the bromine is subsequently recovered.

Iodine may be liberated from iodides by the action of chlorine. An American process was developed in 1934 for the production of iodine, in amounts sufficient for the requirements of this country, from the oil-well brines mentioned previously. A dilute solution of silver nitrate is added to the prepared brine in the amount calculated to precipitate silver iodide, but not the chloride. This is possible because silver iodide is less soluble than the chloride. The addition of clean steel scrap to the suspension of silver iodide displaces silver and produces ferrous iodide.

$$2\ AgI + Fe \longrightarrow FeI_2 + 2\ Ag.$$

Silver is separated and converted into the nitrate, which is used again. Iodine is liberated from ferrous iodide by oxidation with chlorine in water.

$$FeI_2 + Cl_2 \longrightarrow FeCl_2 + I_2.$$

Iodine is also prepared from sodium iodate, which occurs as an impurity in Chile saltpeter. The oxidation number of iodine in the iodate is 5 +. Hence, reduction is necessary to liberate the element. This requires the presence of an acid medium. Sodium hydrogen sulfite may serve as both the reducing agent and the acid.

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

Fluorine was first prepared by Moissan in 1886, by the electrolysis of a solution of potassium fluoride in anhydrous liquid hydrogen fluoride. Scheele had recognized the existence of an element similar to chlorine in fluorspar and is credited with the discovery of fluorine in 1771. The method now used for the preparation of fluorine is the electrolysis of fused potassium hydrogen fluoride, KHF_2, in a copper vessel. The inner surface becomes coated with a thin film of copper fluoride and is thus protected from further corrosion by elementary fluorine.

Properties of the Halogens. Some of the properties of these elements are listed in Table 11.

TABLE 11

PROPERTIES OF THE HALOGENS

	Fluorine	*Chlorine*	*Bromine*	*Iodine*
Atomic Weight . .	19	35.46	79.92	126.92
Atomic Number . .	9	17	35	53
Isotopes	19	35, 37	69, 81	127
Electron Distribution	2, 7	2, 8, 7	2, 8, 18, 7	2, 8, 18, 18, 7
Molecular Weight .	38	70.92	159.84	253.84
State, 20°	Gas	Gas	Liquid	Solid
Melting Point . . .	− 223°	− 102.1°	− 7.3°	113°
Boiling Point . . .	− 188.3°	− 34.7°	58.0°	183°
Critical Temperature	—	144.0°	302.0°	553°

From the table it may be observed that, in the order of their atomic weights, there is a gradual transition in properties from fluorine to iodine. There is an increase in the depth of color in the gaseous state, the density, and in the melting point, boiling point, and critical temperature. The halogens are not highly soluble in water, but fluorine reacts with water, displacing oxygen. These substances are more soluble in alcohol and some other organic solvents than in water, and iodine dissolves readily in aqueous solutions of potassium iodide. In the gaseous state, the halogens exist in the form of diatomic molecules at moderate temperatures. These molecules decompose at high temperatures to form monatomic molecules; and mixtures, the proportions depending on the temperature, are obtained at intermediate temperatures.

In the liquid and solid states the colors of these substances are darker than in the gaseous state. Liquid bromine is a dense, reddish-brown, highly volatile liquid at room temperature. Liquid iodine is brown in color and the solid is a dark gray substance existing in thin, flat crystals. Unless the partial pressure of iodine in the gaseous state in contact with the solid is at least 100 mm., the solid sublimes without melting when it is heated.

In the gaseous state, these substances have disagreeable odors and an irritating effect on the mucous membrane lining the nose and throat. Chlorine gas, breathed in large concentrations, causes severe inflammation and congestion of the lungs, which is likely to prove fatal. The use of chlorine as a military gas during the great war of 1914–1918 was an application of this property. The action of fluorine is more severe, but much less familiar than that of chlorine. Liquid bromine produces severe burns if it comes in contact with the skin, and great care should be exercised to avoid spilling it. At room temperature, iodine has no severe corrosive action on the skin.

Reactions of the Halogens. Since the halogens are composed of atoms which have only one electron less than the number in the next higher inert gas, they react vigorously with a number of substances to gain an additional electron. The stable structure of the inert gas may also be attained by the sharing of electrons to form a single covalent bond. The remaining electrons in the valence shell may now form coördinate links with additional atoms, building up complex molecules and radicals, such as those observed in the oxyacids and their salts.

The halogens react directly with most of the other elements, except the inert gases, oxygen, and nitrogen. Fluorine and chlorine do not unite with each other, and chlorine does not react directly with carbon. Bromine and iodine are less active than fluorine and chlorine, and do not react with some of the less active metals. In the reactions of the halogens with *metals* the molecules of the halogens become broken apart into the atoms, which then gain electrons from the atoms of the metals. The reactions of the halogens with other *non-metals* involve the sharing of electrons, one of the electrons of the bond being contributed by the halogen atom, the other by the atom of the element with which the halogen reacts. Thus, iodine and chlorine react with each other to

form iodine monochloride. This reaction may be illustrated by the use of electronic formulas.

$$:\ddot{I}:\ddot{I}: + :\ddot{Cl}:\ddot{Cl}: \longrightarrow 2:\ddot{I}:\ddot{Cl}:$$

In this compound, the oxidation number of iodine is 1 + and of chlorine 1 −, by arbitrary interpretation. The halogens react with phosphorus in more than one ratio. The first product is the trihalide.

$$2\ P + 3\ Cl_2 \longrightarrow 2\ PCl_3.$$

The trihalides, except the iodide, react with the halogen to form the pentahalide.

$$PCl_3 + Cl_2 \longrightarrow PCl_5.$$

The halogens react with *hydrogen* to form the hydrogen halides. The electron pairs are displaced toward the halogen atoms and these compounds are composed of polar molecules. It has been suggested that a small proportion of the hydrogen halide may break down directly into electrovalent particles. *The difference in the activity of the halogens* is illustrated by the reactions with hydrogen. Moist fluorine and hydrogen react violently, even when they are cold and in the absence of light. Mixtures of hydrogen and chlorine are stable in the dark, but react violently when they are exposed to light. Hydrogen and bromine react with each other at significant rates only when they are heated together or are brought in contact with a catalyst, such as platinum. The reaction of hydrogen with iodine is incomplete even when the substances are heated together. This reaction is reversible; *i.e.*, the products of the one reaction interact to reform the initial substances. The heats of reaction show the order of activity of the halogens:

$$H_2 + F_2 \longrightarrow 2\ HF + 128{,}000\ \text{cal.}$$
$$H_2 + Cl_2 \longrightarrow 2\ HCl + 44{,}000\ \text{cal.}$$
$$H_2 + Br_2 \longrightarrow 2\ HBr + 17{,}280\ \text{cal.}$$
$$H_2 + I_2 \longrightarrow 2\ HI - 12{,}800\ \text{cal.}$$

The halogens react with many binary compounds of non-metals of lower activity. Chlorine displaces bromine and iodine from their binary salts. Similarly, the halogens displace sulfur from sulfides,

$$I_2 + H_2S \longrightarrow S + 2\ HI.$$

The activity relationships of the halogens are shown by their displacement reactions. Each of the halogens may be displaced by those which precede it in a list arranged according to the atomic numbers; but none of them may be displaced by those which follow in the list.

The halogens react with many of the hydrocarbons, binary compounds of carbon and hydrogen. Two types of reaction may be observed. In one of these, a reaction known as *substitution*, atoms of hydrogen are successively replaced by atoms of the halogen, with the formation of halogen derivatives of the hydrocarbon and the hydrogen halide.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl.$$

Carbon tetrachloride is the final product of the reaction of methane with chlorine. In the other type of reaction, known as *addition*, molecules of certain classes of hydrocarbons add halogen atoms in pairs. Thus, ethylene, C_2H_4, may add two atoms of chlorine to form ethylene dichloride,

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2.$$

Hydrocarbons which undergo this type of reaction are known as unsaturated hydrocarbons.

The halogens react with water. The products differ, depending on the activity of the halogen and the experimental conditions. Fluorine reacts vigorously with water, yielding both oxygen and ozone, along with hydrofluoric acid.

$$2\,F_2 + 2\,H_2O \longrightarrow 4\,HF + O_2.$$

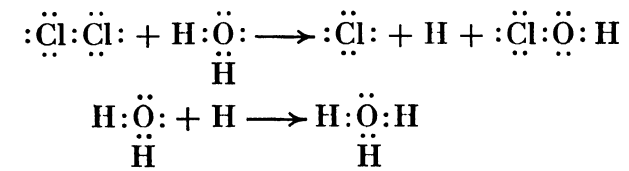
Chlorine reacts with water in direct sunlight, forming hydrochloric acid and oxygen. With bromine, practically no free oxygen is produced; and with iodine, none.

The second and more important reaction of the halogens with water yields the hydrohalic acid and the hypohalous acid. This reaction cannot be detected with fluorine, probably because the reaction liberating oxygen takes place too rapidly. The reaction of the remaining three halogens with water produces the acids, and the reaction is reversible.

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO.$$

This reaction involves the hydrolysis of the halogen. It may be assumed that the reaction occurs in the following manner. The

halogen molecule is split by the action of water; but the pair of electrons constituting the bond remains with one of the atoms, giving it an electrovalence of 1 −. This leaves the other atom of chlorine momentarily in an unstable condition with only six electrons in the outer shell. This particle instantly reacts with the water molecule, combining with the hydroxide radical, including all of its shared electrons and setting free an electrovalent hydrogen ion, which itself reacts with an additional water molecule to form the hydrated hydrogen ion, H_3O^+. These changes may be illustrated by the electronic formulas: [1]



Since hypochlorous acid decomposes when it is exposed to sunlight, the production of oxygen by the reaction of chlorine with water is probably the result of two consecutive reactions, the formation of hypochlorous acid and its decomposition.

In the consideration of the reactions of the halogens, it has been observed that *the activity decreases with increase in the atomic number.* This change is opposite to that observed for the alkali metals. This is to be expected because the activity of the halogens is based on the gain of electrons and of the alkali metals on the loss of electrons. The diagrams, Fig. 60, will aid in interpreting the activity relationships of the halogens. The attraction of the nucleus for an electron in a particular shell depends on the total charge on the nucleus and the extent to which it is screened by intervening electron shells. Although the nuclear charge is greater in atoms of high atomic number than in those of low atomic number, the increased complexity of the atom causes a much greater screening effect than in the elements of similar structure but lower atomic number. Consequently, the additional electron required to complete the valence shell of the halogen is attracted much less energetically in the more complex atoms than in those of simpler structure; *i.e.*, the elements of the higher atomic numbers are the less active.

[1] In the electronic notation, the symbol H does not represent the hydrogen atom, but a charged hydrogen kernel, or proton, from which the valence electron has been removed.

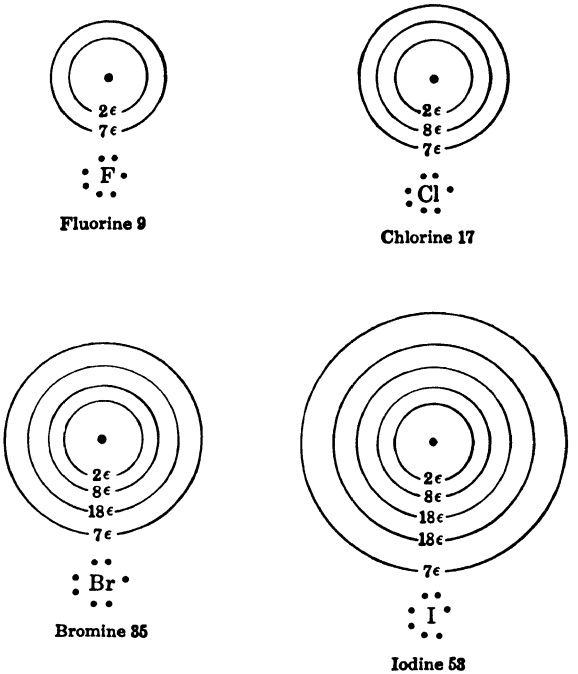


FIG. 60. — Diagrams of the Atoms of the Halogens.

Uses of the Halogens. *Fluorine* has few uses of importance, although some of its compounds are important. The naturally occurring minerals, fluorspar and cryolite, and the manufactured acid, hydrofluoric acid, have important industrial applications. One of the interesting fluorine compounds is the methane substitution product, difluorodichloromethane, prepared by the reaction of carbon tetrachloride with antimony trifluoride in the presence of antimony pentafluoride as a catalyst. This substance is used in some household refrigerating machines. It has the advantage of being nontoxic and noninflammable in the event that leaks develop in the refrigeration system.

Chlorine has a number of important uses; and it is estimated that 605,000 tons of this substance were produced in the United States in 1940. Approximately 525,000 tons were produced as a coproduct of the electrolytic production of sodium hydroxide; and 80,000 tons in the production of metallic sodium and magnesium and from other limited sources. The most extensive use of chlorine, possibly 60% of the production, is in the chemical indus-

tries. It is used not only for the direct formation of many of its compounds, such as the hypochlorites, but also for the preparation of materials which are intermediates in the production of other substances, particularly in the organic chemical industry. A number of uses of chlorine are based on its bleaching and germicidal action. Approximately 21% of the chlorine produced is used in bleaching paper pulp, 5% in the textile industry, and 6% for sanitation. The use of chlorine for these purposes is due to its interaction with water to form hypochlorous acid, and the bleaching action will be discussed further in connection with that substance.

During the great war of 1914–1918, chlorine was used extensively in the production of poison gases for military use. The first extensive use of poison gas as an offensive weapon was made by the German army at Ypres in Belgium in the spring of 1915. This involved the use of chlorine itself, which was liberated from steel cylinders on a day when the wind direction and velocity were suitable to cause it to sweep down over and into the trenches of the Allies. Later, compounds which were much more effective than chlorine were developed and used for military purposes. Among these, one of the most effective was mustard gas, $(C_2H_4Cl)_2S$, which is a liquid substance suitable for use in shells. When the shell explodes, the liquid is scattered over a large area where it remains for a long time, making the area unsuited for human occupation. Hence, it may be used effectively to "deny the ground" to the enemy.

The production of *bromine* in the United States in 1938 was approximately 16,132 tons. It is employed in the production of its compounds, such as the bromides which are used in photography and in medicine. Bromine also finds extensive use as a reagent in chemical industry for the preparation of intermediate compounds, such as ethylene dibromide for the production of lead tetraethyl, "ethyl fluid" for use in gasoline.

A solution of *iodine* in alcohol, "tincture of iodine," is well known as a germicidal agent. The tincture usually contains a high enough concentration of potassium iodide so that it is possible to dilute it to some extent with water without causing the precipitation of the iodine. Iodine is used in the synthesis of some organic compounds and in the production of iodides, which are used to some extent in medicine and in photography.

Halides of the Metals. The halides of metals are salts in which the halogens have an electrovalence of 1 −. Although metal halides result from the reaction of metals with the halogens, they are more commonly prepared by the reaction of the appropriate hydrohalic acid with metals, basic oxides and hydroxides, and with other salts. Some of the important halides are discussed in Chapter XXVIII.

Halides of Hydrogen. The halides of hydrogen are gaseous substances at ordinary temperatures and pressures. They have low boiling points and melting points, except liquid hydrogen fluoride which boils at 20°. They are highly soluble in water, with which they interact to form acidic solutions, the hydrohalic acids, or the hydroacids of the halogens, Chapter XV.

Halides of Non-metals. The halides of a number of the non-metals may be prepared. These substances exist in the molecular state and the halogens have an oxidation number of 1 −, which is due to covalent bonding. These substances do not show the properties of salts. Many of these compounds are decomposed by water, although the nature of the electron bond in some of the non-metal halides is such as to form symmetrical molecules which are stable in contact with water. Those which are decomposed by water yield acidic solutions containing the hydroacid of the halogen and the oxyacid of the other non-metal. Several of these substances are discussed in connection with the other non-metals involved.

Oxycompounds of the Halogens. Although the halogens do not unite directly with oxygen, a number of oxycompounds are known. Oxides of all of the halogens have been prepared; but the oxides of bromine and some of the oxides of chlorine and iodine are very unstable. The oxide of fluorine, F_2O, results from the reaction of the gas with a dilute solution of sodium hydroxide. The more important oxides of chlorine are the *monoxide*, Cl_2O, the *dioxide*, ClO_2, and the *heptoxide*, Cl_2O_7; and of iodine, the *tetroxide*, I_2O_4, and the *pentoxide*, I_2O_5. These oxides result from the decomposition of the various oxyacids. With the exception of fluorine, each of the halogens yields oxyacids and oxysalts. The oxyacids are listed in Table 12.

In all of these compounds the halogens exhibit positive oxidation numbers. The acids possess varying degrees of instability, and

TABLE 12

OXYACIDS OF THE HALOGENS

Oxidation Number	*Name*	*Chlorine*	*Bromine*	*Iodine*
1 +	Hypohalous	$HClO$	$HBrO$	HIO
3 +	Halous	$HClO_2$	—	—
5 +	Halic	$HClO_3$	$HBrO_3$	HIO_3
7 +	Perhalic	$HClO_4$	—	HIO_4

they are usually prepared from their salts as desired for reaction in preference to attempting to store them. The oxycompounds of chlorine are the most important in each of these classes of compounds.

Hypochlorites. Hypochlorous Acid. The reaction of chlorine with water produces a low concentration of hypochlorous and hydrochloric acids in a reversible reaction. In a basic solution the free acids are neutralized and the reaction goes to completion.

$$2\,NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O.$$

Solutions containing the hypochlorite and the chloride are prepared industrially by passing chlorine into cold sodium hydroxide solutions and by the electrolysis of sodium chloride solutions in which the electrodes are in a single compartment. Chlorine, liberated at the anode, reacts with the basic solution formed about the cathode, producing the hypochlorite according to the equation written above. Calcium hydroxide reacts with chlorine to yield a mixed salt in which both chloride and hypochlorite radicals are in combination with calcium.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaClClO + H_2O.$$

This mixed salt is known as *bleaching powder* and as *chloride of lime.* It is prepared by passing chlorine over solid calcium hydroxide spread on trays in a large chamber.

Hypochlorites react with acids, yielding *hypochlorous acid.* If bleaching powder, or a mixture of sodium chloride and sodium hypochlorite, is acidified with a strong acid, both hydrochloric

acid and hypochlorous acid are formed in high enough concentration to react with each other and liberate chlorine.

$$NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4.$$
$$NaClO + H_2SO_4 \longrightarrow HClO + NaHSO_4.$$
$$HCl + HClO \rightleftharpoons Cl_2 + H_2O.$$

If the solution is weakly acidic, the concentrations of the free acids are low and the loss of chlorine is largely prevented. By proper regulation of the acidity, the concentration of hypochlorous acid is also regulated; but it may be maintained at a constant value, if the acidity remains constant, until all of the salt is decomposed. Solutions of this type, known as "Dakin's solution," are used for the irrigation of infected wounds. Sodium hypochlorite in solution decomposes with the liberation of oxygen in the presence of cobalt hydroxide as a catalyst. When a solution of sodium hypochlorite is heated, a mixture of the chlorate and chloride is obtained.

The hypochlorites are important as bleaching, deodorizing, and disinfecting agents. They are used in dairies, public water supplies, sewage disposal plants, the production of paper pulp, and in the laundry. For these purposes, the chloride and hypochlorite mixture produced directly is suitable. Liquid chlorine, stored and transported in steel cylinders, is now used in preference to bleaching powder and solutions of other hypochlorites for many purposes.

Bleaching, both by chlorine and by hypochlorites, is due to the formation of hypochlorous acid, which is an oxidizing agent. Hypochlorous acid decomposes into hydrochloric acid and oxygen with an evolution of energy.

$$2\,HClO \longrightarrow 2\,HCl + O_2 + 18{,}600\ \text{cal.}$$

Consequently, the oxidizing action of hypochlorous acid is greater than that of oxygen. Cotton, linen, and wood pulp are composed chiefly of cellulose, which is inactive chemically and is affected only slowly by dilute solutions of hypochlorous acid. The coloring substances present in the natural materials are more active and they are oxidized to colorless substances. After the bleaching is complete, the excess of hypochlorous acid must be removed by thorough washing or by the use of reducing substances, such as sodium thiosulfate, $Na_2S_2O_3$. Wool, silk, and feathers, which are

largely protein, react with hypochlorous acid, so that they cannot be bleached by hypochlorous acid without injury.

Chlorine monoxide may be prepared by the reaction of chlorine with mercuric oxide at a temperature about 0°.

$$2\,HgO + 2\,Cl_2 \longrightarrow HgCl_2(HgO) + Cl_2O.$$

At room temperature, chlorine monoxide is a yellowish-brown gas which decomposes into the elements in an explosive reaction. This oxide reacts reversibly with water to form hypochlorous acid.

$$Cl_2O + H_2O \rightleftharpoons 2\,HClO.$$

Hypobromites and Hypoiodites. Bromine and iodine react with strongly basic solutions, yielding the halide and the hypobromite and hypoiodite, respectively. These reactions are involved in the preparation of the bromides and iodides from the free halogens. The acids corresponding to these salts are unstable. Bromine monoxide has been prepared by the reaction of bromine with mercuric oxide, a reaction analogous to that which yields chlorine monoxide. Bromine monoxide is very unstable and is not important.

Chlorates. Chloric Acid. When a solution of a hypochlorite is warmed, a mixture of the chlorate and chloride is produced.

$$3\,KClO \longrightarrow 2\,KCl + KClO_3.$$

The mixture containing electrovalent chloride ions together with atoms of chlorine in the oxidation state of 5 + is more stable than the hypochlorite. The most important of the chlorates is *potassium chlorate*. The salt is prepared commercially by the electrolysis of hot, saturated solutions of potassium chloride. For this purpose, the anode and cathode are together in the single compartment of a cell, and the solution is stirred to insure the thorough mixing of the chlorine and potassium hydroxide formed as the direct products of the electrolysis. Since the hypochlorite is not stable in the hot solution, the chlorate is immediately formed. Potassium chlorate is not highly soluble so that it may be crystallized from the solution. Sodium chlorate may be prepared in a similar manner. The decomposition of potassium chlorate to produce oxygen is familiar. When the solid chlorates are carefully heated at moderate temperature, a mixture of the chloride and perchlorate is formed.

A solution of *chloric acid* may be formed by the reaction of sulfuric acid with a solution of barium chlorate, barium sulfate being precipitated.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\,HClO_3.$$

Chloric acid is unstable in concentrated solutions and at temperatures above 40°, decomposing to yield *chlorine dioxide*, water, and oxygen.

$$4\,HClO_3 \longrightarrow 4\,ClO_2 + 2\,H_2O + O_2.$$

Chlorine dioxide is a yellow gas which decomposes with explosive violence at slightly elevated temperatures. Consequently, serious accidents may result from the addition of concentrated sulfuric acid to a chlorate.

Bromates and Iodates. These substances may be prepared by reactions analogous to those used for the preparation of the chlorates. The acids may also be prepared by the reaction of strong oxidizing agents with the free non-metals.

$$3\,I_2 + 10\,HNO_3 \longrightarrow 6\,HIO_3 + 10\,NO + 2\,H_2O.$$

Bromic acid, prepared by a similar reaction, decomposes in concentrated solutions. *Iodic acid* may be separated as a white crystalline solid. By careful heating, the acid may be decomposed to yield *iodine pentoxide*, I_2O_5.

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

The reaction of concentrated sulfuric acid with an iodate yields iodic acid, which decomposes to form *iodine tetroxide*, I_2O_4.

$$4\,HIO_3 \longrightarrow 2\,I_2O_4 + 2\,H_2O + O_2.$$

The salts of iodic acid, *the iodates*, are more stable and less soluble than the other halates. The occurrence of sodium iodate in Chile saltpeter has been mentioned.

Chlorites. Chlorous Acid. Chlorine dioxide reacts with basic hydroxides to form the chlorite and the chlorate.

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

Chlorous acid is liberated from its salts by the action of stronger acids. Both chlorous acid and its salts are moderately unstable, decomposing to give the chloride and oxygen or the chloride and chlorate. The production of sodium chlorite in commercial quantities is expected early in 1941. This substance is active

enough as a bleaching agent to oxidize the coloring matter in cotton, rayon, wood pulp, and other cellulose fibers; but does not attack the fibers themselves. Through the use of this bleaching agent it is possible to produce strong white paper without damaging the fiber. Chlorite acts as a bleaching agent in basic as well as acidic solutions.

Perchlorates. Perchloric Acid. When potassium chlorate is heated just to the melting point and is kept at this temperature for some time, a portion of it decomposes to give up oxygen, while the remainder is converted into a mixture of the chloride and perchlorate.

$$4\ KClO_3 \longrightarrow 3\ KClO_4 + KCl.$$

The perchlorate is much less soluble than the chloride and separation may be effected by fractional crystallization. Sodium perchlorate is prepared industrially by the electrolysis of concentrated solutions of sodium chlorate, using smooth platinum anodes and iron cathodes. The chlorate is converted into the perchlorate at the anode and hydrogen is discharged at the cathode. Potassium and ammonium perchlorates, which are used in fireworks and explosives, are prepared from sodium perchlorate by double decomposition since they are only slightly soluble. Magnesium perchlorate is an excellent drying agent.

Perchloric Acid, $HClO_4$, is prepared by a double decomposition reaction between a perchlorate and a strong acid. It may be concentrated by distillation under reduced pressure. A 70% solution of the acid may be stored safely, but in more concentrated solutions it decomposes explosively. Perchloric acid is an active oxidizing agent in concentrated solution. The dehydration of perchloric acid through the use of phosphorus pentoxide yields the anhydride, *chlorine heptoxide*, Cl_2O_7.

$$6\ HClO_4 + P_2O_5 \longrightarrow 2\ H_3PO_4 + 3\ Cl_2O_7.$$

Since this substance is also unstable, the dehydration must be carried out at low temperature.

Oxidizing Activity of the Oxycompounds of Chlorine. The most stable oxidation state of chlorine is the electrovalent negative ion. In the discussion of the oxycompounds of the halogens, the instability of the substances has been constantly noted. These

compounds are active oxidizing agents, being readily converted into products in which the halogen exhibits the oxidation state of 1 −. The spontaneous changes in oxidation number shown when a solution of a hypochlorite is warmed, producing a mixture of the chloride and chlorate, indicate the increasing stability of the oxycompounds with rise in the oxidation number. The hypochlorites are more vigorous oxidizing agents than the chlorates and perchlorates. When, therefore, a chlorate or a perchlorate is reduced, it yields the chloride, not a lower oxysalt.

EXERCISES

1. How are the alkali metals prepared? Why is it not possible to prepare them satisfactorily by the reduction of their oxides with carbon or by the electrolysis of salt solutions?
2. Write equations which illustrate the common reactions of the alkali metals.
3. In terms of the structure of the atoms, explain:
   (*a*) why the alkali metals exhibit similar reactions;
   (*b*) why the activity increases with increasing atomic number.
4. Explain the use of sodium in photoelectric cells and in sodium vapor lights.
5. Describe the laboratory method for the preparation of chlorine, bromine, and iodine.
6. What are the essential steps in the preparation of:
   (*a*) chlorine from salt deposits;
   (*b*) bromine from sea water;
   (*c*) iodine from certain oil-well brines;
   (*d*) iodine from sodium iodate?
7. Illustrate by equations the common reactions of the halogens.
8. Discuss the relative activities of the halogens, basing the discussion on two series of similar reactions.
9. Account for the differences in the activities of the halogens in terms of the structures of their atoms.
10. Which of the oxycompounds of the halogens are important? How is each of these prepared?
11. Explain the action of chlorine as a bleaching agent.
12. Discuss the relative stability of the compounds of chlorine in different oxidation states.

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CHAPTER VIII

CHEMICAL EQUILIBRIUM

In the discussion of the halogens and their compounds, the reversibility of several reactions was noted. Such reactions do not normally proceed to completion so long as all of the materials remain together. The study of these reactions is important, not only in determining the relative amounts of the products which it is practicable to obtain, but also in determining the effect of changes in conditions on these proportions. The discussion of reversible reactions involving acids, bases, and salts in solution will be deferred to Chapter XII, following the study of the properties of the separate particles in such solutions.

Chemical Equilibrium. If a reversible reaction takes place under such conditions that all of the products remain in intimate contact with each other, the reacting substances constitute a *closed system.* At the outset only one of the two reactions takes place because only the initial substances are present in the system. As the reaction proceeds, however, the concentration of the initial substances becomes lower, since they are consumed in the reaction; and the velocity of the initial reaction becomes progressively less. In the meantime, the reverse reaction has commenced and its velocity has become progressively greater. Since the two reactions occur simultaneously and each tends to counteract the other, the concentrations adjust themselves so that the two reactions attain the same velocity. ***A system is in a state of equilibrium when the two reactions which it involves are opposite in effect and proceed with the same velocity.*** At equilibrium, the concentrations of the reactants remain constant, so long as the conditions are not altered. The equilibria are *homogeneous* when all of the reactants are in the same phase and remain uniformly mixed with one another. The equilibria are *heterogeneous* when two or more distinctly different physical forms of matter are involved.

The products of a great many reactions which are not noticeably

reversible under some conditions react with one another to a significant extent under certain other conditions. In some instances, one of the two reactions involved proceeds so much more slowly than the other that the reaction in one direction is virtually complete. The separation of the products of a reversible reaction prevents their interaction and causes the reaction to go to completion. All of the reactions in which the products are separated, or in which the difference in the rates of reaction causes virtual completion, as well as those which are in reality irreversible, are commonly considered to be *completed reactions*. The name, *reversible reaction*, is commonly applied only to those systems in which the two opposing reactions occur in such a manner that they have a significant bearing on the concentrations of the reactants. The double arrow is usually written to represent reversible reactions. It is sometimes convenient to use arrows of unequal length to express differences in the concentrations of the substances at equilibrium. The longer arrow is directed toward the formulas of the products which are present in the larger proportions in the equilibrium mixture. In many reactions in which the concentrations of the initial reactants are very small at equilibrium, the single arrow is employed unless the reversibility of the reaction is significant in the discussion of the topic under consideration.

The Velocity of Reactions. Since the concentrations of the substances involved in a system in a state of equilibrium depend on the relative velocities of the reactions, it is important to understand the factors which determine reaction velocities. *The velocity of a reaction is the rate of change in the concentrations of the reactants.*

The velocity of any reaction is dependent on the *specific nature* of the substances involved in the change. If the molecules of the reactants are themselves stable, they do not tend to react rapidly. No quantitative rules can be stated relating the velocity of a reaction to the nature of the reacting materials. The velocities of reactions are affected by several conditions which alter the activities of the molecules. The concentrations of the reactants, the pressure, especially for gases, the temperature, and the presence of a catalyst are conditions affecting rates of reaction. If the substances are in different phases, thorough mixing in a

fine state of subdivision, so as to insure the maximum surface contact, plays an important part in securing maximum reaction velocity.

The Effect of Concentration on Reaction Velocity. The velocity of any reaction depends on the concentrations of the reacting substances. The relation of reaction velocity to concentration was stated quantitatively in 1863 by Guldberg and Waage as the **Law of Molecular Concentration, or the Law of Mass Action: The velocity of a chemical reaction is proportional to the product of the molecular concentrations of the reacting substances, each concentration being raised to the power which is numerically equal to the coefficient of that substance in the equation representing the reaction.** The molecular concentrations of substances may be measured as the molar concentrations, the number of moles per liter. The molar concentration is usually represented by writing the symbol or formula inclosed in brackets. Since the number of moles of any gas in one liter under ordinary conditions of temperature and pressure is a small fraction, it is convenient to measure the molecular concentrations of gases in terms of their partial pressures. The partial pressure of each gas in a gas mixture depends on the concentration of that gas in the mixture. Consequently, the pressure-volume relation for each of the gases in the mixture may be stated in terms of the general gas law, the partial pressure being represented by p,

$$pV = nRT; \text{ or } p = \frac{nRT}{V}.$$

However, n, the number of moles, divided by V, the volume, is equal to the molar concentration. Therefore,

$$p = RT \times \text{concentration}.$$

Since the product, RT, is a constant at fixed temperature, the pressure is proportional to the molecular concentration.

Carbon monoxide and steam react with each other at a temperature of 1000° to form carbon dioxide and hydrogen.

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

Applying the law of molecular concentrations,

$$V \propto p_{CO} \times p_{H_2O}$$
$$V = K \times p_{CO} \times p_{H_2O}.$$

In this equation, K is known as a *velocity constant.* Sulfur dioxide and oxygen react to form sulfur trioxide.

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3.$$

$$V \propto p^2_{SO_2} \times p_{O_2}.$$

$$V = K \times p^2_{SO_2} \times p_{O_2}.$$

If the reacting substances are in different states, as in the reaction of a gas with a liquid or a solid, the law of molecular concentrations is applicable only if the assumptions are made that the mechanism of the reaction involves the conversion of the liquid or solid into the gaseous state, and that the concentration of the substance in the gaseous state is constant. This means merely that the velocity of the reaction depends on the concentration or partial pressure of the gaseous substance.

An increase in the partial pressure of a gas causes a corresponding increase in the molecular concentration. Therefore the effect of pressure on the velocity of a reaction involving gaseous substances may be explained in terms of the concentration effect.

The Effect of Temperature on Reaction Velocity. It is a familiar observation that the velocity of chemical reactions increases with rise in temperature. No generalization stating the exact relation between temperature and reaction velocity may be made. It is observed experimentally that the effect of an increase in temperature varies greatly, but that, as an approximate average, the velocity of a reaction is doubled for each ten-degree rise in temperature. Since it may be calculated in accord with the kinetic theory that an increase of ten degrees in temperature increases the kinetic energy, and therefore the rate of motion, of the molecules by only a few per cent, the increased rate of reaction, in some instances as great as 100% to 400%, cannot be attributed to the increased number of molecular collisions. Arrhenius suggested, as an explanation of this relationship, that only a limited number of the molecules of the substances are active enough to enter into the reaction; *i.e.*, the majority of the molecular collisions do not normally lead to any reaction. As the temperature rises, energy is absorbed and the number of the activated molecules increases, so that the rate of reaction likewise increases.

The Effect of Catalysts on Reaction Velocity. In a number of reactions, the velocity is affected by the presence of substances which remain unchanged at the end of the process. These substances are *catalysts.* Some catalysts increase the rate of reaction; and, in other instances, the catalyst decreases the rate of reaction. Catalysts which produce this latter effect are known as *inhibitors.* Only a small amount of the catalyst is required to maintain the catalytic effect for a long time. Some catalysts are homogeneous with the substances in the system which they catalyze, and others are heterogeneous. The function of the positive catalyst is to bring about the desired reaction at suitable velocity by lowering the energy of activation required. Consequently, a larger proportion of the molecules have the requisite amount of energy to cause more rapid reaction in the presence of the catalyst than in its absence, under the same conditions of temperature and concentration. In many instances, the catalytic action is caused through the formation of intermediate compounds with lower energy consumption, and the subsequent decomposition of these compounds with the liberation of the catalyst. The reaction of sulfur dioxide with water and oxygen to form sulfuric acid is catalyzed by the presence of nitric oxide. At moderate temperatures, it is supposed that these substances react rapidly to form the intermediate compound, nitrosyl sulfuric acid, $HNOSO_4$, which then decomposes with the regeneration of the nitric oxide. In other instances, a product of the reaction may serve as a catalyst, called an *autocatalyst.* Oxides of nitrogen may be present in nitrocellulose from its own decomposition. These oxides catalyze the decomposition and promote the detonation of the substance.

The action of heterogeneous catalysts is the result of forces which operate at the surface boundary between the phases. Such catalysts are known as *contact catalysts.* Contact catalysts are usually solids in a finely divided or spongy condition, which gives maximum surface exposure to the reactants for a given weight of the catalyst. Gaseous and dissolved substances become attached to the surface of the solid catalyst in a film limited in thickness to one molecule. This process is called *adsorption.* It is a selective process and all reactions are not affected in the same manner by a particular catalyst. The energy content is changed

by the forces operating in such films; and, in many instances, reactions are catalyzed through the formation of loose adsorption compounds. Adsorption does not always lead to catalytic action. The presence of small proportions of other substances affects the activity of the catalyst. Some of these substances act as *promoters*, increasing the activity of the catalyst, probably by increasing the total area of the surfaces exposed. Finely divided iron is used as the catalyst in the synthesis of ammonia. Its activity is increased in the presence of aluminum oxide and potassium oxide. Other substances act as *catalyst poisons*, inhibiting the action of the catalyst by reacting with its surface molecules to form stable products, thus changing the nature of the surface. The presence of small amounts of arsenic compounds in the gases used in the production of sulfuric acid by the contact process destroys the effectiveness of the platinum contact mass by changing the surface atoms into platinum arsenide.

Inhibitors, or negative catalysts, may operate so as to change the mechanism of the reaction. Lead tetraethyl in ethyl gasoline prevents the oxidation of the hydrocarbons during the compression of the gases before the spark is introduced. In other instances, the negative catalyst may inhibit the action of a positive catalyst which is normally present as an autocatalyst. In the presence of urea, the oxides of nitrogen, formed in nitrocellulose by its slow decomposition, are removed and this explosive substance is stabilized so that it may be handled safely.

The Equilibrium Constant. The velocity of any reaction has been shown to be equal to the product of a velocity constant, characteristic of the specific reaction, and the molecular concentrations of the reacting substances, each raised to the appropriate power shown by the reacting ratio. At equilibrium, two reactions are involved and their velocities are the same. The reaction of carbon monoxide with steam, referred to above, is a reversible reaction which is the basis of one of the important processes for the production of hydrogen for industrial use. It is, therefore, important to select the conditions which will give the maximum yield.

$$H_2O + CO \rightleftharpoons CO_2 + H_2.$$

Representing the velocity of the reaction producing hydrogen and carbon dioxide as V_1, and the other as V_2, and the respective

velocity constants as k_1 and k_2, the following equations may be derived:

$$V_1 = k_1 \times p_{H_2O} \times p_{CO}$$
$$V_2 = k_2 \times p_{H_2} \times p_{CO_2}.$$

But, these velocities are equal at equilibrium.

$$V_1 = V_2$$

$$k_1 \times p_{H_2O} \times p_{CO} = k_2 \times p_{H_2} \times p_{CO_2}.$$

That is,

$$\frac{p_{H_2} \times p_{CO_2}}{p_{H_2O} \times p_{CO}} = \frac{k_1}{k_2} = K_{\text{equilibrium.}}$$

The equilibrium constant is equal to the ratio of the velocity constants of the two reactions, *i.e.*, to the ratio of the product of the molecular concentrations of the substances formed to the product of the molecular concentrations of the reactants, each molecular concentration being raised to the power equal to the coefficient of that substance in the equation which represents the reaction. The reciprocal of this expression is also equal to a constant; but it is customary to place in the numerator of the ratio the concentrations of the substances for which the process is being operated.

It is found by experiment that, at 986° and a pressure of one atmosphere, equilibrium exists in the system involving the reaction of carbon monoxide with steam and the reverse reaction, when the relative amounts of the gases are represented by the following per cents by volume: hydrogen, 80.4%; carbon dioxide, 0.7%; carbon monoxide and hydrogen, each 9.45%. The partial pressures of these gases in fractions of one atmosphere are: hydrogen, 0.804; carbon dioxide, 0.007; carbon monoxide, 0.0945; and water vapor, 0.0945.

$$K = \frac{0.804 \times 0.007}{0.0945 \times 0.0945} = 0.63.$$

From the numerical value of the equilibrium constant, one may observe directly whether the maximum yield of a system is relatively large or small. Through the use of the numerical value of the equilibrium constant, it is possible to determine the changes in yield which would result from changing the concentration of one of the reactants. The numerical value of the equilibrium

constant based on pressures is not appreciably affected by changes in pressure except at very high pressures. The numerical value of the constant changes noticeably with changing temperature. Changes in the constant are due to the fact that the changes in conditions affect the velocity of one of the reactions more than that of the other.

The Effect of Changes in Concentration upon a System at Equilibrium. Suppose that an excess of steam is used in the gaseous mixture for the production of hydrogen by the reaction with carbon monoxide. If no other change in concentrations takes place at the same time, it is apparent that

$$\frac{p_{H_2} \times p_{CO_2}}{p_{CO} \times p_{H_2O}} < K_{\text{equilibrium}},$$

because the partial pressure of the water vapor has been increased. Therefore, the system is out of equilibrium and the reaction of carbon monoxide with water proceeds more rapidly than the reverse reaction. In consequence of this unequal rate of reaction in the two opposite processes, the partial pressures of carbon monoxide and water decrease and of hydrogen and carbon dioxide increase. A new condition of equilibrium is established when the concentrations have become adjusted, as required by the nature of the substances, and expressed by the equilibrium constant. At this new state of equilibrium, the per cents of hydrogen and carbon dioxide are greater and of carbon monoxide less than before the concentration of water vapor was increased. *An increase in the concentration of one of the substances involved in an equilibrium mixture causes a new state of equilibrium with increased concentrations of the products whose formation consumes the substance added.*

From the above example, it is apparent that the proportions of the substances present in the final mixture need not be the same as those expressed by the equation, but that an excess of any of the reactants may be introduced. If all of the substances are in the gaseous state and there is no change in the total number of molecules during the reaction, changes in pressure affect all of the concentrations to the same extent. Since it is the ratio of the concentration products which determines equilibrium, equal changes in all of them do not change this ratio and do not disturb the equilibrium.

The Effect of Changes in Temperature upon a System at Equilibrium. When substances which may react with each other to form an equilibrium mixture are heated, they absorb energy and the temperature rises, causing the molecules to move more rapidly. The proportion of activated molecules is increased and the velocity of the reactions becomes greater, so that equilibrium is established more quickly at high than at low temperatures. Changes in chemical energy accompany reactions. Reactions in which heat is given out are *exothermic reactions;* and those in which heat is absorbed, *endothermic reactions.* The heat energy absorbed by a system may be converted into chemical energy.

If a system at equilibrium is heated, two effects may be caused. One of these effects, the raising of the temperature, has just been discussed. The other effect, an increase in the proportion of the substances whose formation absorbs heat, is the result of a preferential effect on the velocity of the endothermic reaction. This effect is stated in terms of **van't Hoff's Law: If the temperature of a system in a state of equilibrium is raised, the equilibrium is disturbed in the direction of the process which absorbs heat.** A new equilibrium is established in response to this change.

The decomposition of calcium carbonate is a reversible reaction which is endothermic.

$$CaCO_3 \rightleftharpoons CaO + CO_2 - 42{,}900 \text{ cal.}$$

At a temperature of 600°, the pressure of carbon dioxide in equilibrium with calcium oxide is 2.3 mm. If the temperature is raised to 800°, both of the reactions proceed more rapidly than at 600°; but the temperature effect on the rate of decomposition is greater than on the rate of combination, because the decomposition of calcium carbonate absorbs heat. Therefore, in a closed system, the partial pressure of carbon dioxide increases. The increase in the pressure of carbon dioxide causes an increase in the rate of its combination with calcium oxide according to the law of mass action. The reactions again become adjusted to the same velocity, but the pressure of carbon dioxide required for the equilibrium at 800° is 168 mm.

The numerical value of the equilibrium constant for any system

is altered by a change in temperature, since the equilibrium proportions of the reacting substances are changed. From a consideration of the equilibrium constants of a system at several temperatures, it is possible to calculate the conditions which are most favorable for successful industrial operation.

The Effect of Changes in Total Pressure upon a System at Equilibrium. In systems in which there is no change in the total number of molecules, a change in the total pressure would not be expected to cause any change in the equilibrium proportions of the substances. There are, however, a number of systems in which all of the substances are in the gaseous state and the total number of molecules does change during the reaction. In such systems a change in the pressure causes a greater effect on the velocity of the reaction which yields the smaller volume than on the opposite reaction.

The oxidation of gaseous hydrogen chloride by molecular oxygen produces water and chlorine. At the temperature of the reaction water is in the gaseous state. The equation for the reaction is,

$$4\,HCl + O_2 \rightleftharpoons 2\,H_2O + 2\,Cl_2.$$

The volumes of the gases involved in this system are in the ratio of the coefficients which express the molecular ratio; *i.e.*, five volumes of initial gases yield four volumes of the gaseous products. If no change in the equilibrium concentrations should occur, an increase in the total pressure applied to this system would change the partial pressures of all of these gases to the same extent. The result of increasing the partial pressures of all of the gases to the same extent, however, is to throw the system out of equilibrium, because the partial pressure of hydrogen chloride is raised to the fourth power in setting up the equilibrium ratio. Therefore, the reactions occur with unequal velocities, increasing the per cents of chlorine and water, until the partial pressures have become adjusted so that they are again in accord with the equilibrium constant for this system. The value of the equilibrium constant itself is not changed on account of changes in pressure so long as the total concentrations are within the range to which the gas laws are applicable. At high pressures, the value of the equilibrium constant is modified on account of the same properties of gases which cause deviations from the gas laws. *An increase*

in the total pressure applied to an equilibrium mixture causes a change in the equilibrium concentrations, so as to increase the per cent of the substances which occupy the smaller volume.

This effect is applicable also to substances in the solid and liquid states and to physical as well as chemical equilibria. At the freezing point of water, ice and liquid water are in equilibrium at a temperature of 0° under a pressure of one atmosphere. The application of a pressure greater than one atmosphere disturbs this equilibrium, causing enough ice to melt to cool the system to some temperature below zero at which a new equilibrium is established The new system occupies a smaller volume, because the liquid water formed is more dense than the solid ice from which it is formed in establishing the equilibrium.

The Effect of a Catalyst. In reversible reactions, the catalyst does not exert a preferential effect on the velocity of either of the reactions. A catalyst, consequently, causes no change in the proportions of the substances involved in a system in a state of equilibrium. Its function is to increase the velocity of both of the reactions involved and thus bring the system quickly to a condition of equilibrium. The proportions of the substances in the equilibrium mixture depend on the specific nature of the substances, and on the concentration, temperature, and pressure.

The Principle of Le Chatelier. The effects of changes in concentration, pressure, and temperature on systems in a state of equilibrium have now been discussed. It has been found that an equilibrium constant, expressed in terms of molar concentrations, or of the partial pressures if the reactants are gases, may be derived for each system. The numerical value of the constant is independent of changes in pressure, unless these changes are so great that the behavior of the gaseous substances differs greatly from that of an ideal gas. For each equilibrium system, the numerical value of the constant differs at different temperatures. The rules developed for each of these effects separately are special cases of a sweeping generalization, known as the **Principle of Le Chatelier: The application of a stress, *i.e.*, a change in concentration, temperature, or pressure, to a system in a state of equilibrium causes an increase in the concentrations of the substances whose formation tends to relieve the stress.** An increase in the concentration of one of the reactants causes an

increase in the concentrations of the materials whose formation removes the substance added. A rise in temperature increases the velocity of the endothermic reaction more than that of the exothermic reaction involved in the equilibrium. The endothermic reaction converts heat energy into chemical energy and thus tends to relieve the stress of added heat. The application of pressure increases the yield of the substances which occupy the smaller volume. In such gaseous systems, an increase in the concentration of the substances occupying the smaller volume produces a smaller number of molecules. Since gas pressure depends on the number of molecules striking against unit area of the walls of the container in unit time, the formation of a smaller number of molecules tends to reduce the pressure of the gas.

The Stability of Hydrates. A number of substances yield addition compounds with water which are known as hydrates. There are three hydrates of copper sulfate: $CuSO_4(H_2O)_5$, $CuSO_4(H_2O)_3$, and $CuSO_4(H_2O)$. At a fixed temperature, each of these hydrates is stable in contact with concentrations of water vapor which may vary within exactly defined limits. If, however, two hydrates are together in equilibrium with each other, only one specific pressure of water vapor is possible at a definite temperature. The relationships are shown in Fig. 61, in which the number of moles of water in combination with one mole of the salt are represented along the horizontal axis, and the pressure of water vapor on the vertical axis. At a temperature of 50°, anhydrous copper sulfate may exist in contact with water vapor at pressures up to 4.5 mm.; the monohydrate, at pressures from 4.5 mm. to 30 mm.; the trihydrate, from 30 mm. to 47 mm.; and the pentahydrate, from 47 mm. to the pressure of water vapor in equilibrium with the saturated solution. The vertical portions

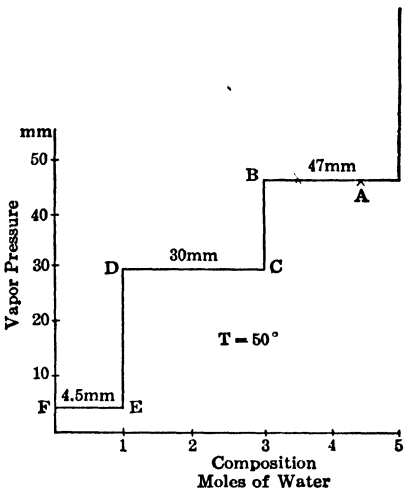


FIG. 61. — Vapor Pressures of Hydrates of Copper Sulfate.

of the curve represent the varying pressures of water vapor which may exist in contact with each pure hydrate. The horizontal portions represent mixtures of two hydrates in varying proportions which may exist at a particular pressure of water vapor.

The equilibria involved are represented by the following equations:

$$CuSO_4 + H_2O \rightleftharpoons CuSO_4(H_2O).$$
$$CuSO_4(H_2O) + 2\,H_2O \rightleftharpoons CuSO_4(H_2O)_3.$$
$$CuSO_4(H_2O)_3 + 2\,H_2O \rightleftharpoons CuSO_4(H_2O)_5.$$

Suppose that a mixture of the trihydrate and the pentahydrate of the composition represented by the point, *A*, is maintained at the fixed temperature of 50°, and that water vapor is removed from the system. The decomposition of the pentahydrate takes place to maintain the pressure of water vapor at 47 mm., as shown by the curve, *AB*. At the point, *B*, the conversion of the pentahydrate into the trihydrate is complete. Further removal of water vapor may decrease its vapor pressure along the curve, *BC*, without causing the decomposition of the trihydrate. At 30 mm., however, a new solid phase, the monohydrate appears; and again a fixed pressure of water vapor exists in equilibrium with this mixture. At the point, *D*, the conversion of the trihydrate into the monohydrate is complete; and at *E* the dehydration of the monohydrate commences. It is to be observed that the change in composition which occurs in response to a change in the pressure of water vapor is immediate and spontaneous, so long as a state of equilibrium exists. Changes in the pressure of water vapor, within certain fixed limits, may be made without affecting the composition of a single hydrate because no question of equilibrium is involved.

The Synthesis of Ammonia. The production of nitrogen compounds from atmospheric nitrogen is extremely important, because of the great number of uses of these compounds and their scarcity in available natural deposits. The importance of nitrogen compounds is discussed in Chapter XVIII, dealing with nitrogen. The production of synthetic ammonia is the most extensively used method for the conversion of nitrogen into useful compounds.

The formation of ammonia by the union of nitrogen and hydrogen was discovered during the latter part of the nineteenth century; but the equilibria were not fully understood and the indus-

trial application of the reaction was not made until 1913. The reaction was investigated extensively, notably by Haber, Nernst, and others in Germany from 1905 to 1908; and the conditions governing the equilibria were worked out quantitatively. The combination of the two elements is an exothermic reaction which is reversible.

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 + 24{,}400 \text{ cal.}$$

The velocity of the reaction is very low even at fairly high temperatures; and the equilibrium yield of ammonia is small at high temperatures. The great decrease in the equilibrium per cent of ammonia at a fixed pressure may be seen by comparing

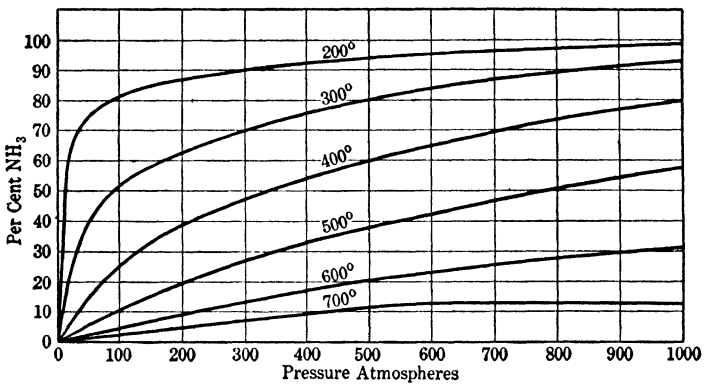


FIG. 62. — Effect of Changes in Temperature and Pressure on the Yield of Ammonia.

the curves of Fig. 62. It is evident that it is necessary to operate the process at the lowest temperature at which the velocity of the reaction is great enough to make it practicable.

In this reaction, four volumes of initial gases yield two volumes of product. Hence, in accord with Le Chatelier's principle, increased pressures give larger proportions of ammonia in the equilibrium mixture of the gases. There is also an additional effect at high pressures which is due to the same causes that lead to the deviations from the gas laws. Since these effects are greater for ammonia than for nitrogen and hydrogen, the numerical value of the equilibrium constant is greater at high than at low pressures. At 450° and a pressure of 10 atmospheres, the value of the constant is 0.00659; at 100 atmospheres, 0.00725; and at

1000 atmospheres, 0.02328. Since both the normal concentration effect and this added effect operate to increase the yield of ammonia, the highest pressure at which the process can be operated economically and safely is desirable.

In order to increase the velocity of the reaction, which proceeds too slowly to be of practical use even at the higher temperatures and pressures, it is necessary to employ catalysts. In his earlier publications on this subject, Haber stressed osmium and uranium. It has been found, however, that the most effective catalysts consist of highly porous iron containing small quantities of "promoters." Best results are secured in the presence of two substances, one strongly basic, as potassium oxide, and the other weakly acidic, as aluminum oxide.

Some of the industrial processes for the synthesis of ammonia operate at temperatures as low as 450°, and others at 600°. There are likewise great differences in the pressure, some of the processes operating at 100 atmospheres, and others going as high as 1000 atmospheres. In order to operate safely at these high pressures and also to prevent the loss of hydrogen through the walls of the vessel, the catalytic bombs are constructed of chrome-vanadium steel. They are usually 15–20 feet long and 3–4 feet in diameter, with walls 3–5 inches thick. The ammonia formed during the passage of the gases through the catalyst is removed from the gas mixture by refrigeration and the uncombined gases are returned to the catalyst. A diagrammatic representation of the process is shown in Fig. 63. The yield of ammonia depends theoretically on the temperature and the pressure; but the practical yield depends also on the purity of the gases, the activity of the catalyst, and the rate of the gas flow. The practical yield is much less than the equilibrium proportion of ammonia at the given temperature and pressure, because it is not economical to hold the gases in contact with the catalyst long enough for equilibrium to be established. The output of the plant is increased by employing a continuous flow of the gases and recirculating the uncombined gases. Improvements in the process now make it possible to secure a practical yield of approximately 40%, whereas the yield of the earlier process was only about 5%.

Nitrogen for use in the synthesis of ammonia may be obtained from liquid air or from a fuel gas, known as producer gas, which

contains approximately 60% of nitrogen. *Hydrogen* may be obtained by the electrolysis of water, by the reaction of steam with hot coke, and by the destructive distillation of coal. The two latter processes are the most extensively used sources of hydrogen. The purification of both the nitrogen and the hydro-

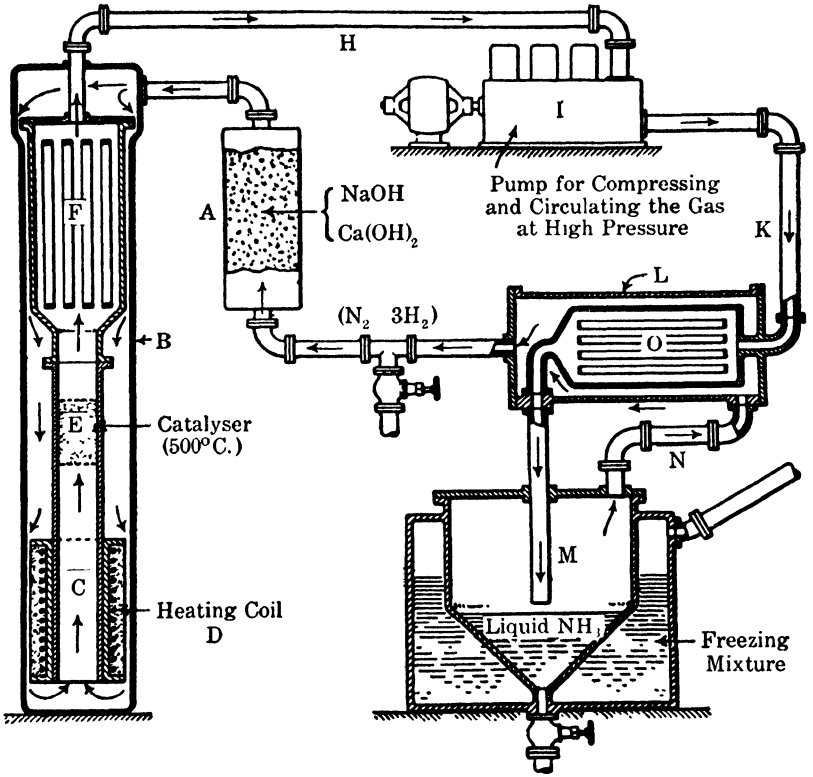


FIG. 63. — Diagram of Synthetic Ammonia Process.

gen is essential because the presence of impurities, especially water and carbon dioxide, greatly decreases the activity of the catalyst. More than one half of the cost of the production of ammonia is due to the preparation and purification of the hydrogen and nitrogen in the one to three proportion by volume required for the reaction.

The Synthesis of Methanol. An important development of industrial chemistry has been the large-scale production of methanol by a synthetic process. This substance has a number of im-

portant uses, the most extensive being for the production of formaldehyde for use in the manufacture of "Bakelite." Methanol is synthesized by the reaction of hydrogen with carbon monoxide.

$$CO + 2\,H_2 \rightleftharpoons CH_3OH.$$

The process is carried out at pressures up to 200 atmospheres and at temperatures between 200° and 400°. The reaction is exothermic, so that the temperature is kept as low as suitable reaction velocity permits. Volume considerations show that high pressures

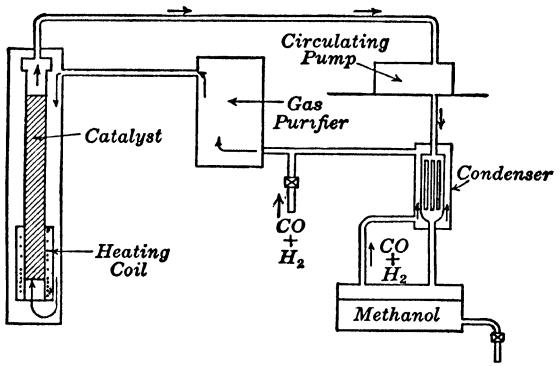


FIG. 64. — Diagram of Synthetic Methanol Process. (From Conant, *The Chemistry of Organic Compounds*, Rev. Ed.)

are favorable. The catalyst for the reaction is a zinc oxide-chromium oxide mixture. This catalyst is not easily poisoned; and water gas, enriched by an additional molecular proportion of hydrogen, is a suitable initial gas mixture. The procedure, both in principle and in practice, is quite similar to that for ammonia, as shown by the diagram illustrating the essential details, Fig. 64.

EXERCISES

1. What is meant by a reversible reaction? chemical equilibrium?
2. What is meant by the velocity of a reaction? Name conditions which affect the velocity of a reaction.
3. What is the effect of changes in the concentration of a reactant on the velocity of a reaction?
4. What is an equilibrium constant? What practical value may be associated with the numerical value of the equilibrium constant?
5. What is the effect of changes in concentration on the proportions of the substances involved in an equilibrium mixture?
6. What is the effect of changes in temperature on the velocity of a reaction?

7. What is the effect of changes in temperature on an equilibrium mixture?
8. What is the effect of a change in pressure upon a reacting system of gases at equilibrium if there is no change in the total number of molecules?
9. What is the effect of an increase in pressure on an equilibrium mixture of gases if the total number of molecules does change during the reaction?
10. State Le Chatelier's Principle and cite examples to show its meaning.
11. Given the following systems in a state of equilibrium; predict the effect of (*a*) the application of heat and (*b*) an increase in pressure.
    1. $2\,H_2 + O_2 \rightleftharpoons 2\,H_2O + 113{,}120$ cal.
    2. $4\,HCl + O_2 \rightleftharpoons 2\,H_2O + 2\,Cl_2 + 28{,}000$ cal.
    3. $PCl_5 \rightleftharpoons PCl_3 + Cl_2 - 30{,}000$ cal.
    4. $CO + H_2O \rightleftharpoons CO_2 + H_2 + 10{,}000$ cal.
    5. $2\,O_3 \rightleftharpoons 3\,O_2 + 61{,}400$ cal.
    6. $N_2 + O_2 \rightleftharpoons 2\,NO - 43{,}200$ cal.
    7. $2\,NO + O_2 \rightleftharpoons 2\,NO_2 + 27{,}800$ cal.
    8. $2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3 + 45{,}200$ cal.
    9. $CaCO_3 \rightleftharpoons CaO + CO_2 - 42{,}900$ cal.
12. Discuss the effect of catalysts on the velocity of reactions.
13. Explain the fact that a mixture of two hydrates of a salt has a definite vapor pressure at a fixed temperature.
14. What conditions are favorable for the production of the maximum yield of ammonia? Why are these conditions favorable?
15. State the conditions which are employed in the synthesis of methanol. Give reasons for the use of each of these conditions.

SUPPLEMENTARY READINGS

Hildebrand, *Principles of Chemistry*, Chapters XI, XII, and XIV.
Meldrum and Gucker, *Introduction to Theoretical Chemistry*, Chapter VII.
Getman and Daniels, *Outlines of Theoretical Chemistry*, Chapters XII and XIII.
Findlay, *The Spirit of Chemistry*, Chapter XX.
Larson, "Increasing Ammonia Production with Improved Catalysts," *Ind. Eng. Chem.* **16**, 1002 (1924).
Mittasch and Frankenburger, "The Historical Development and Theory of Ammonia Synthesis," *J. Chem. Education* **6**, 2097 (1929).
"Nitrogen," *Fortune*, **2**, Number 4, 55 (1930); **6**, Number 2, 43 (1932).

CHAPTER IX

SOLUTIONS

The particles of a substance which is dissolved in a liquid are so finely divided that they do not settle and cannot be separated from the liquid by filtration. These dissolved particles cannot be seen because they are not large enough to furnish reflecting surfaces to the light passing through the solution. The particles of the material in solution are molecules in some solutions and ions in others. These particles become uniformly distributed throughout the entire body of the liquid so that the composition of a solution is uniform throughout. Nevertheless, the proportions of the dissolved substance and the material in which it is dissolved are not definite. *A solution is a homogeneous mixture of two or more materials.* A large proportion of the chemical reactions occur in solution, commonly in aqueous solution. Such reactions are best understood by considering the nature of the particles which are present in solutions.

Types of Solutions. The dissolved substance is known as the *solute* and the dispersing medium as the *solvent.* In many solutions, both materials are in the same phase and are mutually soluble in each other. The designation of one of the substances as the solute and the other as the solvent in such solutions is purely arbitrary. It is customary to consider the liquid present in the larger proportion, in a solution containing two liquids, the solvent; but, if water is one of two liquids in a solution, it is commonly regarded as the solvent, even though the other liquid may be present in the larger proportion. Thus, one speaks of a 95% solution of ethyl alcohol in water.

Substances in each of the three states of matter may serve as solutes, and other substances in each of the three states may be considered solvents. The solutions may be grouped according to the final phase into solid solutions, liquid solutions, and gaseous solutions. Solid solutions are composed of mixed crystals and the

properties of such solids differ from those of the individual substances. Gaseous solutions are the gas mixtures, in which each molecule exerts little effect on the others unless chemical reaction occurs. Liquid solutions are the most familiar of the three classes of solutions. Liquid solutions result from the solution of solids, liquids, or gases in liquids. Attention will be devoted primarily to aqueous solutions.

The Solution of a Substance in Water. The solution of any one substance by another depends on the properties of each. The formation of a solution is the result of the forces which are exerted by the solvent on the solute. When water is added to a soluble *crystalline solid* such as sucrose, cane sugar, molecules at the surface of the solid break away from their positions in the crystal and move about freely as dissolved particles. This process is known as *the solution of the solid.* Some of the dissolved particles, however, are attracted back to the solid and return to an appropriate position in the crystal. This process is *the crystallization of the solute.* As the concentration of the solute increases, the rate of crystallization also increases. If a sufficient amount of the solid is present in contact with the liquid, the velocity of the two changes becomes the same, and equilibrium is established, Fig. 65. The solution is now saturated and no further change in concentration occurs unless the conditions are changed. *A saturated solution contains the concentration of the solute that remains in stable equilibrium with an excess of the undissolved solute at the existing temperature and pressure.*

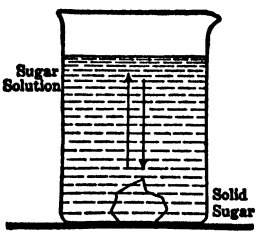


FIG. 65

Some pairs of *liquids* dissolve in each other in all proportions. These are completely miscible. Certain other liquids do not dissolve in each other to an appreciable extent and these liquids are immiscible. Still other liquids dissolve in each other to a limited extent, and are partially miscible. Water and ether are partially miscible, and a mixture separates into two layers if it is allowed to stand after thorough shaking. At the boundary between the two layers, molecules of each substance pass from one layer into the other; and a state of equilibrium is established for each. The concentration of each substance dissolved in the

other is constant under fixed conditions and each solution is saturated.

Solutions of soluble *gases* may be prepared either by bubbling the gas through the liquid, or by inclosing it over the liquid. As the concentration of the dissolved gas increases, the rate at which it escapes also increases. When the two opposite changes, the solution of the gas and its evaporation from the solution, take place at the same rate, the solution is saturated with the gas.

Solubility. At each temperature, the relative amount of the solute in its saturated solution is constant. The amount of a solute required to saturate a specified quantity of a solvent is called the solubility of the substance in that solvent at the given temperature. The solubility of gases is commonly expressed as a volume ratio. The solubility of different substances in water varies greatly. Substances which dissolve in relatively large proportions are said to be very soluble. Thus, 213.4 g. of silver nitrate will dissolve in 100 g. of water at 18°. The substances which have a solubility measured in terms of a few grams, as barium hydroxide, solubility 3.7 g. in 100 g. of water at 18°, are moderately soluble. A substance is called slightly soluble if its solubility is only a few tenths of a gram, as silver sulfate, 0.55 g. in 100 g. of water at 18°. Substances of small solubility, as barium sulfate, 0.00023 g. in 100 g. of water at 18°, are said to be insoluble. These substances are not truly insoluble; but the concentration of the saturated solution is so small as ordinarily to be of no significance.

Conditions Affecting Solubility. The solubility of a substance in a given solvent is a specific property which depends on the nature of both the solute and the solvent. A substance is generally more soluble in a solvent composed of similar particles than in one which is dissimilar. Thus, naphthalene, which is composed of nonpolar molecules, is soluble in benzene which is also nonpolar, but is not soluble in water which is composed of polar molecules. Sucrose, in which the molecules are dipoles, dissolves readily in water, but is not readily soluble in nonpolar solvents. Many crystalline salts, composed of ions, dissolve readily in water, but are not soluble in carbon tetrachloride. There is no adequate theory to account fully for the solubility and insolubility of substances, nor for the differences in solubility.

The solubility of a given solid in water varies to some extent depending on *the size of the particles.* Very small crystals dissolve more rapidly than larger crystals of the same substance. Consequently, in the presence of both large and small crystals, the concentration of the solute maintained by the small particles is greater than that permitted by the large crystals. Therefore, the small crystals dissolve and the larger ones increase in size. The greater solubility of the small crystals is attributed to their greater surface area.

The effect of changes in temperature on solubility is best understood by considering the energy changes which accompany solution. If changes in the state of the solute occur, changes in energy also take place; but if both solute and solvent are in the same state, energy changes may not occur. The solution of a solid by a liquid is an endothermic change; and of a gas by a liquid, an exothermic change. If the change were purely physical in nature, the amount of the energy change should be equal to that which would accompany the same change in state. The solution of a solid hydrocarbon in a liquid hydrocarbon of the same chemical nature approximates this type. Usually other changes in addition to the simple dispersion of the solute, are involved.

The solubility of a solid in a liquid usually increases with rise in temperature, because most solids absorb heat when they dissolve. Sometimes, however, other changes occur when the solid is dissolved and the total effect is an evolution of heat. There is no general rule governing the increased solubility of solids with rise in temperature. Potassium nitrate has a solubility of only 13 g. in 100 g. of water at 0°, but its solubility is 246 g. at 100°; the solubility of sodium chloride increases from 35.6 g. in 100 g. of water at 0° to only 39.8 g. at 100°; and the solubility of calcium sulfate decreases from 0.759 g. in 100 g. of water at 0° to 0.162 g. at 100°.

The solution of one liquid in another does not involve a change in state; and no general prediction can be made about the effect of changes in temperature on solubility. It is found by experiment that the solubility of most partially miscible liquids in each other increases with rise in temperature.

The solubility of a gas in a liquid decreases with rise in temperature because the condensation of a gas is an exothermic change.

Hence, in accord with van't Hoff's law, the application of heat disturbs the equilibrium in the direction of the cooling process, the evaporation of the dissolved gas.

Changes in pressure have little effect on the solubility of liquids and solids in liquids, but exert a great effect on the solubility of gases in liquids and in solids. If the pressure of a gas in contact with its saturated solution is increased, the concentration of the gaseous substance is proportionally increased. Under this new pressure condition, the equilibrium is disturbed, since the gas now dissolves more rapidly than at the lower pressure. Equilibrium is again established when the concentration of the dissolved gas has increased proportionally to the increase in the concentration of the substance in the gaseous condition. If the pressure of a gas in contact with its saturated solution is doubled, the concentration of the gas is also doubled. Consequently, the solubility, by weight, of a gas at a pressure of two atmospheres is twice as great as at a pressure of one atmosphere, provided the temperature remains constant. This relation may be stated in terms of **Henry's Law: At constant temperature, the solubility of a gas in a liquid is proportional to the pressure of the gas.** This law is found to apply only to those cases in which the gas is slightly soluble and does not react with the solvent.

According to the law of partial pressures, each gas in a mixture exerts a part of the total pressure proportional to its molecular concentration. The solubility of a gas from a mixture depends not only on the specific properties of the substance, but also on its partial pressure. At a pressure of 760 mm., the solubility of oxygen from air, which contains 21% by volume of oxygen, is the same as its solubility from oxygen gas at a pressure of 159.6 mm. The passage of insoluble gases through a solution of some other gas aids in the removal of the latter from the solution. The bubbles of the insoluble gas sweep away the escaping gas and reduce its partial pressure virtually to zero. Dissolved gases may be removed rapidly by passing air through the solution which is heated to the boiling point.

Solubility Curves. Solubility data may be represented in a useful and convenient manner by solubility curves, Fig. 66. In these curves, the solubilities of substances are represented along the ordinate and the temperature along the abscissa. If solubility

determinations are made at sufficiently close temperature intervals, a smooth curve may be drawn through the points thus located. This curve then describes the temperature-solubility

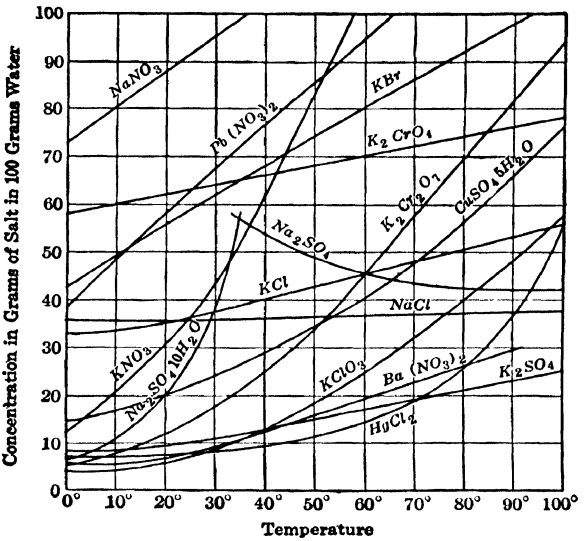


FIG. 66. — Solubility Curves.

relation over the entire range. A break in a solubility curve, a in that of sodium sulfate, Fig. 67, indicates a transition point a which a change in the composition of the solid phase occurs. A

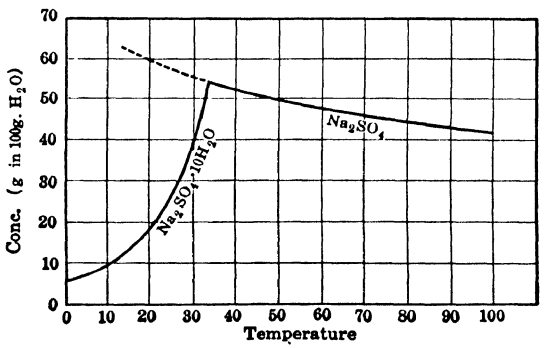


FIG. 67

temperatures above the transition point of this substance, 32.4° anhydrous sodium sulfate, Na_2SO_4, is the solid phase in equilib rium with the saturated solution. At temperatures below th

transition point, the decahydrate, $Na_2SO_4(H_2O)_{10}$, is the solid phase. At the transition temperature, the two solids may exist in equilibrium with the same solution.

Supersaturated Solutions. If a hot, saturated solution of a substance whose solubility increases with rise in temperature is filtered to remove all excess of the solute and all suspended matter, it is often possible to cool the solution so that crystallization of the excess of the solute does not take place. This may be illustrated by considering solutions of sodium sulfate. At a temperature of 30°, the saturated solution in equilibrium with the decahydrate contains 40 g. of sodium sulfate in 100 g. of water. If this solution, free from any excess of the solid, is cooled to 15°, it may retain in solution all of the solute that was dissolved at 30°, although the solubility of sodium sulfate at the lower temperature in direct contact with the decahydrate is only 13 g. in 100 g. of water. Solutions which contain an amount of the solute greater than that which can be dissolved at equilibrium, in contact with an excess of the solid, are called *supersaturated solutions.* If a minute fragment of sodium sulfate decahydrate is now added to this supersaturated solution, a new condition which demands equilibrium is established. Starting from this added fragment of the solid as a center, the excess of the solute rapidly crystallizes from the solution.

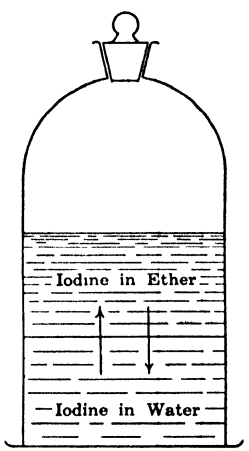


FIG. 68

Extraction. Law of Partition. Some solutes are soluble in each of two solvents which are not very soluble in each other, and are much more soluble in one of these solvents than in the other. Iodine, for example, is about 200 times more soluble in ether than in water. If a solution of iodine in water is shaken with ether and the mixture is then allowed to separate into two layers, most of the iodine is present in the ether layer. Iodine is not removed completely from the water layer, but a condition of equilibrium between the iodine in the one layer and that in the other results, Fig. 68. It is found that the concentration of the iodine in the ether layer is approximately 200 times that in the water layer.

That is, *the solute becomes distributed between the two liquids so that its concentration in each is in the same ratio as the solubility in each.* This statement is known as the *law of partition.* The process of removing a solute from one solvent by the use of another solvent in which it is more soluble is known as *extraction.* The process of extraction has many important industrial applications in the separation and purification of synthetic products.

Vapor Pressure of Liquid Mixtures. Each pure liquid has a definite vapor pressure at a fixed temperature. In a solution of two liquids in each other, the vapor pressure of each liquid is decreased by the presence of the other, so that the actual pressure of the mixed vapors in equilibrium with the solution is less than the sum of the vapor pressures of the two pure liquids. The vapor pressure of the solution is usually intermediate between the vapor pressures of the pure liquids; but there are some liquid mixtures which have lower vapor pressures than either component, and others which have higher vapor pressures than either single component.

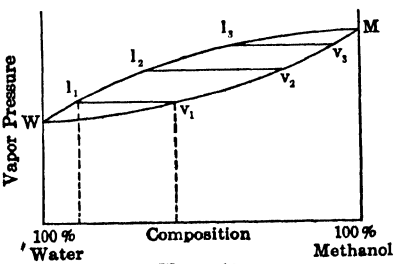


FIG. 69

The vapor pressure relationship for solutions of the first type is shown graphically in Fig. 69. The composition is measured along the base line from 100% of water to 100% of methanol. The vapor pressure of pure water is shown by the point W and of pure methanol by the point M. The curve WlM shows the vapor pressures of all solutions of water and methanol in each other at constant temperature. The point l_1, for instance, represents the composition shown by the point at which a line through l_1 perpendicular to the base intercepts the base line. Since the vapor from solutions of this type always contains a larger proportion of the more volatile substance than the liquid with which it is in equilibrium, the composition of the vapor is shown by the curve WvM. Thus, the liquid of the composition shown by l_1 is in equilibrium with the vapor of the composition v_1; liquid of the composition l_2, in equilibrium with the vapor v_2; etc.

The vapor pressure relationship for liquid pairs which yield a solution of definite composition having a minimum vapor pressure

is shown in Fig. 70. As in the preceding type, the liquids of the composition shown by the points l_1 and l_2 are in equilibrium with the gas mixtures of the composition v_1 and v_2, respectively. With increasing percentages of the liquid B dissolved in A, the vapor pressure of the solution decreases as shown by points on the curve Al_1M; and the composition of the vapor is shown by the corresponding points on the curve Av_1M. Likewise, with increasing percentages of A in B, the vapor pressure of the solution decreases as shown by the curve Bl_2M; and the composition of the vapor is shown by the curve Bv_2M. The lowest point on the curves at M represents the composition and vapor pressure of the solution of the two liquids in each other which shows the minimum vapor pressure. Solutions of nitric acid in water illustrate this type. A third type is that in which liquid pairs yield a solution having a greater vapor pressure than any other solution of the two liquids in each other. Grain alcohol and water form a solution which exhibits maximum vapor pressure.

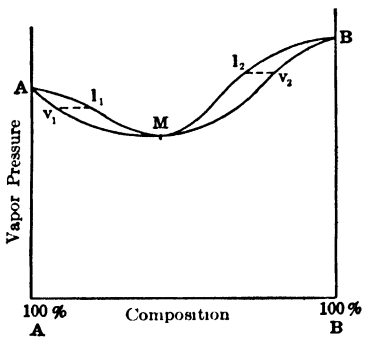


FIG. 70

Fractional Distillation. When a solution, such as that of methanol in water, is heated, the vapor pressure of each component increases; and the solution boils when the sum of the two partial pressures is equal to the atmospheric pressure. Both of the substances are present in the gas emerging from the boiling solution; but, as shown in Fig. 69, the vapor contains a larger proportion of the more volatile component than the liquid with which it is in equilibrium. This results in a gradual change in the composition of the solution and a corresponding change in the boiling temperature. The vapors which emerge from the solution over arbitrarily selected ranges in boiling point may be condensed and collected in separate containers. The first fraction contains a higher concentration of the more volatile component than the original solution; and the last fraction, a higher concentration of the less volatile component. Redistillation of the first fraction again yields a fraction which is still richer in the more volatile

material. By continuing the processes of redistillation and condensation in separate fractions, it is possible to separate the liquid mixture more or less completely into the pure liquids. This process is known as *fractional distillation.* Liquid mixtures having vapor pressures intermediate between those of the pure components may be separated by fractional distillation. No change in the composition of either substance occurs during fractional distillation, so that a solution of the same composition as that originally distilled results from the mixing of all of the fractions.

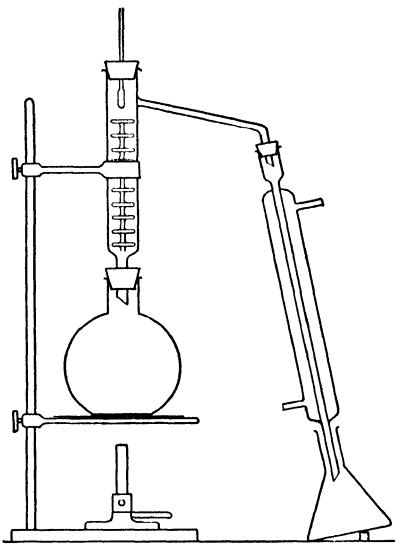


FIG. 71. — Laboratory Apparatus for Fractional Distillation.

In practice, the separation of the two substances in a liquid mixture, such as that described in the preceding paragraph, is accomplished by the use of a fractionating column into which the vapors from the boiling solution pass, Fig. 71. In this way, the repeated separate distillations are eliminated and the separation is accomplished in a single operation. In a fractionating column such as this, each plate gives the effect of a separate distillation. The liquid which condenses in the lower part of the column is richer in the more volatile component than the solution in the still, as is apparent from the study of Fig. 69. The vapor which passes on from this condensed liquid is likewise richer in the more volatile component than the liquid itself. At a second plate, at a lower temperature, some of this vapor condenses and a vapor still richer in the more volatile component passes on up the fractionating column. The condensed liquid flows down from the top of the column, meeting a counter current of the rising vapor. Since this liquid is cooler than the gases, the less volatile material in the gas condenses in the liquid. At the same time, the more volatile materials in the returning liquid are evaporated. There is thus a continual approach toward equilibrium between the liquid and

the vapor in the column; but equilibrium is not attained. Eventually, the nearly pure volatile component passes from the top of the fractionating column into the condenser, while the less volatile material is returned to the still. Fractional distillation is used extensively in chemical industry as a means of separating and purifying many commercial products. The atmospheric gases are obtained separately by the fractionation of liquid air; and a number of commercial products are obtained by the fractional distillation of petroleum.

Constant Boiling Solutions. Liquid solutions which have vapor pressures less than those of either of the pure components cannot be separated completely by fractional distillation. In such mixtures, some solution of definite composition has a lower vapor pressure, and consequently a higher boiling point, than either pure component or any other solution of the two substances.

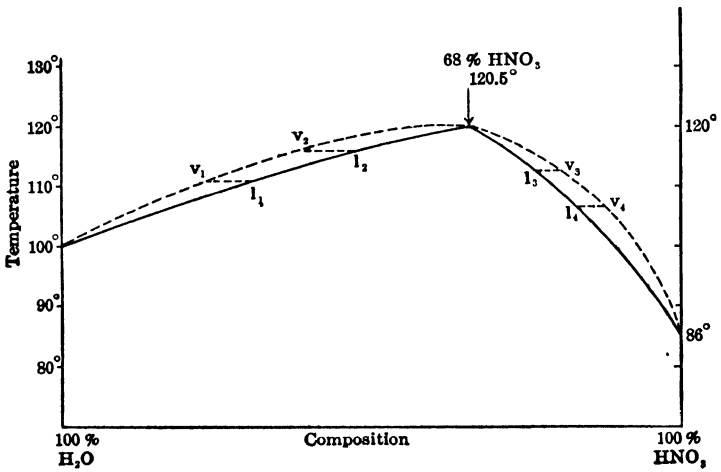


FIG. 72. — Constant Boiling Solution of Nitric Acid.

Nitric acid and water yield a solution of this type. During the distillation of any solution of nitric acid and water, either nitric acid or water predominates in the vapor, depending on the original proportions of these substances in the solution. The boiling point gradually rises as the evaporation proceeds; and, in this respect, the behavior is similar to that discussed in the preceding paragraph. In this solution, however, the boiling point becomes constant when the concentrations have become adjusted to those

of the solution of minimum vapor pressure; and the distillate now has the same composition as the liquid in the still. Such solutions are *constant boiling solutions;* and repeated distillation does not alter the composition of the solution so long as the external pressure is not changed. The composition and boiling points of solutions of nitric acid and water are plotted in Fig. 72. The broken line shows the composition of the gaseous phase in equilibrium with the solution at each temperature. The composition of several constant boiling solutions of this type is shown in Table 13.

TABLE 13

SOME CONSTANT BOILING AQUEOUS SOLUTIONS

Solute	*Boiling Point*	*Per Cent of Solute*
Nitric acid	120.5°	68.0
Hydrochloric acid	110°	20.2
Hydrobromic acid	126°	47.5
Hydriodic acid	127°	57.0
Hydrofluoric acid	120°	35.4
Sulfuric acid	338°	98.3

Liquid pairs which yield solutions having maximum vapor pressure also form constant boiling solutions. The solution of this type is the first fraction which is obtained by distillation. Ethyl alcohol, boiling point 78.3°, and water yield a constant boiling solution of this type. This solution contains 95.57% of ethyl alcohol and boils at 78.13° under a pressure of 760 mm. It is possible to fractionate solutions containing a smaller per cent of alcohol to obtain the solution of this composition but not to obtain absolute alcohol.

The Concentration of Solutions. The concentration of a single substance is defined by the weight in unit volume. To express the concentration of a solution requires consideration of the quantity of both solute and solvent. Several plans are in use, each having certain advantages. The most familiar basis for the description of the proportions of substances in a complex body is the *weight per cent.* Thus, a 10% solution of a salt is one which contains 10 parts by weight of the salt dissolved in 90 parts by weight of the solvent to produce 100 parts by weight of

the solution. No significant relationship can be observed in the properties of solutions containing the same weight per cent of different solutes, and other units are preferred for use in scientific work.

Solutions are extensively used to supply a solute for use in chemical reactions. For such uses it is customary to express the amount of the solute in chemical units of weight in one liter of solution. The familiar chemical units of weight are the mole and the gram equivalent weight. *The molarity of a solution is equal to the number of moles of a solute in one liter of solution.* The ratio by volume in which solutions of the same molarity react is the same as the molar ratio. In order to calculate the volume of one molar, 1 M., sulfuric acid required to react with 500 ml. of 1 M. sodium hydroxide, the molar ratio is observed from the equation for the reaction,

$$2\ NaOH + H_2SO_4 \longrightarrow 2\ H_2O + Na_2SO_4.$$

Only one half as many moles of sulfuric acid are required as of sodium hydroxide. Since equal volumes of the solutions of the same molarity contain the same number of moles, it is obvious that the volume of sulfuric acid required is one half that of the sodium hydroxide, or 250 ml.

The concentration in terms of the gram equivalent weight is stated in normality. *The normality of a solution is equal to the number of gram equivalent weights of the solute in one liter of solution.* The gram equivalent weight of a compound has been defined as the weight which contains one gram equivalent weight of the element or radical for which the substance is being used. The gram equivalent weight is based on the weight corresponding to an oxidation number of one or a change in oxidation number equal to one. A single substance may have more than one equivalent weight, depending on the reactions into which it enters. One gram equivalent weight of potassium hydrogen sulfate, $KHSO_4$, as an acid, is equal to one mole, 136.16 g.; but, for the precipitation of barium sulfate, one gram equivalent weight of this substance is equal to one half of one mole, 68.08 g. In Table 14, the amounts of several substances, per liter, in solutions of the same molarity and normality are shown.

TABLE 14

WEIGHTS OF SOLUTE FOR ONE LITER OF SOLUTIONS OF DIFFERENT CONCENTRATIONS

Substance	*1 M.*	*0.5 M.*	*1 N.*	*0.5 N.*
Hydrochloric acid, HCl	36.45 g.	18.22 g.	36.45 g.	18.22 g.
Phosphoric acid, H_3PO_4	98.00 g.	49.00 g.	32.66 g.	16.33 g.
Calcium chloride, $CaCl_2$	111.00 g.	55.50 g.	55.50 g.	27.75 g.
Cupric nitrate, $Cu(NO_3)_2$	187.60 g.	93.80 g.	93.80 g.	46.90 g.
Aluminum sulfate, $Al_2(SO_4)_3$ . . .	342.00 g.	171.00 g.	57.00 g.	28.50 g.
Ammonium sulfate, $(NH_4)_2SO_4$ . .	132.00 g.	66.00 g.	66.00 g.	33.00 g.
Potassium hydroxide, KOH . . .	56.10 g.	28.05 g.	56.10 g.	28.05 g.

Solutions of the same normality, based on similar reactions, react with each other in a ratio of equal volumes. If they are not of the same normality, the volumes required are inversely proportional to the normalities of the solutions. This follows as a necessary consequence of the law of equivalent weights, that the weights of two substances which are equivalent to the same weight of a third substance are equivalent to each other. The calculation of the volume of a solution of specified concentration required to react with a given weight of a substance may be done by the method illustrated in Chapter IV. From the equation, the molar ratio is observed. This ratio is expressed in the units required by the problem, and the calculation is then completed. Suppose that the problem is to calculate the volume of 0.5 N. hydrochloric acid required to react with 10 g. of calcium carbonate.

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2.$$

1 mole of $CaCO_3$ requires 2 moles of HCl.
100 g. of $CaCO_3$ require 4 liters of 0.5 N. HCl.
10 g. of $CaCO_3$ require $10/100 \times 4$ liters, or 0.4 liters of 0.5 N. HCl.

Several properties of solutions are dependent on the effect of the solute particles on the solvent particles. For the comparison of such effects, it is necessary that the measurements be based on solutions which contain the same relative numbers of solute and solvent particles. One liter of different solutions of the same molarity may contain the same number of solute particles or it

may contain different numbers, depending on the nature of the solute. The number of solvent particles in one liter of different solutions may differ greatly. A specific weight of a given solvent always contains the same number of molecules except for errors inherent in measuring the weight, and chemical reactions which may occur with the consumption of the solvent when the solute is dissolved. For the investigation of effects which are dependent on molecular ratios, both the solute and the solvent are measured by weight. *The molality of a solution is equal to the number of moles of a solute dissolved in 1000 g. of the solvent.* If the solute becomes dispersed into particles which contain either more than one molecule, or fragments of molecules, it is clear that the relative number of the solute particles will differ from that in solutions in which the solute is in the molecular state.

In a number of important scientific derivations, the *mole fraction* is a significant ratio. This is equal to the ratio of the number of moles of one component of the solution to the total number of moles. In a solution prepared by dissolving 1 mole of ethanol, 46 g., in 9 moles of water, 162 g., the total number of moles is 10. The mole fraction of ethanol is 0.1 and the mole fraction of water is 0.9. Mole per cent is this same ratio based on 100 total moles of the mixture. In the solution just considered, the mole per cent of ethanol is 10 and the mole per cent of water is 90.

PROPERTIES OF SOLUTIONS

Many of the physical properties of solutions differ from those of both the solute and the solvent. In general, solutions possess properties which more closely resemble those of the solvent than of the solute. Thus, the solution of a solid in a liquid has the properties of a liquid, not of a solid. If, however, the solute has characteristic color or taste, the solution may also exhibit these properties of the solute. The density of a solution of a solid in a liquid is usually greater than that of the solvent itself. Consequently, a saturated solution is formed in contact with a solid placed in the bottom of a vessel of water; and the rate of solution is slow because the solute diffuses only very slowly into the upper, unsaturated solution. Shaking, stirring, or suspending the solid in the upper part of the vessel of water increases the rate of solution by main-

taining more nearly uniform concentrations throughout the entire body of the liquid. The presence of the dissolved solute causes a change in the vapor pressure, freezing point, and boiling point of the solvent.

The consideration of these effects in the following paragraphs is limited to non-volatile solutes, and attention is devoted primarily to those which are not ionic in nature.

The Lowering of the Vapor Pressure of the Solvent. In the discussion of the distillation of solutions of liquids in each other, it was noted that each liquid causes a decrease in the vapor pressure of the other. This is a general effect which may be observed in all solutions of solutes in liquid solvents. In terms of the kinetic theory, the lowering of the vapor pressure is caused by the fact that the solute particles decrease the rate of evaporation of the solvent. Since the solute is uniformly distributed throughout the whole of the solution, some of the molecules at the surface of the solution are solute molecules. The attractive forces which these molecules exert upon the solvent prevent the escape of the solvent molecules as freely as in the absence of the solute. Therefore, the concentration of the vapor required for equilibrium is decreased; and the vapor pressure is lower than that of the pure liquid at the same temperature. It seems logical to conclude that the vapor pressure of the solvent depends on the relative number of its molecules in the solution. This conclusion, based on experimental observations, may be stated as **Raoult's Law: The vapor pressure of a liquid solvent is proportional to its mole fraction in the solution.** This relation is shown by the following equation:

$$p = p^0 N_1^0,$$

in which p is the vapor pressure of the solvent from the solution, p^0, the vapor pressure of the pure solvent, and N_1^0, the mole fraction of the solvent.

The pressure of water vapor in equilibrium with a solution containing 10 g. of dextrose in 1000 g. of water is less than the vapor pressure of pure water at the same temperature; and 20 g. of dextrose in the same weight of water produce double the effect of 10 g. The same weights of different solutes, such as glycerol and glycol, dissolved in the same weight of water, do not cause the same lowering of the vapor pressure; but the same fraction of

one mole of each of these solutes does cause the same effect in the same weight of water. It is obvious that the vapor pressure effect does not depend on the relative masses of the solutes or on the density of the solutions. One mole of each of these solutes contains the same number of molecules; and the same weight of water naturally contains the same number of molecules. The fact stated in Raoult's law may be restated: **The lowering of the vapor pressure of the solvent is proportional to the mole fraction of the solute.** This is shown by the equation,

$$p^0 - p = p^0 N_2,$$

in which N_2 is the mole fraction of the solute.

In its fundamental form, Raoult's law, expressed in terms of mole fractions, applies directly only to "ideal solutions." An *ideal solution* is one in which no change in energy accompanies the mixing of the materials if they are in the same state; and the energy change is the same as that accompanying the change in state if they are not in the same state. In such solutions the solute is in the form of single molecules which have no effect on each other or on the molecules of the solvent, except the diluting effect accompanying the mixing of the substances. Although most solutions do not show the properties of the ideal solution, Raoult's law is applicable to "infinitely dilute" solutions of many non-polar solutes. It may be applied as an approximate generalization to solutions of many solutes in ordinary concentrations.

An approximate form of the fundamental law of vapor pressure depression may be stated in terms of molal concentrations. The number of moles of the solute in dilute solutions is small compared to the number of moles of the solvent. Consequently, the difference between the mole fraction and the ratio between the numbers of moles of the solute and solvent is so small that the two may be considered to be approximately the same. In a solution which contains 0.1 mole of a solute in 1000 g. of water, the number of moles of water is 55.55 and the total number of moles is 55.65. The mole fraction in this solution is 0.1/55.65, 0.00179. In a 0.2 molal solution, the mole fraction is 0.2/55.75, 0.00358. Since the vapor pressure depressions in these two solutions are proportional to the mole fractions, they are in the ratio, 0.00179 to 0.00358, or 1 to 2. These numbers are in the same ratio as the molalities of

the two solutions. Hence, *the lowering of the vapor pressure of the solvent is approximately proportional to the molal concentration of the solute.*

The simple form of Raoult's law may be applied in solutions of ordinary concentration by the introduction of an empirical constant, called the *activity coefficient.* This function takes into account the deviations from ideality caused by the forces existing in solution. In terms of activity coefficients, the equations for the two forms of the vapor depression law are written:

$$p = p^0(f_1 N_1);$$

and

$$p^0 - p = p^0(f_2 N_2).$$

These functions, represented by f_1 and f_2, are evaluated from experimental data as a means of describing the behavior of substances in solution. The quantity obtained by multiplying the mole fraction by the activity coefficient is known as the *activity*, a function introduced by G. N. Lewis.

The deviations from Raoult's law are greater in concentrated solutions than in dilute solutions. *The vapor pressure effects caused by acids, basic hydroxides, and salts in aqueous solution are much greater than those summarized by Raoult's law.* The effects approach as a limit some multiple of those predicted by this law.

Deliquescence. Drying Agents. The vapor pressure of water in equilibrium with highly concentrated solutions is much less than the pressure of water vapor normally present in the air. Such solutions absorb moisture from the air. This may be illustrated by placing a beaker containing a concentrated solution of calcium chloride and a beaker of pure water under a bell-jar, Fig. 73. The pressure of the water vapor from the pure water is greater than is tolerated at equilibrium by the calcium chloride solution. Hence, water continually evaporates from the pure water and condenses in the calcium chloride solution, until all of the water is distilled into the solution. Highly soluble solids exhibit the property of absorbing moisture from the air. At first a small volume of saturated solution is formed at the surface of the

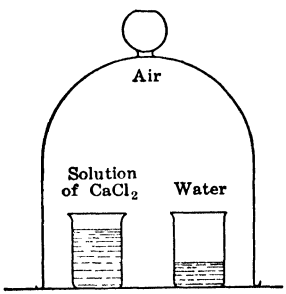


FIG. 73

solid and water from the air condenses into this solution as already described. The solution becomes more dilute as it stands exposed to air; and the pressure of the water vapor required for equilibrium increases until it becomes equal to the pressure of the water vapor in the air. This phenomenon in which soluble substances take up water from the air to form solutions is called *deliquescence*. It is on account of this property that calcium chloride is used on the surface of dirt roads to absorb moisture from the air and keep down the dust.

There are a number of substances which absorb water because the pressure of water vapor which can exist in equilibrium with them is very low. These substances are suitable for use as *drying agents*. Concentrated sulfuric acid is often used in a desiccator, Fig. 74, to provide a dry atmosphere. For this purpose the exposed surface of the acid may be increased by pouring it over some inert substance. Some drying agents absorb moisture on account of a chemical reaction, as in the combination of phosphorus pentoxide with water to form phosphoric acid, and of barium and calcium oxides with water to form the hydroxides. Other drying agents combine with water to form hydrated compounds. Examples of this type are anhydrous copper sulfate, calcium chloride, and sulfuric acid. Another group of drying agents includes substances which are so highly soluble that their solutions have very low vapor pressures. The dehydrating action of sodium and potassium hydroxides, and in part of calcium chloride and sulfuric acid, may be ascribed to this property. Still another group of drying agents includes substances which have a very porous structure, so that water condenses on the surface in the many fine capillaries. Silica and alumina in especially prepared forms exhibit this property.

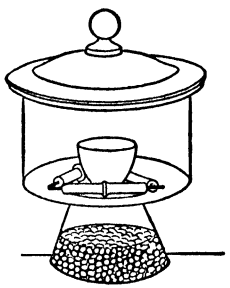


FIG. 74.—Desiccator.

The Elevation of the Boiling Point of the Solvent. The normal boiling point of a liquid is, by definition, the temperature at which its vapor pressure is equal to 760 mm. Since the presence of a non-volatile solute lowers the vapor pressure of the solvent, it is obvious that the vapor pressure of the solution is less than 760 mm. at the boiling point of the pure solvent. For this reason it is necessary to heat an aqueous solution of a solute of this type

to a temperature above 100° to bring the vapor pressure up to 760 mm., Fig. 75. According to Raoult's law, the depression of the vapor pressure of the solvent depends on the mole fraction of the solute. *The elevation of the boiling point of the solvent is proportional to the mole fraction of the solute. It is approximately proportional to the molal concentration. Acids, bases, and salts in aqueous solution cause abnormally great effects on the boiling point of water.* The elevation of the boiling point of the solvent in a one-molal solution is known as the *molal elevation of the boiling point.* The molal elevation of the boiling point is shown for several liquids in Table 15.

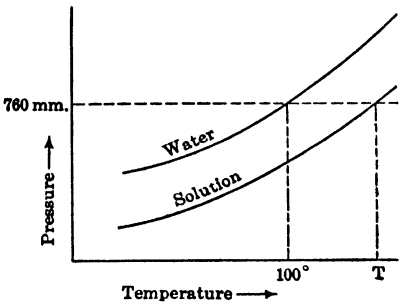


FIG. 75

TABLE 15

MOLAL ELEVATION OF THE BOILING POINT OF SEVERAL SOLVENTS

Solvent	*Boiling Point*	*Molal Elevation*
Water	100.0°	0.52°
Benzene	80.3°	2.43°
Acetic acid	118.1°	2.93°
Ethanol	78.5°	1.14°
Chloroform	61.2°	3.41°
Naphthalene	218.0°	5.80°
Ethyl ether	34.5°	2.01°
Phenol	183.0°	3.0°

The Depression of the Freezing Point of the Solvent. That lower temperatures are required to freeze salt water than fresh water is a fact generally well-known from common observation. The use of alcohol and other substances in the water in an automobile radiator in winter is a familiar application of the principle of freezing point lowering. The effects of the presence of several solutes, in the concentrations given, on the freezing point of water are shown in Table 16.

TABLE 16

DEPRESSION OF THE FREEZING POINT OF WATER
(DEGREES C.)

(1000 g. of water in each solution)

Compound	*Formula*	*Molecular Weight*	*10 g.*	*20 g.*	*30 g.*	*0.1 Mole*
Dextrose .	$C_6H_{12}O_6$	180	0.1	0.2	0.3	0.186
Ethanol . .	C_2H_5OH	46	0.4	0.8	1.2	0.186
Methanol .	CH_3OH	32	0.58	1.16	1.74	0.186
Glycerol . .	$C_3H_8O_3$	92	0.2	0.4	0.6	0.186
Glycol . .	$C_2H_6O_2$	62	0.3	0.6	0.9	0.186

The freezing point depression caused by the same weights of the three solutes, glycol, glycerol, and dextrose, in the same weight of water are shown graphically in Fig. 76. It is observed that these effects are not the same, as was noted also in the vapor pressure lowering. When, however, the depression is plotted against the molality, Fig. 77, it is found that the effects for the different solutes fall on a single curve. The similarity to the vapor pressure effect is a consequence of the fact that the freezing point of a liquid is the temperature at which the solid and liquid phases of the substance have the same vapor pressure under a total pressure of one atmosphere. The presence of the dissolved solute decreases the vapor pressure of the liquid solvent. The solid phase which freezes from a dilute solution is the solvent free from any of the solute. Hence, as shown in Fig. 78, the vapor pressure of water from the solution is less than that of the solid at 0°. The effect of changes in temperature

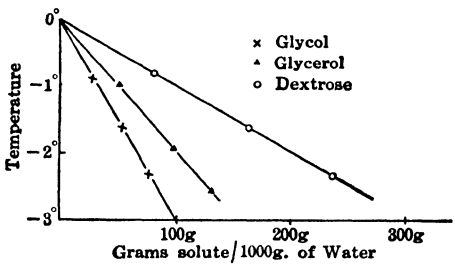


FIG. 76. — Freezing Point Depression.

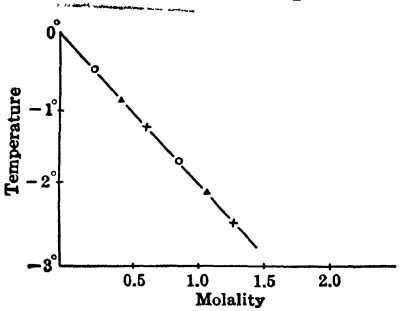


FIG. 77. — Freezing Point Depression.

on the vapor pressure of the solid is greater than on the vapor pressure of the liquid. By cooling the solution to a temperature below 0°, it is possible for the solid pure ice and the liquid solution to exhibit the same pressure of water vapor. *The depression of the freezing point of the solvent is proportional to the mole fraction of the solute, and approximately to the molality of the solution. Acids, bases, and salts cause abnormally great effects on the freezing point also.* The depression of the freezing point of the solvent in a one-molal solution is called the *molal depression of the freezing point.* In Table 17, the molal depression constants for several solvents are shown.

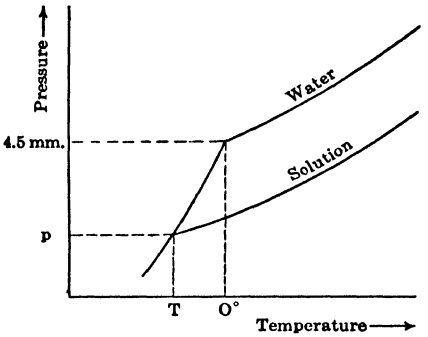


FIG. 78

TABLE 17

MOLAL DEPRESSION OF THE FREEZING POINT OF SEVERAL SOLVENTS

Solvent	*Freezing Point*	*Molal Depression*
Water	0.0°	1.86°
Acetic acid	17.0°	3.9°
Benzene	5.4°	5.12°
Dioxane	11.78°	4.63°
Ethylene bromide	10.0°	12.5°
Naphthalene	80.0°	6.8°
Phenol	38.5°	7.4°
Tribromophenol	95.0°	20.4°

The Determination of the Molecular Weights of Substances in Solution. The effects of different solutes on the properties of the solvent give a basis for the determination of the molecular weights of many substances. According to Raoult's law, the mole fraction of different solutes is the same if they cause the same vapor pressure lowering of a given solvent. If the weight of one mole of one of the substances is known, that of the others may be calculated. Methods based on this principle are applicable only to solutions in which the solute is present in the molecular

state of dispersion. They, therefore, cannot be used for substances to which Raoult's law is not applicable.

Temperature changes may be measured more simply than the changes in the vapor pressure. Experimental procedures are therefore usually based on measuring the freezing point depression or the boiling point elevation, in preference to making direct measurement of the vapor pressure effect. In the determination of the molecular weight by the freezing point method, it is assumed that the lowering of the freezing point is directly proportional to the molality. A weighed sample of the solute is dissolved in a known weight of the solvent in the inner tube of the apparatus shown in Fig. 79. This tube is then placed in a freezing mixture and the temperature at which the solid and solution are in equilibrium before much of the solvent has solidified is measured. Knowing the freezing point of the pure solvent, the freezing point depression is calculated. The molal depression for this solvent must also be known or must be determined through the use of another solute whose molecular weight is known. Suppose that 1.5 g. of a solid dissolved in 100 g. of water cause a freezing point depression of 0.465°. The weight of one mole is calculated in the following manner.

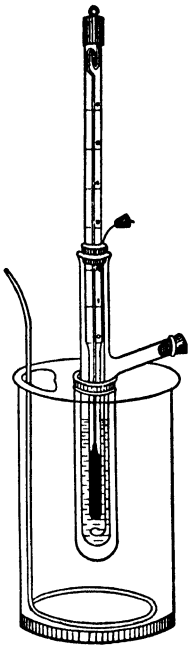


FIG. 79

1.5 g. in 100 g. of water = 15 g. in 1000 g. of water.

0.465° depression is caused by 15 g. in 1000 g. of water.

$$1.86° \text{ depression is caused by } 15 \times \frac{1.86}{0.465} = 60 \text{ g.}$$

One mole of this substance is 60 g. and the molecular weight is 60.

Methods of making the molecular weight determinations based on the freezing and boiling point effects supplement those already considered, which are based on the volumes of definite weights of substances in the gaseous state. In all of these methods, effects caused by equal numbers of molecules are applied to the determination of the weight of the molecule in terms of the standard of molecular weights.

Osmotic Pressure. The uniform dispersal of a solute throughout the whole of a solution is an important property of dissolved substances. If the diffusion of the solute is in some way prevented, an effect which may be observed and measured is caused. This result may be accomplished through the use of a partition which allows the free passage of the solvent, but not of the solute, between a solution and some of the pure solvent. A partition which will show these properties is known as a semipermeable membrane. For laboratory use, a semipermeable cell wall may be prepared by the deposition of cupric ferrocyanide in the pores of an unglazed clay cup. If such a cell is now filled with a solution of cane sugar, closed with a stopper carrying a long glass tube, and placed in a beaker of pure water, Fig. 80, it will be observed that the level of the water in the tube gradually rises. *This phenomenon, called osmosis, is the selective flow of the solvent through a semipermeable membrane from the pure solvent into the solution, or from a more dilute into a more concentrated solution.*

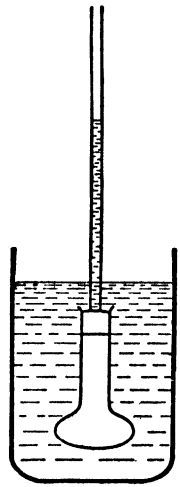


FIG. 80

Since the membrane is permeable to water, it is assumed that water molecules may pass through the cell wall in both directions; but it is obvious that water enters the cell more rapidly than it emerges. Suppose that the mole per cent of the solvent in a solution is 90. One molecule out of ten in contact with a certain minute area of the cell wall is, as an average, a solute molecule which cannot pass through the wall. Outside of the cell, the mole per cent of the solvent in the pure liquid is 100 and all of the molecules striking the cell wall may pass through. There are also molecular forces between the molecules of the solute and solvent, which are greater than the forces exerted between the molecules of the solvent alone. On account of these effects, the water molecules in the solution cannot pass through the cell wall as freely as those in the pure solvent. As the amount of the water entering the cell increases, two effects tend to equalize the rate of entrance and escape of water from the cell. The dilution of the solution decreases the difference in the rates of flow; and the pressure, due to the difference in water level, tends to increase the rate at which

water emerges. After a time a condition of equilibrium is reached and water molecules pass through the semipermeable membrane in both directions at the same rate. No further diffusion of water into the cell is now observed. *The pressure necessary to establish equilibrium at a semipermeable membrane, between a solution and the pure solvent, is called the osmotic pressure of the solution.*

Osmosis is related to the vapor pressure effect. Solutes which cause normal vapor pressure effects also exhibit regularities in their osmotic pressure relationships. Up to concentrations which are approximately one molal, the osmotic pressure is proportional to the molal concentration of the solute. Osmotic pressures increase rapidly with increasing concentration of the solution. According to the measurements of Morse, the osmotic pressure of a one-molal solution at 0° is equal to approximately 25 atmospheres. The osmotic pressure increases with the absolute temperature in the same manner as gas pressure. Solutions which have the same osmotic pressure are *isotonic*.

The natural membranes which surround animal and plant cells are semipermeable membranes; but, in addition to permitting the diffusion of water, they also allow the diffusion of certain dissolved substances into the cells. In this manner, the substances needed for cell growth and repair may be supplied. Two of the many examples which show important applications of osmosis will be discussed. Sometimes it is necessary to inject a fluid into the blood stream of an animal. The blood consists of corpuscles floating in a clear liquid which contains a certain concentration of dissolved substances. The walls of these corpuscles are semipermeable. The contents of the corpuscles are isotonic to the solution in which they are suspended and water passes at the same rate in both directions through this cell wall. If pure water is injected, the liquid in which the corpuscles are suspended is diluted and water enters the corpuscles more rapidly than it emerges. The result is that the corpuscles burst under the pressure which is built up. If, on the contrary, a strong salt solution is injected, the concentration of the liquid outside of the corpuscles is increased, and water emerges more rapidly than it enters. As a result, the blood corpuscles shrink and become useless for performing their natural functions. For injections of this kind solutions which are isotonic to the blood must be used.

Some solutes also may diffuse slowly through a cell wall, and the rate at which this occurs differs for different substances. Soluble salts may pass through the cell walls, but complex organic substances cannot do so. In growing plants the walls of the cells in the very fine roots are freely permeable to water. Since the sap within these cells is a dilute solution, water enters the cells more rapidly than it flows in the opposite direction. From the more dilute solution thus formed, water passes on from cell to cell and offsets the evaporation from the foliage of the plant. The passage of soluble salts in solution through the walls of the root cells furnishes the plant with its mineral foods. As these salts slowly circulate through the cells of the plant, they may undergo reaction with other substances present in the cells to form products which cannot pass out of the cell. In this way the growing parts of the plant are built up. Overfertilizing the plant results in the formation of a solution in the soil around the roots of the plant which is more concentrated than the sap within the cells. This causes a more rapid flow of water out from cells than into the cells, and the plant withers.

EXERCISES

1. What is a solution? Distinguish between solutions and mechanical mixtures.
2. What is meant by the following: saturated solution; solubility; supersaturated solution; molar solution; normal solution; molal solution?
3. What conditions affect the rate of solution of a solid?
4. What conditions affect the solubility of a solid in water? of a gas?
5. Explain the extraction of a solute from one solvent by the use of another solvent.
6. What is meant by fractional distillation? Under what conditions may two liquids be separated into the pure components by fractional distillation?
7. Which types of solutions cannot be completely separated by fractional distillation? What is a constant boiling solution?
8. What different methods are used to describe quantitatively the concentration of solutions? What are the advantages of each?
9. What three properties of water are affected in a regular manner by the presence of a non-volatile solute which is not an acid, a base, or a salt?
10. State Raoult's law and account for the effect described in this law in terms of the kinetic theory.
11. What is the relation between the vapor pressure depression and the lowering of the freezing point? the elevation of the boiling point?

12. What is meant by the molal elevation of the boiling point and the molal depression of the freezing point? Show how these effects may be applied in the determination of the molecular weights of dissolved substances.
13. What is meant by osmosis? osmotic pressure? Explain the fact that one feels thirsty after eating salty food.
14. Examples dealing with the concentrations of solutions and the freezing point and boiling point effects and their application in the determination of molecular weights may be found in the general list of problems.

SUPPLEMENTARY READINGS

Findlay, *The Spirit of Chemistry*, Chapter XV.
Getman and Daniels, *Outlines of Theoretical Chemistry*, Chapters VII and VIII.
Meldrum and Gucker, *Introduction to Theoretical Chemistry*, Chapter IV.
Hildebrand, *Solubility of Non-Electrolytes* (Reinhold Publishing Corporation, 1936).

CHAPTER X

THE COLLOIDAL STATE

In the preceding chapter some of the properties of solutions have been discussed. Solutions are homogeneous mixtures in which the solute is dispersed into the molecular or ionic state of subdivision. A true solute particle diffuses rapidly into a supernatant layer of the solvent. Finely divided solids which are not soluble in a given liquid produce heterogeneous mixtures when they are shaken or stirred with the liquid. In coarse suspensions, the particles of the solid are visible to the unaided eye. They usually settle to the bottom of the container if the suspension is allowed to stand; and they may be separated from the liquid by filtration. Between the true solution and the ordinary mechanical suspension, there is an intermediate degree of dispersion in which the particles do not separate on standing and cannot be removed by the ordinary processes of filtration. The particles do not diffuse rapidly into a supernatant layer of the dispersing liquid. Graham made a detailed investigation of such systems about 1861 and applied the name *colloid*, from the Greek word meaning *glue*, to the substances which show little or no tendency to diffuse. Substances which form true solutions were called *crystalloids*. It was soon recognized, however, that certain crystalline substances, as well as amorphous materials, may be dispersed in liquids to form systems which do not exhibit the general properties of solutions. It was thus made evident that no distinction between colloids and crystalloids on the basis of the nature and constitution of the material is valid. The colloidal condition is in reality a state of matter differing from the solid, liquid, and gaseous states. The name, *colloid*, does not refer to a particular substance but to a system made up usually of two or more substances. A *colloidal dispersion* is intermediate between the solution and the mechanical mixture. The essential difference is in the *degree of dispersion*. The particles of the dispersed

material in colloidal systems are many times ordinary molecular size, but are smaller than the visible particles in ordinary suspensions.

Size of the Particles in the Colloidal State. A colloidal system is a heterogeneous system in which the dispersed material is uniformly distributed in a fine state of subdivision throughout the dispersing medium. Ostwald first classified such systems on the basis of the size of the particles of the dispersed phase. The smallest particles in the ordinary coarse suspensions are about 5×10^{-5} cm. along any dimension. These particles do not pass through a filter paper and do not diffuse. They are visible with the aid of the microscope. Particles having dimensions less than 1×10^{-7} cm. diffuse rapidly, pass through filter paper, and exhibit all of the properties of solute particles. *Colloidal dispersions* are systems in which the dispersed phase consists of particles having at least one dimension which ranges between 1×10^{-7} cm. and 5×10^{-5} cm. These limits are between microscopic visibility and particles somewhat larger than ordinary molecules. There is no sharp line of distinction between colloidal dispersions and slow-settling suspensions at one extreme, nor between colloidal dispersions and true solutions at the other. The limits assigned to the colloidal state are arbitrary. There are substances such as egg albumen which may be dispersed into molecular particles which, nevertheless, fall in the colloidal range because they are composed of such large molecules.

Types of Colloidal Dispersions. Colloidal dispersions may be classified according to the states of matter involved. Consequently, there are eight types of colloidal dispersions: *viz.*, solids, liquids, and gases in liquids; solids, liquids, and gases in solids; and solids and liquids in gases. The more familiar systems are those in which the dispersing phase is liquid or gaseous. Colloidally dispersed solid materials are commonly called *colloidal solutions* or *sols*, such as water containing particles which are so finely divided that they do not settle even on long standing. A prefix may be employed to indicate the dispersing medium. Colloidal dispersions of solids in water are *hydrosols* and dispersions in alcohol are *alcosols*. Dispersions of liquids in liquids are called *emulsions*. Milk and mayonnaise are emulsions. Dispersions involving gases in liquids, like lather from a soap solution, are

foams. Solids and liquids dispersed in gases are known as *aerosols.* *Smoke* and finely divided *dust* particles, such as the ammonium chloride smoke so familiar in the laboratory, are solid aerosols. *Clouds* and *mists*, such as the fumes from concentrated solutions of hydrochloric acid, are liquid aerosols. In addition, there are semisolid systems known as *gels.* The solid and liquid phases in the gel are continuous so that they have a network structure of the interlacing type. There are two familiar forms of gels: *viz.*, *gelatinous precipitates* which separate, leaving an excess of the liquid; and *jellies* which set so as to include all of the liquid. Gels containing water are known as *hydrogels* and those containing alcohol as *alcogels.*

A useful classification of liquid colloidal dispersions may be based on the stability of the system. If the attraction between the dispersed material and the dispersing medium is small, the dispersion is called a *lyophobic* system. If water is the dispersing liquid the term is *hydrophobic*, from the Greek root signifying "water-fearing." In the hydrophobic systems the dispersed material is readily coagulated and does not usually become dispersed again into the colloidal state simply by the addition of water. Such systems are called irreversible colloidal dispersions. If the attraction of the dispersing medium for the dispersed phase is great, the dispersion is a *lyophilic* system, called a *hydrophilic*, "water-loving," system in an aqueous medium. Such systems are relatively stable, and the separated materials may again be mixed into a colloidal dispersion by shaking or stirring them together. Hydrophilic systems are called reversible colloidal dispersions.

Properties of Colloidal Dispersions. Colloidally dispersed materials in liquid media pass through filter paper; and they do not settle out on long standing, although they tend to become more dense in the lower portions of the dispersion if the sol is more dense than the dispersing liquid. The particles are not visible even with the aid of the microscope. The dispersed particles do not diffuse readily into a supernatant layer of the dispersing medium. Colloidal systems show slight osmotic pressure if they are separated from the pure liquid by a semipermeable membrane. Certain material, such as parchment paper, animal membranes, and cellophane, may be used as a porous diaphragm which will

permit the diffusion of the dissolved materials, but will not permit the passage of particles of colloidal magnitude. This difference is the basis of a process, known as *dialysis*, by which dissolved substances may be washed out of colloidal dispersions. For this purpose, the colloidal suspension containing dissolved substances is placed in a dialyzing cup, such as that which may be made by binding parchment paper over the end of an open glass cylinder, to serve as a porous diaphragm, Fig. 81. The cup is now suspended in a vessel through which fresh water flows; and the dissolved substances pass out through the parchment and are washed away, while the colloidally dispersed material remains in suspension in the cup.

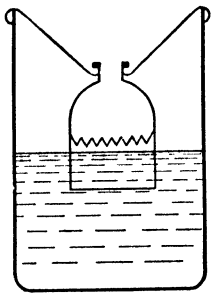


FIG. 81. — Dialyzing Cup.

The vapor pressure, boiling point, and freezing point effects caused by colloidally dispersed substances are so slight as to be almost inappreciable. These effects depend on the relative numbers of dispersed particles in some particular weight of the solvent. Since the particles in colloidal dispersions are usually many times molecular in composition, they are relatively few in number compared to those in the same molal quantity of a true solute.

The most noticeable differences in properties between colloidal dispersions and coarser suspensions are due to the fine state of subdivision of the colloidal particles. The more finely divided the substances are, the greater are the number of particles and the total area of the surface exposed for the same weight of material. In the surface between two phases the atoms and molecules are in a different relation to adjacent atoms and molecules than are those in the interior of a solid, so that there are specific properties which are dependent on the forces existing at the surface interface. The surface energy depends on the surface tension and the area of the surface. It has been observed previously that adsorption and contact catalysis depend on surface forces. Hence, these effects are increasingly prominent as the size of the particles in the heterogeneous mixture decreases. The solubility of a substance varies somewhat depending on the size of the particles in the excess of the solid in suspension. It is for this reason that fine crystals disappear and the large crystals become somewhat larger

when a mixture of the two is allowed to stand in a saturated solution of the substance. The solubility of colloidally dispersed solids is significantly greater than that of the same substances in an ordinary coarse state of aggregation. *In colloidal systems the dispersed particles are so minute that surface forces play an important rôle in determining the properties of the substance.*

The Tyndall Effect. The path of a beam of light passing through a colloidal suspension is visible as a turbid area extending through the liquid or gas, Fig. 82. This phenomenon, known as the Tyndall effect, is due to the fact that the dispersed particles are large enough to present reflecting surfaces to light. It is not observed in solutions because the particles of most solutes are too small to have reflecting surfaces for light. This effect is familiar in the illuminated area of a beam of light passing through air which contains dust or fog. If the illuminated area in a colloidal dispersion is examined by means of a high-power microscope at right angles to the beam of light, the position of an individual particle may be located as a point from which light appears to originate. This device is known as the *ultramicroscope.*

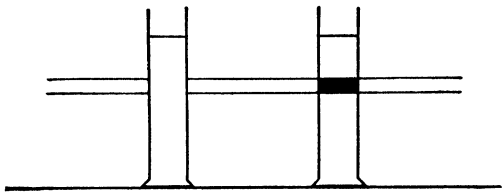


FIG. 82. — The Tyndall Effect.

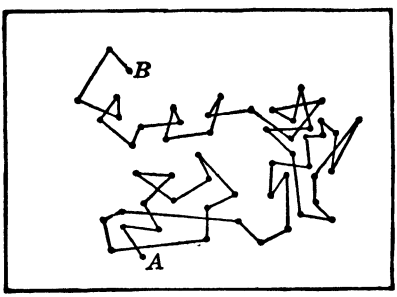


FIG. 83. — Brownian Movement.

The Brownian Movement. By examining colloidal suspensions through the use of the ultramicroscope, it may be observed that the particles do not remain in fixed positions but are in constant motion. They move short distances in straight lines so that the motion follows a zigzag path. A single particle may remain for some time within the field of vision, Fig. 83. This phenomenon was first noticed in 1827 by Brown, a Scottish botanist, and is called the Brownian movement. The motion is due to the bombardment of the suspended particles by the molecules of the dispersing medium. The

effect of these collisions is to knock the dispersed particles about in a haphazard manner. The motion is greater for light particles than for heavy particles. The Brownian movement tends to cause the particles to remain suspended and uniformly distributed throughout the dispersing medium.

The Electric Charges of the Particles. Colloidally dispersed particles almost always carry an electric charge. This may be shown by placing a colloidal suspension beneath water in a large U-tube and inserting electrodes connected with a source of direct current into the clear liquid. When colloidal arsenious sulfide is tested in this way, it is found that the colloidal particles move toward the anode, showing that they bear negative charges, Fig. 84. Many of the metal sulfides and free noble metals produce negatively charged colloidal particles. Metal oxides and their hydrated products are commonly positively charged in the colloidal state. The source of this charge cannot be stated with certainty in all suspensions, although it is probably due to the adsorption of specific electrically charged ions from the solution. The effect of the electrical charges borne by the dispersed particles is to cause them to repel one another and to prevent their coalescence to form heavier particles.

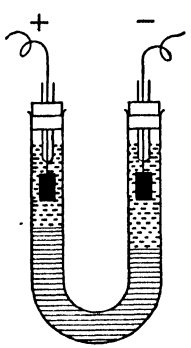


FIG. 84

Preparation of Colloidal Dispersions. The methods which may be used for the preparation of colloidal dispersions fall into two classes, dispersion methods and condensation methods. *The dispersion methods* consist in the subdivision of coarser aggregates of matter into particles of colloidal size. The disintegrating action of the dispersing medium causes many substances to become dispersed into colloidal particles, as the solvent action of water on water-soluble substances produces molecular and ionic dispersions. This process of sol formation is called *peptization.* Water is absorbed by such substances as gelatin, tannin, and agar, and these substances are peptized by water. Many substances are peptized by solutions containing the specific ions which they readily adsorb. Some of the metal sulfides are peptized by sulfide and hydrosulfide ions. This is due to the fact that the adsorption of these negative ions leads to the formation of negatively charged

colloidal particles which repel one another and cause the coarse solid to disintegrate. In other instances the stability of the precipitate is due to the presence of an adsorbed salt. Such substances are called agglomerating agents. If the salt is washed out of the precipitate, a colloidal dispersion sometimes results. Peptization by ions and by the removal of the agglomerating agent are frequently encountered in analytical chemistry and often cause trouble in handling precipitated sulfides and hydrated metal oxides.

Many solids may be broken down into particles of colloidal magnitude by *grinding*. The finely ground powder produces a colloidal suspension when it is agitated with a liquid, unless particles coalesce during the latter stage of the process. Colloidal silica may be produced by suspending finely ground quartz in hot water. "Colloid mills" have been devised for grinding solids to produce colloidal suspensions. The pigment zinc oxide consists of aggregates of very fine particles which must be suspended uniformly throughout the oil in the preparation of paint. This may be accomplished by grinding the oxide with the vehicle in a colloid mill.

Some of the metals of low activity may be dispersed into colloidal particles by the *Bredig arc method*. This process consists in causing an electrical discharge between wires of the metal beneath the surface of water. Minute particles of the metal are torn off during the discharge and remain in suspension.

The condensation methods of preparing colloidal suspensions involve the formation of particles of colloidal size by the union of smaller particles. Molecules and ions are the smaller particles which are available to put into this process, and chemical reactions forming insoluble products are required to produce the larger particles. The conditions under which the reactions occur must be controlled so as to produce particles of appropriate size to exist in colloidal suspension. Such reactions are usually carried out in dilute solution and in the absence of any excess of the ionic materials which would cause the precipitation of an insoluble product.

Colloidal suspensions of some of the metals of low activity result from *the reduction of the metal ions* by certain soluble reducing agents. Colloidal gold may be prepared by the reduction

of gold chloride in dilute solution by the action of reducing agents such as phosphorous acid and hydroquinone. Colloidal gold exhibits different colors, red, blue, or purple, depending on the size of the particles which are formed. Colloidal silver may be prepared by the reduction of a faintly ammoniacal solution of silver nitrate with tannin or with certain other reducing agents. The stability of the metal hydrosols may be greatly increased by their preparation in the presence of hydrophilic colloids such as gelatin or glue.

Precipitation reactions ordinarily lead to the formation of insoluble products in the form of particles which are much larger than those in the colloidal state. However, many reactions which produce insoluble products may be carried out under special conditions so as to form colloidal dispersions. The passage of hydrogen sulfide into an acidic solution of an arsenious compound produces a precipitate of arsenious sulfide.

$$2\,AsCl_3 + 3\,H_2S \longrightarrow As_2S_3\downarrow + 6\,HCl.$$

The reaction of hydrogen sulfide with a dilute solution of arsenious acid yields a yellow colloidal suspension of the sulfide.

$$2\,H_3AsO_3 + 3\,H_2S \longrightarrow As_2S_3 + 6\,H_2O.$$

The presence of the free acid in the first solution prevents the formation of the charged particles of colloidal size and the larger aggregates are formed and precipitated. The concentration of the free acid in arsenious acid solutions is so low that it is possible for the particles to acquire an electrical charge by the adsorption of negative sulfide or hydrosulfide ions from solution. The coalescence of the particles is thus prevented and the colloidal suspension is stable. Different colloidal materials are sensitive to specific ions which prevent the retention of the charges of the particles. Hence, the formation of any colloidal dispersion requires the absence of significant concentrations of the ions to which it is sensitive.

There are also instances in which the stability of a colloidal dispersion is increased by the presence of ions. This may be the result when the ions in solution are those which are adsorbed by the dispersed particles. An example of this effect may be found in the formation of silver halide sols. At sufficiently low concentrations, the interaction of silver nitrate with a solution of a

sodium halide produces the colloidally dispersed silver halide if either of the reactants is present in excess. The particles of the sol are positively charged if an excess of the silver salt is used and are negatively charged in the presence of an excess of the halide.

Colloidal metal hydroxides are frequently prepared by the interaction of a salt with water, a reaction known as *hydrolysis*. In these products, such as ferric hydroxide, the substance does not contain definite proportions of water relative to the oxide of the metal and it is more accurately named an hydrous oxide. The ferric oxide sol is readily prepared by the slow addition of a concentrated solution of ferric chloride to boiling water.

$$2\,FeCl_3 + (x + 3)H_2O \longrightarrow Fe_2O_3(H_2O)_x + 6\,HCl.$$

The Coagulation of Colloidally Dispersed Solids. The colloidal particles of these materials remain in the dispersed phase in a liquid medium primarily because of the electric charges which they bear. These charges are considered to be due either to the selective adsorption of specific ions from solution or to the formation of ions by molecules at the surface of the solid. Because all of the particles bear a charge of the same kind, they repel one another and do not coalesce. The agitation caused by the random motion of the molecules of the dispersing liquid causes the particles to remain in suspension so long as they are very finely divided. In order to cause the coagulation of the colloidal particles, it is necessary to alter their charges so that they may coalesce. This is accomplished by the addition of ionized substances which combine with and thus remove the adsorbed ions, or are adsorbed and thus balance the charges of the colloidal particles. The precipitating ions must have the opposite charge to that of the particle and the precipitating power increases with the charge of the ion. Many colloidal particles are capable of reacting in such a manner that they may give up hydrogen ions and they may also react to take on hydrogen ions. The stability of the colloidal particle is least under the ion concentrations at which these two effects are balanced. Under these conditions the colloidal particle does not migrate if an electrical field is applied. The concentration of the hydrogen ion at which such colloidally dispersed particles do not migrate in an electrical field is called the *isoelectric point*.

The particles in arsenious sulfide are negatively charged. This colloidal system may be broken down with the coagulation of the arsenious sulfide by the addition of a solution containing the ions to which this dispersion is sensitive. The addition of acids and of aluminum salts causes the coagulation of colloidal arsenious sulfide. The particles of colloidal hydrous ferric oxide bear positive charges. The coagulation of this material is caused by the addition of a solution containing highly charged negative ions such as sulfates and phosphates. Oppositely charged colloidal particles will mutually coagulate each other. Thus, both colloidal arsenious sulfide and hydrous ferric oxide are coagulated when the two suspensions are mixed in the proper proportions.

Many rivers carry large quantities of colloidally dispersed solids in addition to those in mechanical suspension in the form of muddy water. When this water becomes mixed with sea water, the suspended matter precipitates on account of the coagulating effect of the dissolved salts.

Protective Colloids. Many colloidal suspensions are stabilized by the use of the proper proportion of some other colloidal substance. If dilute solutions containing equivalent quantities of silver nitrate and potassium bromide are mixed, a precipitate of silver bromide is formed at once. If, however, gelatin is added to each of the solutions before they are mixed, a clear colloidal dispersion of silver bromide is produced. Gelatin is itself a colloidally dispersed material and it acts as a protective colloid in stabilizing the silver bromide suspension. The use of gelatin is of great importance in the preparation of light-sensitive silver salts in the proper state of subdivision for use in the manufacture of photographic films, plates, and printing papers. The protective colloid is in general hydrophilic in nature and its effect is due to the formation of a thin film of the protective colloid which is adsorbed on the surface of the dispersed solid.

Gels. Precipitates which contain relatively large proportions of the liquid in which they are formed are known as gelatinous precipitates. If the insoluble substance coagulates in such a manner that it retains all of the liquid, the product is a jelly. The setting of jellies may be attributed to the formation of minute fibers and films of the dispersed material in an interlacing structure, with the liquid held in this structure by combination with

these fibers. When jellies are allowed to stand, it frequently happens that free liquid separates with a corresponding decrease in the volume of the jelly. This phenomenon is known as *syneresis*. It is commonly attributed to the gradual growth of the minute particles of the dispersed material into larger aggregates with a decrease in the surface area for the same weight of material. On account of this change some of the dispersing liquid is set free.

Fruit juices containing enough pectin, as the juices of apples, currants, and grapes, yield jellies when sugar is added and the solutions are concentrated to the proper degree. In making "solidified alcohol," employed for special purposes as a fuel, cellulose esters are used to cause the formation of the jelly. When hydrochloric acid is added to a solution of a soluble silicate, insoluble hydrated silica is formed. Under certain conditions this reaction yields a clear colloidal suspension which soon sets to form silicic acid jelly. The dehydration of this jelly produces a very porous solid, known as *silica gel*, which has extensive commercial applications as an adsorbent.

Emulsions. The preparation of emulsions is usually accomplished by shaking, beating, or stirring immiscible liquids together. Such emulsions are usually temporary and soon separate into layers of the original components when they are allowed to stand. In order to prepare a more stable emulsion, a third substance must be present in the mixture. Such substances are called *emulsifying agents.* The nature of these substances is different for different liquids. The emulsifying agents used in aqueous emulsions are usually lyophilic colloids. The effect of the emulsifying agent is partly due to a decrease in the surface tension of the liquid in which it is soluble, thus decreasing the tendency for the small drops to unite to produce larger drops and finally separate layers of the liquids. The essential condition for emulsification is to disperse one of the liquids into fine droplets and to cause these droplets to become coated with a protecting film of the emulsifying agent. In the preparation of an emulsion of kerosene and water, such as those used in spraying fruit trees, soap is the emulsifying agent. Eggs are used to furnish the emulsifying agent in the production of mayonnaise from olive oil and vinegar. Milk and cream are emulsions of drops of butter fat in water with casein as the emulsifying agent. The fat droplets

vary in size from 2×10^{-4} cm. to 1×10^{-3} cm. in diameter. In the process of homogenization the droplets are reduced to a small fraction of these sizes, so that the surface area of the droplets is greatly increased for the same quantity of material, and the stabilizing action of the emulsifying agent is correspondingly increased.

The breaking of an emulsion is caused by the destruction of the protecting film. The emulsifying agent may be decomposed by the addition of a substance which reacts with it, thus causing the emulsion to break and separate into layers of the component liquids. Soap is an emulsifying agent for the kerosene-water emulsion. The addition of an acid converts the sodium oleate into free oleic acid and the emulsion is destroyed. Calcium and magnesium salts react with sodium and potassium oleates forming insoluble compounds, so that soap is not effective as an emulsifying agent in hard water until these salts have been precipitated. The emulsifying film may be broken by a number of procedures, such as the addition of an excess of the dispersed phase, "salting out" by the addition of an excess of salt which dehydrates the films, heating, freezing, the application of a high electrical potential, and centrifuging. The breaking of emulsions is frequently of great industrial importance.

Foams. A foam is a dispersion of a gas in a liquid. The gas bubbles, like the liquid droplets in emulsions, are inclosed in films. Even though the bubbles are much larger than the droplets in emulsions and larger than the colloidal range of magnitudes, the inclosing films are of such thickness that they fall within the colloidal state of dispersion and may be treated by the same principles used in the consideration of other colloidal materials. Foams are ordinarily formed by shaking liquids in air. In order to produce a stable foam the liquid must be sufficiently viscous to form long-lived films or must be stabilized by the presence of finely divided solids at the liquid-gas boundary. Many hydrophilic colloidal materials, such as soap, saponin, and proteins, yield stable foams. Soap bubbles and lathers are familiar examples. In some carbon dioxide fire extinguishers the gas is produced by the reaction of sodium bicarbonate with a solution of aluminum sulfate in the presence of saponin. The foam produced in this way is stabilized by the hydrous aluminum oxide

and by the saponin. Such a froth extinguishes the fire by blanketing it with an atmosphere of carbon dioxide. In the flotation process for the concentration of certain types of ores, especially the sulfides, the finely ground ore is agitated in water containing an oil and an emulsifying agent and air is blown through the mixture to produce a foam. The foams are stabilized by the adsorption of the metal compound in the surface film of the oil froth, while the silicate minerals remain in the water layer.

The formation of foams is troublesome in many processes, so that it is desirable to prevent foaming in such instances. This is accomplished, as in the breaking of liquid-liquid emulsions, by the addition of materials which prevent the formation of films or produce weak films which are short-lived, and by breaking the film through physical means. The foam which forms during the evaporation of many solutions may be broken by blowing a current of cold air over the surface of the liquid. The sudden condensation of the vapor inside of the bubble causes the film to break. The foaming of boiler waters is due to the presence of dissolved salts, such as sodium chloride and sodium sulfate, and to the presence of finely divided solid matter which tends to stabilize the foam.

Dust, Smoke, and Fog. These colloidal dispersions consist of finely divided materials in air. Such materials are known as *aerosols*. Dusts contain solid particles; smokes usually contain both solid and liquid particles; and fogs, mists, and clouds consist primarily of liquid particles. Nevertheless, these liquid aerosols are usually formed by the condensation of moisture about dust particles as nuclei and there is no sharp line of separation between liquid and solid aerosols in natural materials.

Dusts are usually formed by dispersion methods such as grinding processes and explosions. Dust clouds are raised by explosions in mining and quarrying operations. Dusts from drilling and blasting in granite and other silicate rocks, particularly in the boring of tunnels, cause the disease *silicosis* to develop if large quantities of the dusts get into the lungs. In recent years dust storms originating in drouth-stricken areas have spread across the country and have caused enormous damage, not only in the region where they originate, but also where the dust settles. The most spectacular dust cloud in history originated in the volcanic ex-

plosion at Krakatoa in 1883. The dust was carried completely around the earth in a cloud approximately fifteen miles thick and the effects of this dust persisted through 1884 and 1885. Dusts containing combustible materials frequently ignite spontaneously, causing explosions, as in flour mills, grain elevators, and similar situations. Finely divided coal dust blown into furnaces is a very efficient use of the material as a fuel.

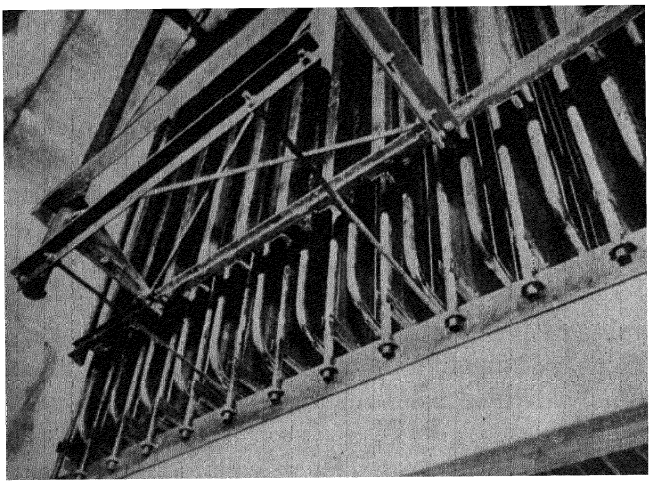


FIG. 85. — (Courtesy of Western Precipitation Company.)

Smoke and fog usually result from the condensation of gaseous materials and from the interaction of gases. These materials also usually contain solid particles carried along mechanically. An interesting and scientifically important application of fog formation is in the Wilson cloud chamber for the investigation of rapidly-moving minute particles. Smoke, dusts, and fogs are evident in all industrialized areas. The sudden cooling of warm moisture-laden air produces mists, fogs, and clouds.

Many of the materials carried along in smokes, dusts, and fumes are objectionable and dangerous. Many of these materials have great industrial value. The heat value of the carbon contained in the smoke from chimneys in industrial plants in the entire country represents a very large amount. The *Cottrell process* for the elimination of such smokes and the recovery of valuable materials which they contain depends on the passage of the flue

gases between plates bearing high electric charges, Fig. 85. The charged particles in the dispersion are attracted to the plates of opposite charge and are deposited, allowing only the uncharged gaseous molecules to pass on into the air, Fig. 86.

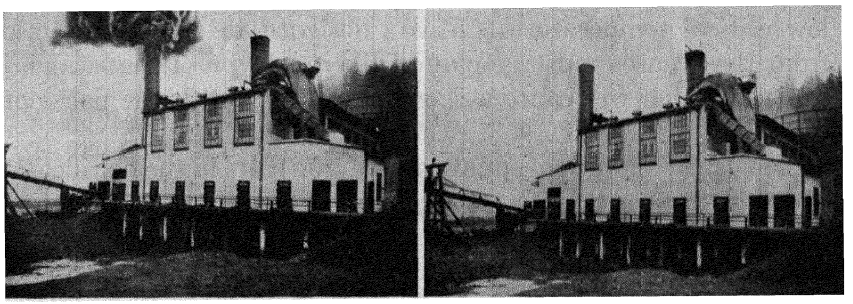


FIG. 86. — Effect Caused by Cottrell Precipitator.
(Courtesy of Western Precipitation Company.)

Adsorption. In a preceding chapter, the adsorption of gases and of substances in solution on the surface of heterogeneous catalysts has been discussed. *Adsorption is dependent on surface forces*, so that the extent of adsorption is greatest when the adsorbent is in a finely divided or porous condition, so as to furnish maximum surface area between the phases involved. The amount of a substance adsorbed is not, however, dependent merely on the state of subdivision of the adsorbent, but depends on the properties of both the adsorbent and the adsorbed substance. *Adsorption is a selective process.* Gases having high critical temperatures are in general adsorbed to a greater extent than those having low critical temperatures. The quantity of a gas adsorbed by a given weight of an adsorbent is increased by increasing the pressure. These results are in accord with the general behavior of gases previously discussed. Larger proportions of a specific gas condense on the surface of a solid if the temperature and pressure are near those at which the substance liquefies than if they differ widely from liquefying conditions.

A very porous form of charcoal may be prepared from cocoanut shells. This material is particularly efficient for the adsorption of gases. It is extensively used in the canisters of gas masks for protection from some military gases and from poisonous gases liberated in many industrial accidents. These gases have high

enough critical temperatures so that they are adsorbed as the air is drawn through the charcoal in the canister, and the proportions remaining in the air are not toxic; but oxygen and nitrogen are not appreciably adsorbed at ordinary temperatures. Such gas masks are not effective for carbon monoxide and other gases of low critical temperatures. Masks designed to afford protection from these gases must employ a different type of material in a canister which will cause a chemical reaction with the poisonous gas.

The use of aluminum sulfate and of iron salts in the clarification of water in filtration plants depends on two effects. The highly charged positive ions of these salts aid in coagulating the negatively charged colloidally dispersed particles in the water. These ions also interact with water and basic solutions to form positively charged colloidal particles of a gelatinous nature, which adsorb suspended particles and themselves coagulate to form easily filterable precipitates. The coagulation of colloidal materials in sewage disposal plants is an important process.

Most dyes go into colloidal suspension in the dye solution. Many dyes are adsorbed directly by animal and vegetable fibers; but there are few direct dyes for cotton cloth. In order to dye such materials a mordant is used. The *mordant* is a salt of some high-valent metal ion, such as aluminum or tin, which may be caused to form a gelatinous, colloidal hydrous oxide throughout the fiber. Such materials are adsorbed by the fiber and they, in turn, adsorb the dye. The mordant may be stamped in a pattern in the cloth which is then soaked in the dye. When the dyed cloth is subsequently washed, the dye is washed out except in the mordanted portions, leaving the desired printed goods.

The applications of colloid chemistry are too numerous for detailed discussion here. The production of wood pulp and of paper involves colloidal phenomena. The synthetic plastics are colloidal materials which may be coagulated, molded, and shaped into a great variety of objects of industrial importance. "Rayon," "Nylon," and other synthetic textile fibers are produced as fine threads through the coagulation of colloidally dispersed materials. Rubber latex is a colloidal substance and the different steps in the production of the great number of important products made of rubber modify the properties of this colloid. A large proportion

of the foods are colloidal in nature; and cooking such substances modifies the nature of these materials. Many of the chemical industries are confronted with problems which are solved through the application of knowledge acquired in the study of colloidal systems.

EXERCISES

1. What are colloidal dispersions? How do they differ from ordinary coarse suspensions?
2. How do colloidally dispersed materials differ from solutes in (*a*) diffusibility, (*b*) osmotic pressure effect, (*c*) vapor pressure effect? Explain these differences.
3. What is meant by dialysis? How is it related to filtration?
4. What are the various classes of colloidal systems?
5. What is the Tyndall effect? To what is it due?
6. What is the Brownian movement? How does this effect aid in causing colloidal dispersions to persist?
7. What is the effect of electric charges on the stability of colloidal systems?
8. What two classes of methods may be used for the preparation of colloidal dispersions? Give examples to illustrate each class.
9. How may the particles in colloidal suspensions be coagulated? Give examples to show the importance of coagulating such materials.
10. How are emulsions prepared? How may they be caused to break?
11. What is a protective colloid? Explain its action in stabilizing colloidal dispersions.
12. How do gels and jellies differ in structure from the other types of colloidal systems discussed?
13. Account for the formation of colloidal dusts, smokes, and fogs.
14. What is meant by adsorption? Discuss some of the important applications of adsorption in industrial processes and in analytical separations.

SUPPLEMENTARY READINGS

Weiser, *Colloid Chemistry* (John Wiley and Sons, 1939).
Hildebrand, *Principles of Chemistry*, Chapter XIX.
Getman and Daniels, *Outlines of Theoretical Chemistry*, Chapter X.
Alexander, *Colloid Chemistry, Theoretical and Applied* (The Chemical Catalog Company, 1932).
Hatschek, *An Introduction to the Physics and Chemistry of Colloids* (P. Blakiston's

CHAPTER XI

IONIZATION

The formation of gas ions by the passage of streams of electrons or of alpha rays through gases has been discussed. That a transfer of electrons from the atoms of metals to the atoms of non-metals occurs during the direct union of active metals with active non-metals has also been noted. In consequence of such electronic changes, positively and negatively charged ions are formed during chemical reactions. These charged particles are structural units in the space lattice of the crystal of a solid product. When soluble solids dissolve in water, they become dispersed into a fine state of subdivision throughout the water. The vapor pressure effects caused by a number of solutes leads to the conclusion that they yield molecules in solution; but the effects caused by soluble salts, basic hydroxides, and acids indicate a larger number of particles.

The Solution of Crystalline Salts in Water. Crystalline substances dissolve in a solvent if the force exerted by the solvent is great enough to overcome the attraction of the particles of the solid for each other. When an ionic solid, such as potassium chloride, is placed in water, the molecules of the water become oriented about the ions in the surface of the crystal. The water molecules are dipoles and the negative part of the molecule is attracted toward the positive potassium ions, while the positive part of the molecule is attracted toward negative chloride ions. In consequence of this arrangement, the forces of attraction of the ions for each other are weakened and the ions separate from the crystal as free ions, surrounded by molecules of water. These changes are represented in Fig. 87. The name *ion*, given by Faraday, at first represented only the free charged particle capable of wandering about in the solution. According to current usage, the name is applied to the charged particle without regard to its location or freedom of motion, and the independent particles in solution may be designated "free ions."

The dispersion of a solute into ions may be represented by an equation in which the formula signifies the solid substance. In order to show that the solid itself is composed of charged particles,

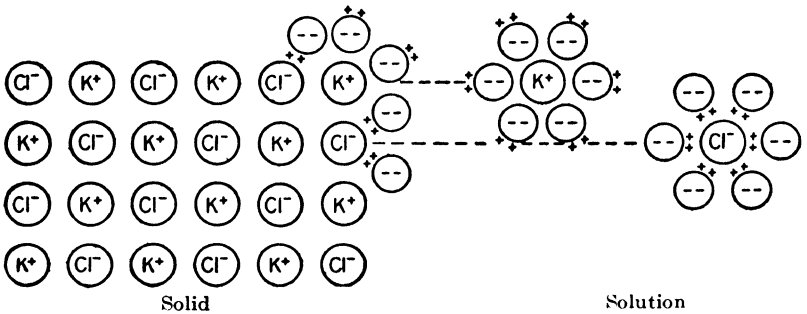


FIG. 87. — Dissolving of a Crystalline Salt in Water. (From Hildebrand, *Principles of Chemistry*, 4th Ed.)

positive and negative signs may be written into this formula. The formulas of the free ions must show the charges which they bear in order to differentiate them from atoms.

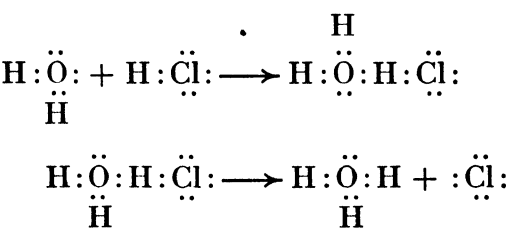
$$K^+Cl^- \longrightarrow K^+ + Cl^-.$$
$$Na^+OH^- \longrightarrow Na^+ + OH^-.$$
$$(K^+)_2SO_4^{--} \longrightarrow 2\,K^+ + SO_4^{--}.$$

The first of these equations should be read: one mole of potassium chloride yields one gram ion each of free potassium and chloride ions. Since the ions exist as free and independent particles, it is customary to call one gram ion of a substance one mole of that variety of ion. Consequently, a one-molar solution of an ion contains one gram ion per liter of solution.

Many crystalline solids dissolve in water to produce solutions containing the ions of the solute. In a saturated solution of such substances, there is an equilibrium between the excess of the solid and the ions in solution. In some crystalline solids, however, the forces of attraction between the ions are not weakened enough by the action of water to cause the presence of more than an extremely small concentration of the dissolved material at equilibrium. These salts are practically insoluble. The hydroxides of the active metals yield ions in a manner similar to the salts. There are also certain classes of molecular substances which are decomposed into ions in solution.

The Solution of Molecular Acids in Water. The common acids, in the pure condition, are composed of molecular units. Pure hydrogen chloride is a gas and hydrogen nitrate and hydrogen sulfate are liquids at ordinary temperatures and pressures. These substances yield ions when they dissolve in water. Clearly, the formation of the ions of these solutes involves a change which differs from that of the salts. As a part of a system of definitions dealing with acids and bases in general, Lowry and Brönsted, independently, in 1923 postulated the formation of ions from molecular substances in terms of their interaction with the solvent.

The molecules of these substances are polar in nature. Since water molecules are also polar, it is assumed that there is an attraction between the hydrogen atom of the acid molecule and the oxygen atom of the water molecule, and that a coördinate bond is formed attaching the water molecule to the acid. In this way a complex structure is built up; and the bond between the hydrogen atom, hydrated by the attached molecules of the solvent, and the remainder of the acid molecule is weakened. This leads to the decomposition of the complex structure with the formation of the hydrated hydrogen ion, known as the *hydronium ion*, H_3O^+, as the positive ion in the solution. The remainder of the acid molecule constitutes the negative ion. The simple hydrogen ion, formed by the removal of an electron from an atom of hydrogen, is a single proton. On account of its small size relative to its charge, it is unlikely that this particle can remain in the free condition, except temporarily as a gas ion. In terms of these assumptions, the formation of ions when hydrogen chloride dissolves may be illustrated by the following equation in which the electronic formulas are written.



In ordinary form, this equation is written,

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-.$$

This reaction involving the transfer of a proton from one substance to another is known as *protolysis*. Similarly, the formation of ions in solutions of nitric and sulfuric acids may be shown by the following equations:

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-.$$

$$H_2SO_4 + 2\,H_2O \longrightarrow 2\,H_3O^+ + SO_4^{--}.$$

Many ions, probably most of them, are hydrated in aqueous solution. Frequently, the number of molecules of water associated with each ion is not definitely known. Hence, in order to simplify the writing of ordinary equations, it is customary to omit the water of hydration from the formulas of the ions, unless some specific point is clarified by introducing it; and the simple symbols are used to represent the ions even though they may be hydrated.

In concentrated solutions, the reaction producing ions is incomplete; but it is virtually complete in the dilute solutions of some of the acids. Nevertheless, the reaction is incomplete in solutions of the majority of the acids, even in dilute solutions; and a state of equilibrium is established.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-.$$

The Vapor Pressure Effects. The conclusion that many solutes yield ions in solution is supported by a consideration of the vapor pressure effects. It has been shown in a preceding chapter that the lowering of the vapor pressure of the solvent, together with the resulting elevation of the boiling point and the depression of the freezing point, depends on the relative numbers of the solute and solvent particles. The relative numbers of particles in one-molal solutions of several solutes may be estimated by comparing the effect that each produces on the vapor pressure, boiling point, or freezing point of the solvent. It is observed that the effects caused by salts, basic hydroxides, and acids in aqueous solutions are greater than those caused by other substances in the same molal concentration. In a one-molal solution of common salt, the freezing point depression is found to be 3.33° and the boiling point elevation, 0.93°. Each of these effects is nearly 1.8 times the molal effect caused by non-electrolytes. Some solutes may show an effect which is greater than double but less than

triple the normal molal effect. From the consideration of a large amount of data, two conclusions may be drawn: *viz.*, the effects caused by salts, basic hydroxides, and acids on the physical constants of water are greater than proportional to the molal concentration; and the effects are less than, but approach as a limit, an integral multiple of the regular molal effect. From these observations it follows logically that *solutions of salts, basic hydroxides, and acids in aqueous solution contain a greater number of solute particles per mole than the molecular solutions. The effective concentration of the ions is somewhat less than an integral multiple of the number of molecules in a molecular dispersion of the same molality.*

The first of these conclusions is easily explained in terms of the dispersion of solutes in aqueous solution. In one mole of potassium chloride there are the same number of potassium and chloride ions, 6.064×10^{23} of each. This is also the number of molecules in one mole of a molecular substance. Since the salt dissolves to yield ions, it is evident that the number of particles is double the number of molecules in one mole. According to the ionic concentrations, however, the freezing point effect should be double the regular effect. Two explanations of the difference between the observed depression of the freezing point and an integral multiple may be suggested. One may assume that a portion of the solute is in a molecular state in solution, and stands in equilibrium with its ions. This explanation is valid for solutions of molecular substances which are not highly ionized; but is not valid for the salts and other solutes which yield high concentrations of ions. A second assumption is that the ions suffer interferences on account of their electrical charges. This is a reasonable hypothesis. The attraction resulting from the charges borne by the ions decreases to some extent the freedom of the ions without forming molecules in the solution. The essential difference in the two assumptions is that in the former, two ions are actually in combination through electron bonding to form molecules, and a large per cent of the solute is in the molecular state; while in the latter, the solute is entirely in the ionic state, but each ion is affected to some extent by all of the ions which are near it.

Chemical Reactions of Salt Solutions. There are groups of salts having properties in common. Thus, the soluble metal

chlorides show in common the property of reacting with a solution of silver nitrate to form a precipitate of silver chloride. Certain other chlorine compounds, such as carbon tetrachloride, chloroform, and potassium chlorate, do not show this property. The common property of solutions of the metal chlorides indicates that they contain a common constituent, the chloride ion. It is not likely that this common reaction is due to the molecules of the salts, particularly since the evidence is all against the existence of molecules of such salts in solution. But, even if it be granted that the molecules might exist in solution, it would still be necessary to maintain that the molecules of different substances are different particles. It is not logical to attribute an identical reaction to a number of different particles. The simpler explanation is that the salts are present in solution in the form of the free ions; and this explanation is in accord with the other observations already noted.

If dilute solutions of potassium chloride and sodium nitrate are mixed, there is no evidence of an energy change to indicate a chemical reaction. Nevertheless, not only sodium nitrate and potassium chloride, but also sodium chloride and potassium nitrate, may be obtained in the crystalline state from this solution. The heats of formation of sodium chloride and potassium nitrate are different from those of sodium nitrate and potassium chloride. Hence, an energy change would necessarily accompany any chemical change which occurred during the mixing of the solutions. If, however, the solutions contain only the ions of the solutes, both before and after they are mixed, because by nature all of the substances are soluble and ionized, no energy change would be expected to occur.

The Electric Charges of Ions. The particles which are present in the solutions of salts, basic hydroxides, and acids bear electric charges. Solutions of these substances conduct the electric current and are known as *electrolytes*. Substances which do not dissociate to yield conducting solutions are known as *non-electrolytes*. A more restricted definition classifies as true electrolytes only the substances which are composed of ions and exhibit electrovalence in the anhydrous state. The molecular substances which interact with water to form ions are not true electrolytes, but the aqueous solutions are electrolytic solutions.

Substances which are composed of molecular particles with covalent bonding of the constituent atoms are non-electrolytes.

In a solution of an electrolyte, the total charge of all of the positive ions is equal to the total charge of all of the negative ions, and the solution is electrically neutral. Sodium chloride solution, for example, contains positive sodium ions having unit charge and negative chloride ions which also have unit charge. A solution of common salt contains the same number of sodium and chloride ions. The origin of the charge of an ion may be traced to the electronic change which occurs when elementary particles undergo chemical change. In the direct union of sodium with chlorine, one electron is transferred from each sodium atom to a chlorine atom. The sodium ion, therefore, contains one electron less than the atom, while the chloride ion contains one electron more than the atom. The differences between atoms and ions of these elements are shown diagrammatically in Figs. 88 and 89.

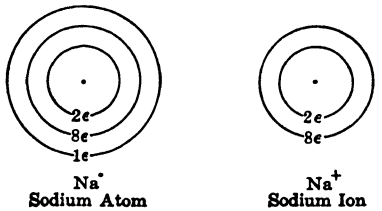


FIG. 88

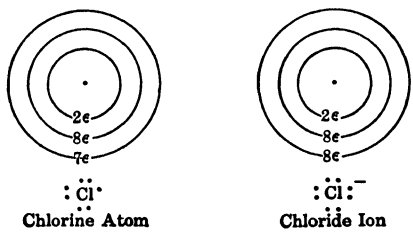


FIG. 89

Compound ions are composed of groups of atoms bound together by the sharing of electrons. The entire group behaves chemically as a unit particle which contains a different number of electrons than the individual atoms contain in the free state. Ions containing a smaller number of electrons than the uncombined atoms composing them have positive electrovalences; and ions containing a larger number of electrons have negative electrovalences. Thus, the sulfate ion contains one atom of sulfur and four atoms of oxygen. Each of these five atoms has six valence electrons when it is in the elementary state. The sulfate ion contains two additional electrons, giving it a total of thirty-two instead of thirty electrons in the valence shells of the atoms. This ion is repre-

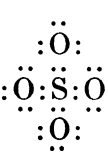


FIG. 90. — Diagram of Sulfate Ion, SO_4^{--}.

sented by the electronic formula in Fig. 90. The sulfate ion has a negative electrovalence of 2; and the group of atoms is held together as a group only when the ion contains these two additional electrons.

Electrolysis. The passage of a direct current of electricity through a solution of an electrolyte is accompanied by the transport of ions toward the electrodes bearing the opposite charges. Positive ions travel to the negative electrode, the cathode, so that they are called *cations*. Negative ions are at-

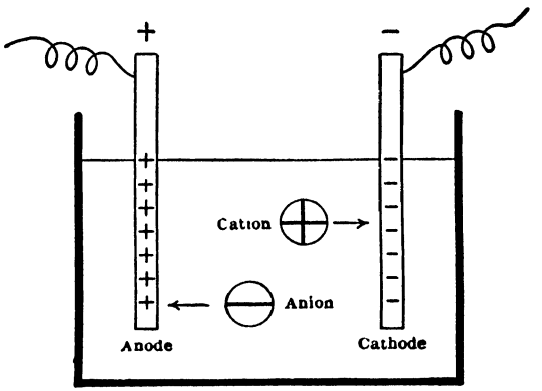


FIG. 91

tracted to the positive electrode, the anode, and are called *anions*, Fig. 91. The electrodes are strips of solid electrical conductors, such as metals or graphite, which are electrically connected to the source of the current. If inactive electrodes are used, positive ions gain electrons at the cathode and are converted into electrically neutral particles. Simultaneously, an equivalent number of negative ions lose electrons to the anode and become neutral particles. The gain of electrons is defined as *reduction* and the loss of electrons as *oxidation*. During the passage of electricity through a solution of an electrolyte, electronic reactions take place at the electrodes, reduction at the cathode and oxidation at the anode. The entire process, the migration of ions and the reactions at the electrodes, is known as *electrolysis*.

Products of Electrolysis. The nature of the products obtained at the electrodes depends on the properties of the ions in the solution. The electrodes are in different parts of the cell and the products

at each electrode are deposited separately. Consequently, it is possible to investigate each electrode reaction as a distinctly separate part of the entire process of electrolysis. The charge of an ion, whether positive or negative, may be determined by observing the electrode toward which it migrates during electrolysis. Metal ions and hydronium ions travel toward the cathode, showing that they are positively charged ions. Simple non-metal ions, hydroxide ions, and oxyions of non-metals are the common negatively charged ions.

Aqueous solutions of electrolytes contain not only the ions of the solute, but also low concentrations of hydronium and hydroxide ions from water, which is itself slightly ionized. *At the cathode*, cations of metals which do not actively displace hydrogen from water are discharged when a direct current of electricity is passed through solutions containing various metal ions. If the cations of the salts are ions of metals which displace hydrogen vigorously from water, hydrogen is discharged instead of the metal. *At the anode*, simple anions of salts are discharged unless hydroxide ions of water may be set free more readily. Compound anions, such as sulfate and nitrate ions, are not discharged directly at the anode; but hydroxide ions are oxidized, with the formation of oxygen and water. The products formed by the direct discharge of ions from solution are known as *primary products*. The description of the electrolysis of three salt solutions, cupric chloride, sodium chloride, and potassium sulfate, will serve to illustrate the principles involved.

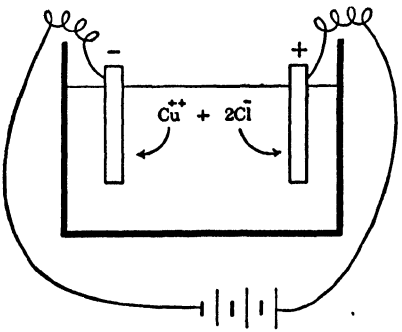


FIG. 92

The electrolysis of a solution of cupric chloride illustrates the *discharge of the ions of the solute* at both the cathode and the anode. The salt becomes dispersed into ions when it dissolves in water. During the passage of the current through the solution, cupric ions migrate to the cathode, and chloride ions to the anode, Fig. 92. Each cupric ion gains two electrons from the cathode and is reduced to a copper atom which is deposited on the cathode. This reaction may be

shown by an ion-electron equation as one half of the reaction in the cell.

$$Cu^{++} + 2\epsilon \longrightarrow Cu.$$

An equivalent number of chloride ions lose electrons at the anode and are oxidized to free chlorine. This reaction, the other half of the chemical change in the cell, is also represented by an ion-electron equation.

$$2\,Cl^- - 2\epsilon \longrightarrow Cl_2.$$

Although the solution contains both hydronium and hydroxide ions, these ions are not discharged to a significant extent during the electrolysis of this salt solution, because cupric and chloride ions are set free more readily. If a solution contains several other varieties of ions, it is possible to regulate the voltage so that at first only the ions of the least active metal are deposited at the cathode and of the least active non-metallic constituent at the anode.

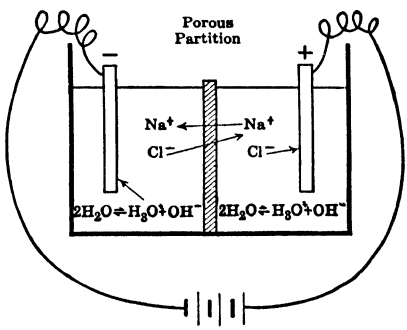


FIG. 93

Cations of metals of high activity are more stable than hydronium ions. Consequently, hydrogen is obtained at the cathode during the electrolysis of solutions of the ions of active metals. Metals of high activity may be obtained by the electrolysis of fused compounds, as described in Chapter VII for the production of metallic sodium. The passage of a direct current of electricity through an aqueous solution of sodium chloride is accompanied by the migration of both sodium and hydronium ions to the cathode and of both chloride and hydroxide ions to the anode, Fig. 93. On account of differences in the stability of the ions, hydronium ions are discharged at the cathode with the production of gaseous hydrogen; and sodium ions remain in solution.

$$2\,H_3O^+ + 2\epsilon \longrightarrow H_2 + 2\,H_2O.$$

Chloride ions are discharged at the anode, as in the electrolysis of cupric chloride.

$$2\,Cl^- - 2\epsilon \longrightarrow Cl_2.$$

Hydroxide ions accumulate in the solution about the cathode because of the discharge of hydronium ions. Chlorine reacts with solutions containing an excess of hydroxide ions, so that a special type of cell is used to prevent the mixing of these materials. The cell is divided into two compartments by a porous partition through which ions may pass in response to the attraction of the electrodes; but the mechanical mixing caused by diffusion is largely prevented.

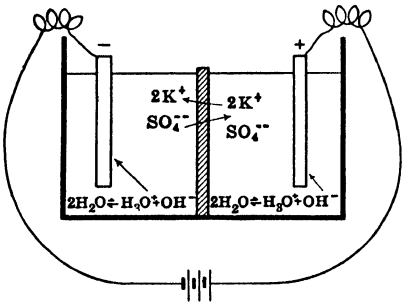


FIG. 94

Solutions containing *compound anions* or the *anions of highly active non-metals*, such as the fluoride ion, yield oxygen at the anode during electrolysis. The evolution of oxygen results from the discharge of hydroxide ions. Water is the other product. When a solution of potassium sulfate is electrolyzed, hydrogen is produced at the cathode and oxygen at the anode, Fig. 94. The migration of ions takes place as in the examples already discussed. Hydronium ions are discharged at the cathode.

$$2\,H_3O^+ + 2\,\epsilon \longrightarrow H_2 + 2\,H_2O.$$

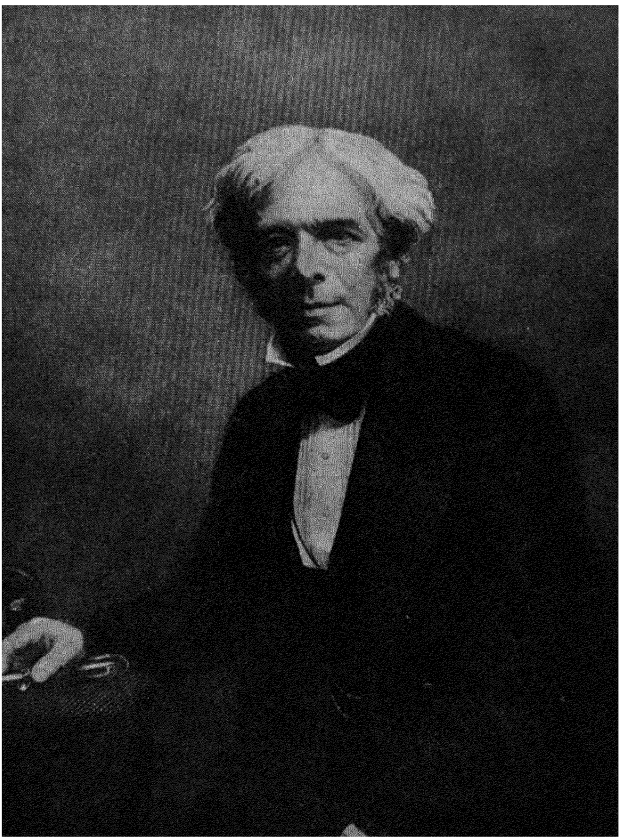
Hydroxide ions are oxidized at the anode with the production of oxygen and water.

$$4\,OH^- - 4\,\epsilon \longrightarrow O_2 + 2\,H_2O.$$

The electrolysis of solutions such as this leads to the decomposition of the solvent.

In a number of instances, the products which are obtained as the result of the electrolysis of solutions are not the primary products. Such products may result from secondary reactions into which the primary products enter, or from electrode reactions in which the ions are not discharged. Examples of some of these changes will be discussed in other sections.

Faraday's Laws. The relation between the quantity of electricity passing through a solution and the weights of the products formed at the electrodes was determined by Faraday in 1833. This relation may be stated in two generalizations known as **Faraday's Laws: The quantities of substances set free**



MICHAEL FARADAY (1791–1867).

Michael Faraday was the son of a blacksmith. He became an errand boy for a bookbinder at the age of thirteen, and a bookbinder's apprentice a year later. In 1813, Sir Humphry Davy appointed him laboratory assistant at the Royal Institution. He was appointed Director of the Laboratory when Davy retired in 1825 and Professor of Chemistry in 1827. An active research worker, his investigations covered many fields. He liquefied chlorine and other gases, then believed to be permanent gases, discovered benzene, and made many other major contributions to chemistry. He is best known, however, for his studies of magnetism, electricity, electro-magnetic induction, the magnetic rotation of the plane of polarized light, and electrochemical equivalents.

at the electrodes are directly proportional to the quantity of electricity passing through the solution. The same quantity of electricity liberates weights of different substances which are proportional to their equivalent weights. Measurement of these quantities may be used for the determination of the equivalent weights of different products of electrolysis and of the electric charges of the ions in solution. If an electric current is passed through separate solutions of cupric sulfate, silver nitrate, and hydrochloric acid connected in series, Fig. 95,

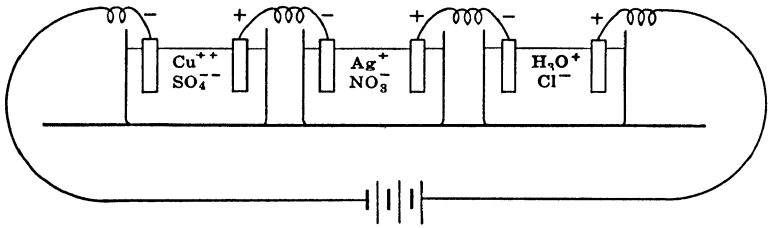


FIG. 95

the same quantity of electricity passes through each solution. It is found that 96,500 coulombs of electricity set free 1.008 g. of hydrogen, 107.88 g. of silver, and 31.78 g. of copper at the respective cathodes. *One coulomb* is the quantity of electricity transferred in one second by a current flowing at the rate of one ampere. It is observed that the weights of hydrogen and of silver are equal to the gram atoms of these elements, but that the weight of copper is only one half of one gram atom. From these weights it is evident that the charge of the cupric ion is double that of the hydronium ion and that the charges of the silver and hydronium ions are the same. Each hydronium ion requires one electron to discharge it from solution. In the gram equivalent weight of hydrogen, which is the same as its gram atom, there are 6.064×10^{23} atoms. Hence, the gram ion of hydronium ions contains 6.064×10^{23} ions. Therefore, 96,500 coulombs is a sufficient quantity of electricity to furnish one electron to each ion in one gram ion of a substance. Since 96,500 coulombs of electricity deposit one gram equivalent of silver, it follows that the gram equivalent of this substance contains 6.064×10^{23} atoms. This is also the number of atoms in one gram atom, so that it is evident that the charge of the silver ion is one. Only one half of an atomic weight of

copper is deposited by the same quantity of electricity. Hence, it is necessary to conclude that each cupric ion requires two electrons to convert it to a neutral atom and that the charge of this ion is two. Chlorine is produced at the anode in one of these cells and oxygen in the other two. It is found that 96,500 coulombs of electricity liberate one gram atom of chlorine, but only one half of one gram atom of oxygen. The quantity of electricity required to set free one gram equivalent of a substance, 96,500 coulombs, is known as one *faraday*.

The weights of substances deposited by a current of known amperage in a specified time may be calculated by the application of Faraday's laws. If a current flowing at the rate of one and one-half amperes is passed through a solution of cupric sulfate for two hours and it is assumed that the only reaction at the cathode is the discharge of cupric ions, the weight of copper deposited may be calculated in the following manner:

$$\begin{aligned}
\text{The quantity of electricity} &= 2 \times 60 \times 60 \times 1.5 \\
&= 10{,}800 \text{ coulombs.} \\
\text{The gram equivalent of copper} &= 63.57/2 = 31.78 \text{ g.} \\
96{,}500 \text{ coulombs deposit} &\quad 31.78 \text{ g. of copper.} \\
10{,}800 \text{ coulombs deposit} &\quad \frac{31.78 \times 10{,}800}{96{,}500} \\
&= 3.556 \text{ g. of copper.}
\end{aligned}$$

The weight of bismuth deposited from a solution of bismuth sulfate by a current which sets free 5.394 g. of silver is calculated on the basis of the equivalent weight fractions.

$$\begin{aligned}
\text{The gram equivalent of silver} &= 107.88 \text{ g.} \\
\text{The gram equivalent of bismuth} &= 209/3 = 69.67 \text{ g.} \\
5.394 \text{ g. of silver} &= \frac{5.294}{107.88} \\
&= 0.05 \text{ gram equivalents} \\
\text{The weight of bismuth} &= 69.67 \times 0.05 = 3.4825 \text{ g.}
\end{aligned}$$

The Arrhenius Theory of Ionization. In the attempt to devise a consistent theory to account for the properties of solutions of electrolytes, Arrhenius published a ***Theory of Ionization*** in 1887. There are three essential points in this theory.

Molecules of acids, bases, and salts in aqueous solution dissociate into ions which bear electric charges.
In dilute solution, ionization is practically complete.
In more concentrated solutions, ionization is incomplete and a condition of equilibrium is established between the molecules of the solute and the ions which it forms.

A great deal of experimental data dealing with electrolytic solutions was available to Arrhenius. In 1833, Faraday determined the relationships between the quantities of electricity passed through solutions and the weights of the products appearing at the electrodes. In 1853, Hittorf measured the relative speeds of migration of charged particles through a solution during electrolysis; but he did not emphasize the existence of free charged particles in solution. In 1857, Clausius concluded that dissociation in solution is not caused by the passage of the current, but that a small proportion of the molecules of an electrolyte breaks up into ions when it is dissolved. In 1885, Raoult published the results of his measurements on the freezing point depression. It thus appears that a number of preliminary suggestions had been made and that the theory was based on a large background of data which Arrhenius succeeded in relating to each other and interpreting by a consistent, logical theory.

The Arrhenius theory accounts for the reactions of solutions of electrolytes as being due to the properties of the ions which they contain. Each solution contains two varieties of ions so that the properties of solutions of electrolytes are additive. Since all of these substances were believed to be composed of molecules, and since the vapor pressure effects were found to be somewhat less than an integral multiple of those of non-electrolytes in the same molal concentration, it was assumed that equilibrium is established between molecules and ions. This idea of incomplete ionization is supported by the observation that solutions of electrolytes do not show as great a conductivity of electricity as they should if completely ionized. The theory at once attracted a great deal of attention and has been productive of a large amount of experimental and theoretical research, so that it occupies an important place in the science of chemistry.

In the attempt to check experimentally the conclusions based on the ionization theory, it has been necessary to modify some

SVANTE ARRHENIUS (1859–1927).

Arrhenius, a Swedish chemist, was educated at Upsala and was highly trained in mathematics and physics. In 1887 he advanced the theory of ionization, which has become one of the most useful theories in the development of modern chemistry. Many of the important applications of this theory have been further extended by the work of Ostwald, who early became an adherent of the Arrhenius theory. In 1895 Arrhenius was appointed professor in Stockholm, and afterwards Director of the Nobel Institute for Physical Chemistry.

of its assumptions and to recognize its limitations. With certain modifications, the theory has been found adequate to account for the properties of solutions in which equilibrium actually exists between molecular and ionic material, with only a small per cent of the solute in the ionized condition. It was soon recognized that this theory does not account satisfactorily for the behavior of salts, and of other solutes which exist largely in the ionic state in solution. Many attempts were made to reconcile the Arrhenius theory with the behavior of these substances by introducing modifications before an acceptable theory dealing with the salts was developed.

The Interionic Attraction Theory. Substances which are completely, or almost completely, ionized in dilute solution are called *strong electrolytes.* These substances fall into two groups: *viz.*, crystalline substances composed of electrically charged ions, and molecular substances which become practically completely decomposed into ions in aqueous solution. Although strong electrolytes are now considered to be completely ionized in dilute solution, they show increasingly wide differences from the behavior which completely ionized substances should exhibit as the concentration of the solute increases. Consequently, the apparent ionization or effective ionization is somewhat less than equivalent to complete ionization. This behavior of strong electrolytes is now explained in terms of the *interionic attraction theory.* The quantitative aspects of the theory are beyond the scope of this text; but a mechanical picture of its results may be given. The forces of attraction of the oppositely charged ions in dilute solutions are not strong enough to cause the formation of crystals of soluble substances; but they are great enough to cause some interferences in their behavior as free particles. The attraction of the oppositely charged particles for each other varies directly as the magnitude of the charges, and inversely as the square of the distances between the ions. Since the average distance between the ions is less in concentrated than in dilute solutions, the effects of ionic attraction are greater, and the activities of the ions less, in concentrated than in dilute solutions.

The attraction of the oppositely charged ions for each other results in an effective ion concentration which is less than the actual concentration of the ions. Hence, the vapor pressure lower-

ing is less than that calculated on the assumption that all of the ions are unaffected by such forces. The rate of migration of the ions through the solution is decreased, because they must move through an ionic atmosphere. In addition, many of the ions must draw water molecules along with them as they move. Since the conductivity of an electrolytic solution involves ion migration, it is decreased by the forces of interionic attraction. The chemical activity is also decreased. The properties of a solution of an electrolyte depend on the individual ions in solution. Therefore, interionic attraction decreases the activity of the solute. On the basis of these interionic effects, Debye and Hückel succeeded in calculating the activity coefficients of dilute solutions of strong electrolytes.

The Apparent Degree of Ionization. In the preceding paragraph, it has been observed that substances which are completely dispersed into ions in solution are strong electrolytes. Substances which are largely in the molecular state in equilibrium with low concentrations of ions are *weak electrolytes.* In all solutions of electrolytes in ordinary concentrations, such as those used in laboratory and industrial work, the effective ionic concentration corresponds to the incomplete dissociation of the solute. The term "apparent degree of ionization" is used to indicate the per cent of the solute which would give the ionic properties observed, if it were in the ionic state unaffected by other ions, and if all of the remainder of the solute were in a non-ionic state. It is not intended to convey the impression that this state necessarily exists in all solutions; but this assumption is useful in making comparisons of the different ionic properties of solutes of both the strong and weak types.

The apparent degree of ionization depends on the nature of the solute. Salts composed of ions having the same electrovalences have approximately the same apparent degree of ionization in aqueous solutions of the same concentration; but the higher the electrovalence of the ions, the lower is the apparent degree of ionization. There are also a few salts which behave as weak electrolytes. Among these are lead acetate, the halides of cadmium and divalent mercury, and mercuric cyanide. Similar relationships are observed among the soluble hydroxides of metals. The degree of ionization of the acids varies from those which are com-

pletely ionized in dilute solution to those which are only slightly ionized. The apparent degree of ionization of some of the common solutes in aqueous solution is shown in Table 18. In this table, the 1–1 salts are those in which both the anion and the cation have electrovalences of one; *e.g.*, potassium chloride, KCl; and the 1–2 salts are those in which the cation has a valence of 1 + and the anion a valence of 2 −, *e.g.*, sodium sulfate, Na_2SO_4.

TABLE 18

APPARENT DEGREE OF IONIZATION IN 0.1 M. SOLUTION, 25°

Solute	*Ions*		*Approximate Per Cent*
1–1 Salts	M^+	A^-	85
1–2 Salts	$2\,M^+$	A^{--}	73
2–1 Salts	M^{++}	$2\,A^-$	73
1–3 Salts	$3\,M^+$	A^{---}	65
3–1 Salts	M^{+++}	$3\,A^-$	65
2–2 Salts	M^{++}	A^{--}	40
Sodium hydroxide	Na^+	OH^-	90
Potassium hydroxide	K^+	OH^-	90
Barium hydroxide	Ba^{++}	$2\,OH^-$	80
Ammonia water	NH_4^+	OH^-	1.3
Hydrochloric acid	H_3O^+	Cl^-	90
Nitric acid	H_3O^+	NO_3^-	90
Sulfuric acid	H_3O^+	HSO_4^-	90
Oxalic acid	H_3O^+	$HC_2O_4^-$	50
Sulfurous acid	H_3O^+	HSO_3^-	33
Phosphoric acid	H_3O^+	$H_2PO_4^-$	27
Hydrofluoric acid	H_3O^+	F^-	8.5
Nitrous acid	H_3O^+	NO_2^-	6.5
Acetic acid	H_3O^+	$C_2H_3O_2^-$	1.33
Carbonic acid	H_3O^+	HCO_3^-	0.17
Hydrogen sulfide	H_3O^+	HS^-	0.07
Hydrocyanic acid	H_3O^+	CN^-	0.01
Boric acid	H_3O^+	$H_2BO_3^-$	0.01

The apparent degree of ionization of a solute is affected by the nature of the solvent. The formation of ions in solution is the result of the action of the solute and solvent on each other. Water, ethyl alcohol, methyl alcohol, and ammonia are the most important of the ionizing solvents. Many liquids exhibit low ionizing power. These are composed of nonpolar molecules or of molecules in which the polarity is slight, while the best ionizing solvents are composed of molecules which are strongly polar. The forces exerted between two free charged particles depend not only on

their charges and the distance between them, but also on the nature of the medium which separates them. The *dielectric constant* is a measure of this specific property of the solvent, and it is related to the polar nature of the molecules. The dielectric constant is so defined that the force between two charged particles varies inversely as the dielectric constant. In Table 19 the dielectric constants of a few liquids at 18° are given.

TABLE 19

DIELECTRIC CONSTANTS OF A FEW SOLVENTS AT 18°

Water	80	Acetic Acid	9.7
Methyl Alcohol	33	Chloroform	5.0
Ethyl Alcohol	26	Diethyl Ether	4.0
Ammonia	22	Benzene	2.3

According to the Nernst-Thomson rule, the ionizing power of a solvent is greater, the greater the dielectric constant, because the forces of attraction of solute ions for each other are progressively decreased as the dielectric constant increases. In solvents of low ionizing power, the interaction of the solvent with a molecular solute is much less extensive than in solvents of high ionizing power. Bjerrum pointed out that ionic solids, when dissolved in solvents of low dielectric constants, form associated *ion-pairs* which behave as unit particles having no electrical charges. Hydrochloric acid in solution in a solvent of dielectric constant 10 is a weak acid, little stronger than acetic acid in aqueous solution.

The apparent degree of ionization increases with increasing dilution. In solutions of strong electrolytes, the forces of interionic attraction are decreased as the particles are farther apart. Equilibrium in solutions of weak electrolytes is determined by the rates of dissociation and recombination; and at the lower concentrations a larger per cent of the solute may exist in the ionic state. The effect of dilution on the apparent degree of ionization of a few solutes is shown in Table 20.

The apparent degree of ionization of an electrolyte is affected also by the presence of other ions in solution. This effect is small in dilute solutions of strong electrolytes, except in the saturated solutions of slightly soluble salts. In solutions of weak electrolytes, however, the addition of another electrolyte which furnishes an

TABLE 20

EFFECT OF DILUTION ON THE APPARENT DEGREE OF IONIZATION

Concentration	*1 N.*	*0.1 N.*	*0 01 N.*	*0.001 N.*
Hydrochloric acid	78%	90%	97%	100%
Potassium hydroxide . . .	77%	90%	95%	98%
Potassium chloride	76%	85%	94%	98%
Copper sulfate	22%	40%	62%	85%
Acetic acid	0.42%	1.33%	4.1%	12.5%

ion in common has a great effect upon the ionization of the weak electrolyte. Acetic acid in solution produces a pink color with the indicator, methyl orange. The addition of sodium acetate to a solution of acetic acid containing methyl orange causes the pink color to disappear, and the solution to assume a yellow color. In the presence of sodium acetate, a strong electrolyte, the concentration of acetate ions is greatly increased, causing a new state of equilibrium in which the concentration of hydrogen ions is greatly decreased. The extent of ionization of a weak electrolyte is decreased by the addition of ions which are common to this solute.

Weak Electrolytes. Ionization Constants. In solutions of weak electrolytes, only a small part of the solute is in the ionized condition, and the solutions are poor conductors of the electric current. Equilibrium exists between the undissociated molecules and the ions which they yield. The relation of the equilibrium concentrations may be stated mathematically.

The dissociation of acetic acid in aqueous solution may be represented by the equation,

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-.$$

The velocity of the dissociation reaction, V_1, is

$$V_1 = [HC_2H_3O_2] \times [H_2O] \times k_1.$$

The bracketed formulas represent the molar concentrations. The velocity of the reverse reaction, V_2, is

$$V_2 = [H_3O^+] \times [C_2H_3O_2^-] \times k_2.$$

At equilibrium, $V_2 = V_1$

$$[H_3O^+] \times [C_2H_3O_2^-] \times k_2 = [HC_2H_3O_2] \times [H_2O] \times k_1.$$

This may be expressed,

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2] \times [H_2O]} = \frac{k_1}{k_2}.$$

The molar concentration of water in a solution, the number of moles in one liter, is so nearly the same as in pure water and in solutions of other concentrations, that it may be considered to be a constant without significant error, unless the solutions are very highly concentrated.

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{k_1}{k_2} \times H_2O = \frac{k_1}{k_2} \times \text{a constant.}$$

Hence,

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_{\text{ionization.}}$$

The ionization constant of a substance is equal to the ratio of the product of the molar concentrations of its ions to the molar concentration of the molecular solute in solution. Each ion concentration is raised to a power numerically equal to the number of ions of that variety formed from one molecule of the solute. The numerical value of this constant is characteristic of the substance and is independent of changes in concentration. It is altered by changes in temperature. The value of the constant is affected to some extent by changes in the concentration of other ions not actually involved in the equilibrium, although these changes are usually small unless the concentration of the foreign ions is great.

Acetic acid is ionized to the extent of 0.42% in 1 M. solution at 18°. The molar concentration of each ion variety is 0.0042 molar and the concentration of the undissociated material is 0.9958 molar. Substituting these numbers in the formula, the numerical value of the ratio is found to be

$$\frac{0.0042 \times 0.0042}{0.9958} = K = 0.0000177 = 1.77 \times 10^{-5}.$$

The extent of the ionization in 0.1 M. solution is 1.33%. The concentration of each ion variety is 0.00133 M. and of the molecular material 0.09867 M.

$$\frac{0.00133 \times 0.00133}{0.09867} = K = 0.0000178 = 1.78 \times 10^{-5}.$$

The values of the ionization constants of several weak electrolytes are shown in Appendix XI.

The concentration of an ion in a solution of given molarity may be calculated if the value of the ionization constant is known. Suppose that the concentration of the hydronium ion furnished by the primary ionization of boric acid in 0.15 M. solution at 25° is to be calculated.

$$H_3BO_3 + H_2O \rightleftharpoons H_3O^+ + H_2BO_3^-.$$

From the tabulated data it is found that the constant for the primary ionization of boric acid at 25° is 5.8×10^{-10}.

$$\frac{[H_3O^+] \times [H_2BO_3^-]}{[H_3BO_3]} = K = 5.8 \times 10^{-10}.$$

Let C represent the concentration of the hydronium ion.

$$[H_3O^+] = [H_2BO_3^-] = C.$$

$$[H_3BO_3] = 0.15 - C.$$

$$\frac{C \times C}{0.15 - C} = 5.8 \times 10^{-10}.$$

$$C^2 = 5.8 \times 10^{-10} \times (0.15 - C).$$

The ionization constant of this acid is so small as to indicate that the difference between $(0.15 - C)$ and 0.15 is negligible.

$$C^2 = 5.8 \times 10^{-10} \times 0.15 = 8.7 \times 10^{-11}.$$

$$C = \sqrt{87 \times 10^{-12}} = 9.3 \times 10^{-6}.$$

If the concentration of the undissociated material does differ significantly from the entire concentration of the solute, the calculation must take into account the concentration of the undissociated solute.

The Common Ion Effect. It has been noted in a preceding paragraph that the ionization of a weak electrolyte is decreased by the addition of another solute which furnishes an ion in common. Suppose that sodium acetate is added to a one-molar solution of acetic acid in sufficient quantity to maintain the concentration of the acetate ion at one molar. It is apparent that the concentration of the hydronium ion cannot remain equal to 0.0042 molar, because

$$\frac{0.0042 \times 1}{0.9958} > 1.8 \times 10^{-5}.$$

Therefore, hydronium and acetate ions combine to form acetic acid molecules, giving decreased ion concentrations and increased concentration of the molecular acid at a new equilibrium. The additional small increase in the concentration of the molecular acid is almost insignificant compared to 0.9958. Hence, it follows that the hydronium ion concentration is decreased to almost the same extent that the acetate ion concentration is increased. Under the conditions mentioned the concentration of the hydronium ion is decreased from 4×10^{-3} to 1.8×10^{-5}.

The common ion effect is an important means of regulating ion concentrations at some particular value. For this purpose, a weak electrolyte is employed as the source of the ions, in the presence of a strong electrolyte which furnishes an ion in common. The high concentration of the molecular weak electrolyte serves as a source of supply for its ions, preventing any significant decrease in the ion concentration, even though chemical reactions consume some of these ions. The excess of one of the ions of the weak electrolyte counteracts any tendency toward an increase in the concentration of the other variety of ion furnished by the weak electrolyte. This effect is important in many analytical separations, because such separations are frequently based on moderately small differences in solubility.

Acetic acid solutions in the presence of an acetate are often employed for a regulated concentration of the hydronium ion. The acetates of the metals are, for the most part, sufficiently soluble so that no difficulties are introduced by maintaining relatively large concentrations of the acetate ion. A number of ion separations are based on the use of a regulated concentration of the sulfide ion. Hydrogen sulfide in aqueous solution is a weak electrolyte yielding hydronium and sulfide ions. Consequently, through the use of varied concentrations of the hydronium ion, the concentration of the sulfide ion may be maintained at different selected values. If a regulated small hydroxide concentration is required, it may be secured through the use of the soluble weak base, ammonia water, in the presence of an ammonium salt, such as ammonium nitrate or ammonium chloride. Some of the analytical applications of the common ion effect will be discussed further in connection with the particular substances involved.

EXERCISES

1. How may you account for the presence of ions in a solution of potassium chloride? in a solution of hydrogen chloride?
2. How do the vapor pressure effects observed in solutions of salts, basic hydroxides, and acids confirm the conclusion that these substances yield ions in solution?
3. How is the fact that the freezing point depression in a solution of a salt, a base, or an acid is less than an integral multiple of the regular molal effect explained?
4. How do the chemical reactions of certain salt solutions indicate the presence of ions in these solutions?
5. How may the sign and magnitude of the charge borne by an ion be determined experimentally?
6. What is the origin of the charge of an ion?
7. What is meant by electrolysis? What is the nature of the changes which occur during electrolysis?
8. What conditions determine the nature of the products formed at each electrode during electrolysis?
9. Describe the electrolysis of solutions of the following substances, representing the electrode reactions by ion-electron equations: (*a*) cadmium iodide; (*b*) silver nitrate; (*c*) barium chloride; (*d*) silver fluoride; (*e*) potassium hydroxide.
10. State the assumptions of the Arrhenius theory of ionization and cite experimental evidence to support each assumption.
11. To which class of electrolytes may this theory be applied successfully? Explain.
12. How does the interionic attraction theory account for the magnitude of the vapor pressure effects in solutions of salts?
13. What is meant by apparent degree of ionization? weak electrolyte? strong electrolyte?
14. What conditions affect the apparent degree of ionization of a solute? What is the effect of each?
15. What is an ionization constant?
16. What is the common ion effect? Show how this effect may be employed to regulate ion concentrations.

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CHAPTER XII

COMPLETED IONIC REACTIONS

The type of reaction to be discussed in this chapter is that in which the ions undergo no change in oxidation number, but two initial substances react with each other to form two different products. These reactions are frequently called *double decomposition reactions* because it may be assumed that such reactions between electrolytes involve the ionization of the initial substances when they go into solution, followed by the combination of the ions when the solutions are mixed, with the formation of the products which are secured. Completed ionic reactions are those in which the initial substances are practically completely consumed during the reaction. Equilibria which are involved in regulating ion concentrations so as to establish the conditions necessary for the reaction are important.

Conditions Leading to the Completion of Ionic Reactions. The general condition which is required for the extensive reaction of ionized substances with each other is that ions be removed from solution. So long as all of the ions introduced into a solution may remain together in the free condition no reaction occurs. The combination of ions disturbs all of the equilibria which formerly existed in the separate solutions. Ions are removed from solution by the formation of slightly soluble solids, of slightly ionized molecules in solution, of slightly soluble gases, and of stable complex ions.

The Precipitation of Solids. When solutions containing equivalent quantities of a soluble lead salt and a soluble chloride are mixed, a precipitate of lead chloride is formed if the concentrations are great enough.

$$Pb^{++} + 2\ NO_3^- + 2\ Na^+ + 2\ Cl^- \longrightarrow PbCl_2\downarrow + 2\ Na^+ + 2\ NO_3^-.$$

Inspection of this equation shows that the sodium and nitrate ions play no part in the reaction. Hence, the ionic equation may be written,

$$Pb^{++} + 2\ Cl^- \longrightarrow PbCl_2\downarrow.$$

If the suspension is filtered to remove the precipitated chloride, it is possible to show by tests that the filtrate contains both lead and chloride ions. The addition of dilute nitric acid and a solution of silver nitrate to a portion of the filtrate produces a white precipitate, showing that the solution contains chloride ions. Silver chloride is less soluble than lead chloride.

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow .$$

The addition of potassium chromate to another portion of the filtrate from the lead chloride produces a yellow precipitate of lead chromate, which is less soluble than the chloride, thus showing the presence of lead ions.

$$Pb^{++} + CrO_4^{--} \longrightarrow PbCrO_4\downarrow .$$

Both lead and chloride ions remain in solution in equilibrium with the precipitated lead chloride, so that the equation for the precipitation reaction is written

$$Pb^{++} + 2\,Cl^- \rightleftharpoons PbCl_2\downarrow .$$

By the use of arrows of unequal length, the fact that most of the material is in the precipitate at equilibrium is represented. If solid lead chloride is stirred into water and the excess is removed by filtration, it may be shown that both lead and chloride ions are present together in this solution also. Measurement of the concentrations of the ions shows that the same conditions of equilibrium are attained whether it be reached by the solution of the solid or by the interaction of its ions.

When silver chloride is formed by the reaction of silver nitrate and hydrochloric acid in solutions of equivalent concentrations, the reaction goes virtually to completion on account of the removal of silver and chloride ions by the formation of the slightly soluble silver chloride. Nevertheless, the liquid in which the precipitate is suspended is a saturated solution of this salt.

$$Ag^+ + Cl^- \rightleftharpoons AgCl\downarrow .$$

Ionic reactions go virtually to completion if ions are removed from the solution by the formation of a slightly soluble solid.

Solubility Product. In a saturated solution of silver chloride, the solute is completely ionized and there is little interference due

to interionic attraction because this salt is so slightly soluble that the concentrations of the ions are low. The equilibrium in this saturated solution is between the solid and its free ions in solution. Since the surface of the solid is the active portion and this is constant at equilibrium, the application of the law of molecular concentrations to this system gives the equation:

$$\frac{[Ag^+] \times [Cl^-]}{\text{a constant}} = K,$$

or

$$[Ag^+] \times [Cl^-] = K \times \text{a constant.}$$

This product is itself a constant which is usually designated by the letter S, with which the formula of the salt may be written to identify the system to which the constant applies.

$$[Ag^+] \times [Cl^-] = S_{AgCl}.$$

This constant is known as the solubility product, or the ion concentration product. It is numerically equal to the product of the molar concentrations of the ions in the saturated solution of a solid strong electrolyte at a given temperature, each ion concentration being raised to a power which is the same as that shown by the ion ratio. For lead chloride, the equation is,

$$[Pb^{++}] \times [Cl^-]^2 = S_{PbCl_2}$$

It is not necessary that equivalent concentrations of the ions be used, for an excess of one of the reagents may be added. If the concentration of one variety of ion is greater than the equivalent proportion, the other is necessarily less. The numerical value of the solubility product is altered by changes in temperature. For most substances, it increases with rise in temperature. There is, however, no regularity in this effect.

The solubility product is affected by the nature of the solvent. The addition of other solutes, without an ion in common, changes the nature of the solvent from water to a salt solution and increases the solubility of the slightly soluble salt. Consequently, the solubility product increases somewhat as the total concentration of the ions in solution increases. Although the solubility product principle does not hold rigidly except in dilute solutions, it is a useful guide in the treatment of saturated solutions of solutes which are not highly soluble.

Suppose that the solubility of lead chloride at 20° is 0.993 g. of the salt in 100 g. of water. The molal solubility is calculated by dividing the weight in 1000 g. of water by one mole.

$$9.93 \text{ g.} \div 278.12 \text{ g.} = 0.0357 \text{ mole.}$$

$$PbCl_2\downarrow \rightleftharpoons Pb^{++} + 2\,Cl^-.$$

$$[Pb^{++}] = 0.0357 \text{ molar.}$$

$$[Cl^-] = 0.0357 \times 2 = 0.0714 \text{ molar.}$$

$$[Pb^{++}] \times [Cl^-]^2 = S_{PbCl_2}.$$

$$0.0357 \times 0.0714^2 = S_{PbCl_2}\,(20°) = 1.8 \times 10^{-4}.$$

The solubility of a slightly soluble strong electrolyte may be calculated from its solubility product; and the solubility product may be calculated from the solubility, for it may be assumed that these electrolytes are completely dissociated into free ions at such great dilutions. The solubility product of silver chloride is 1×10^{-10}. The molar concentration of the silver ion is equal to the molar concentration of the chloride ion, so that the molar concentration of each ion is equal to the square root of the solubility product.

$$[Ag^+] = [Cl^-] = \sqrt{1 \times 10^{-10}} = 1 \times 10^{-5}.$$

Hence, the molar solubility of silver chloride at room temperature is 1×10^{-5}, because each mole of silver chloride yields one mole of silver ion and one mole of chloride ion. One liter of a saturated solution of silver chloride contains only 0.00001×143.337 g., or 0.0014 g., of the dissolved salt.

The solubility of silver iodide is 1×10^{-8} moles per liter at 18°. Assuming complete ionization, the molar concentration of the silver ion is equal to that of the iodide ion, each being 1×10^{-8} molar.

$$AgI\downarrow \rightleftharpoons Ag^+ + I^-.$$

The solubility product of silver iodide is:

$$[Ag^+] \times [I^-] = 1 \times 10^{-8} \times 1 \times 10^{-8} = 1 \times 10^{-16}.$$

The solubility products of a number of common substances are tabulated in Appendix X.

Conditions for the Formation of Precipitates. The formation of any precipitate results from the mixing of solutions containing its ions in greater concentrations than equilibrium permits. Consequently, the concentrations of the ions brought

together in solution must be so great that their product would exceed the solubility product of the substance if the ions could remain together in the solution. Since this condition cannot exist at equilibrium, a precipitate is formed, thus reducing the concentrations of the ions to the equilibrium values. When solutions of barium chloride and a soluble sulfate are mixed, barium sulfate is precipitated,

$$Ba^{++} + SO_4^{--} \rightleftharpoons BaSO_4 \downarrow .$$

The maximum concentrations of these ions which may exist in solution together is defined by the solubility product of barium sulfate.

$$[Ba^{++}] \times [SO_4^{--}] = S_{BaSO_4}.$$

Therefore, precipitation of barium sulfate takes place when solutions of barium and sulfate ions are mixed, because the product of the molar concentrations of the ions is greater than the solubility product of this substance at the moment the solutions are mixed. *Solid strong electrolytes may be precipitated by mixing solutions which supply their ions in such concentrations that the actual product of the molar concentrations of the ions, raised to the proper powers, is greater than the solubility product of the substance.*

In analytical chemistry, many separations of ions must be made in order to establish conditions for the detection of certain ions and the measurement of the amounts which are present. The equilibria dealing with both saturated and unsaturated solutions are extensively applied in qualitative and in quantitative analysis. The familiar ions are grouped on the basis of their behavior with specific reagents or mixtures of reagents. In this way, small groups of ions may be successively separated from a solution containing many ions. The individual members of a group are then detected by specific tests to which none of the other ions in the group responds.

One of the analytical groups of ions is known as the *silver group of cations*. The three common ions in the group form slightly soluble chlorides. Inspection of the tabulated list of solubility products shows that the solubility products of silver, lead, and mercurous chlorides are small. Consequently, these three chlorides may be precipitated together as a mixture, free from the chlorides of the other common metal ions which might be present,

by the addition of dilute hydrochloric acid to a solution containing the metal ions.

$$Pb^{++} + 2\,Cl^- \rightleftharpoons PbCl_2\downarrow.$$
$$Ag^+ + Cl^- \rightleftharpoons AgCl\downarrow.$$
$$Hg_2^{++} + 2\,Cl^- \rightleftharpoons Hg_2Cl_2\downarrow.$$

No special regulation of the concentration of the chloride ion is necessary to effect the separation of this group of chlorides, because the chlorides of the other metal ions likely to be present are much more soluble.

There are, however, many instances in which the regulation of the ion concentrations is necessary to bring about the desired separation. Aluminum and magnesium ions may be separated by the precipitation of aluminum hydroxide, if the concentration of the hydroxide ion is properly controlled. The solubility products of aluminum hydroxide and magnesium hydroxide are 1.9×10^{-33} and 5×10^{-12}, respectively. The size of these numbers indicates that both of these hydroxides may be precipitated easily. To bring about a separation, however, the hydroxide ion concentration must be so regulated that

$$[Al^{+++}] \times [OH^-]^3 > S_{Al(OH)_3},\ 1.9 \times 10^{-33};$$
but $$[Mg^{++}] \times [OH^-]^2 < S_{Mg(OH)_2},\ 5 \times 10^{-12}.$$

Regulated low concentrations of the hydroxide ion may be secured by the use of solutions of ammonia containing ammonium chloride. Suppose that a solution which is 0.1 M. with respect to ammonia contains ammonium chloride to give an effective ammonium ion concentration which is one molar. Since the degree of the ionization of ammonia is small, slight error is introduced into the calculations if it is assumed that the concentration of molecular ammonia in this system is 0.1 M., and the total ammonium ion concentration 1 M.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-.$$
$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = K = 1.8 \times 10^{-5}$$
or, $$[NH_4^+] \times [OH^-] = 1.8 \times 10^{-5} \times [NH_3].$$

Since the concentration of molecular ammonia is 0.1 M.,

$$[NH_4^+] \times [OH^-] = 1.8 \times 10^{-5} \times 0.1 = 1.8 \times 10^{-6};$$
$$[OH^-] = 1.8 \times 10^{-6} \div [NH_4^+].$$

The concentration of the ammonium ion is 1 M.

$$[OH^-] = 1.8 \times 10^{-6} \div 1 = 1.8 \times 10^{-6}.$$

This concentration of the hydroxide ion is great enough to cause the precipitation of aluminum hydroxide, but not great enough to cause the precipitation of magnesium hydroxide unless the concentration of the magnesium ion is relatively large. Suppose the concentration of the magnesium ion to be 0.1 M. The product of the concentrations of the ions actually present in the solution would be: $0.1 \times (1.8 \times 10^{-6})^2 = 3.2 \times 10^{-13}$.

Since this product is less than the solubility product constant, magnesium hydroxide does not precipitate.

The separation of the barium and strontium ions on the basis of differences in the solubility products of their chromates furnishes a second example of the analytical application of this principle. The solubility products of barium chromate and strontium chromate are 2×10^{-10} and 5×10^{-5}, respectively. The concentration of the chromate ion must be regulated so that

$$[Ba^{++}] \times [CrO_4^{--}] > S_{BaCrO_4},\ 2 \times 10^{-10};$$

but

$$[Sr^{++}] \times [CrO_4^{--}] < S_{SrCrO_4},\ 5 \times 10^{-5}.$$

This condition causes the precipitation of barium chromate but not of strontium chromate. The chromate ion concentration is governed by the hydronium ion concentration,

$$2\ CrO_4^{--} + 2\ H_3O^+ \rightleftharpoons Cr_2O_7^{--} + 3\ H_2O.$$

If the concentration of the hydronium ion is high, the chromate ion concentration is so low that barium chromate will not precipitate. A regulated low concentration of the hydronium ion is obtained through the use of acetic acid solutions containing sodium acetate; and the chromate ion concentration in a solution such as this is correctly adjusted to bring about the separation of barium and strontium ions. Not only is the concentration of the chromate ion great enough to cause the precipitation of barium chromate, but the large concentration of the dichromate ion maintains the chromate ion concentration at the required level by interaction with water.

Many similar separations are based on the application of the solubility product principle and the common ion effect. The

sulfide equilibria are employed in a number of separations. The equilibria involving hydrogen sulfide are discussed in the chapter dealing with that substance.

Conditions for the Solution of Precipitates. A substance continues to dissolve so long as the solution in contact with the solid is unsaturated. *A solid electrolyte may be dissolved by maintaining in solution such conditions that the actual product of the molar concentrations of the ions, raised to the proper powers, is kept lower than the solubility product of that substance.* If the solid is at least moderately soluble, a simple method of dissolving any excess is the addition of the solvent. *The addition of the solvent decreases the molar concentration of each of the ions so that their product is less than the solubility product.* The solid now dissolves more rapidly than it deposits, until the solution again becomes saturated or all of the solid is dissolved. Unless the substance has at least moderate solubility this method is not practical. The solubility product of barium sulfate at 20° is 1×10^{-10}. One liter of saturated solution of barium sulfate at this temperature contains only 0.00001 mole. One hundred thousand liters of water would be required to dissolve one mole of barium sulfate, or four hundred and twenty-eight liters to dissolve one gram.

A second method of dissolving precipitates is based on the increased solubility of the solute at high temperatures. This method is applicable practically to those precipitates which are among the more soluble of the slightly soluble substances, and which are much more soluble at high than at low temperatures. If a suspension of lead chloride in water is heated to 100°, a much greater amount of the solid may be dissolved by the same amount of water. In the suspension at room temperature,

$$[Pb^{++}] \times [Cl^-]^2 = S_{PbCl_2}\ (20°).$$

The solubility product of lead chloride increases greatly with rise in temperature.

$$S_{PbCl_2}\ (20°) < S_{PbCl_2}\ (100°).$$

Therefore, the concentrations of lead and chloride ions which are present in the saturated solution at 20° are far below the equilibrium concentrations at 100°.

$$[Pb^{++}] \times [Cl^-]^2 < S_{PbCl_2}\ (100°).$$

Hence, the suspended chloride dissolves completely at the higher temperature, unless indeed the amount present is greater than that required to produce a saturated solution even at the higher temperature.

The most generally used method of dissolving slightly soluble precipitates involves chemical reactions by which soluble products are formed. This is accomplished by the addition of substances which react with one of the varieties of the ions furnished by the precipitate, even though it be present in only low concentrations. This may be pictured as a competition between the added reagent and the precipitate for the ions furnished by the precipitate. In practice, precipitates are dissolved by the formation of molecular products or complex ions in solution or of insoluble gases.

Limestone dissolves in water containing dissolved carbon dioxide, forming a solution of calcium bicarbonate. The equilibria illustrate the principle involved in dissolving many solids.

$$CaCO_3\downarrow \rightleftharpoons Ca^{++} + CO_3^{--}.$$
$$[Ca^{++}] \times [CO_3^{--}] = S_{CaCO_3},\ 9 \times 10^{-10}.$$

The reaction of carbon dioxide with water yields a low concentration of hydronium ions, which combine with the carbonate ions from calcium carbonate to form bicarbonate ions.

$$CO_2 + 2\,H_2O \rightleftharpoons H_3O^+ + HCO_3^-.$$
$$CO_3^{--} + H_3O^+ \rightleftharpoons H_2O + HCO_3^-.$$

In consequence of these reactions the concentration of the carbonate ions is reduced and the solid dissolves.

$$[Ca^{++}] \times [CO_3^{--}] < S_{CaCO_3}.$$

Whether or not the solid dissolves completely depends on the amount of it which is present and on all of the equilibria in the solution. A number of other slightly soluble salts of weak acids may be dissolved by the addition of solutions which furnish hydronium ions.

The Formation of Weak Electrolytes in Solution. Reactions in which the ions of weak electrolytes combine to form molecular products in solution are the reverse of the reactions involved in the ionization of weak electrolytes. The same state of equilibrium is involved whether molecules of acetic acid dissociate in aqueous solution by interaction with water to form ions, or the

ions react to form the molecular substance. Consequently, the ionization constant of the weak electrolyte describes the equilibria in the reaction of an acid with an acetate and the common ion effect is fully applicable.

$$H_3O^+ + C_2H_3O_2^- \rightleftharpoons H_2O + HC_2H_3O_2.$$

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K.$$

In the reaction of hydrochloric acid with sodium acetate, the chloride and sodium ions remain free in the solution. At low concentrations, they have no significant effect on the ionization constant of acetic acid.

Silver phosphate dissolves in dilute nitric acid solution, on account of the formation of the weakly dissociated dihydrogen phosphate ion.

$$Ag_3PO_4 \downarrow \rightleftharpoons 3\,Ag^+ + PO_4^{---}.$$

$$[Ag^+]^3 \times [PO_4^{---}] = S_{Ag_3PO_4}.$$

$$2\,H_3O^+ + PO_4^{---} \rightleftharpoons H_2PO_4^- + 2\,H_2O.$$

Hence, $$[Ag^+]^3 \times [PO_4^{---}] < S_{Ag_3PO_4}.$$

The reaction of acids with metal hydroxides is a virtually completed reaction which is characteristic of both of these classes of substances. This reaction results in the formation of the slightly ionized product, water, leaving the ions of the salt in solution if the salt is soluble. Hydrochloric acid and sodium hydroxide are strong electrolytes. When solutions containing equivalent amounts of these substances are mixed, the concentrations of the hydronium and hydroxide ions are greater than the water equilibrium permits. Therefore, these ions unite, leaving ionized sodium chloride in the solution.

$$Na^+ + OH^- + H_3O^+ + Cl^- \rightleftharpoons 2\,H_2O + Na^+ + Cl^-.$$

The significant equilibrium in this reaction is,

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O.$$

In a similar manner, salts of weak bases react with strongly basic substances. The reaction of sodium hydroxide with ammonium chloride yields molecular ammonia in equilibrium with the ammonium and hydroxide ions, provided ammonia gas does not escape.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O.$$

The Formation of a Slightly Soluble Gas. If the molecular product formed in solution by the union of the ions is a slightly soluble gas, an added factor affecting the extent of the reaction is involved. If the gas is allowed to escape from the solution, the equilibrium is destroyed by the complete removal of the product. If, however, the slightly soluble gas is retained in contact with the liquid in a closed vessel, its solubility, under the existing conditions of temperature and pressure, determines the concentration of the molecular substance in the solution, and thus, indirectly, the concentration of the ions. *The reaction between dissolved electrolytes commonly proceeds practically to completion if one of the products formed by the union of the ions is a slightly soluble gas.* When hydrochloric acid is added to sodium sulfide solution, the weak acid, hydrogen sulfide is formed. Hydrogen sulfide is only slightly soluble, so that equilibrium is established only if some of the substance is kept in solution in a closed container, in equilibrium both with its ions and with the gas.

$$2\,H_3O^+ + S^{--} \rightleftharpoons 2\,H_2O + H_2S\ (\text{dissolved}) \rightleftharpoons H_2S\ (\text{gas}).$$

The reaction is also completed if the molecular product is unstable and its decomposition products leave the solution. The reaction of hydrochloric acid with a solution of sodium carbonate in an open vessel is a completed reaction. The escape of carbon dioxide leaves so little of the material in solution that the carbonate ions are removed almost completely.

$$CO_3^{--} + 2\,H_3O^+ \longrightarrow 2\,H_2O + H_2CO_3 \longrightarrow H_2O + CO_2\uparrow.$$

When a strong base is added to a solution of an ammonium salt and the solution is then heated in an open vessel, the reaction is completed, because ammonia is slightly soluble at elevated temperatures.

Complex Ions. There are a number of ions, known as complex ions, which are formed by the union of two or more simple ions or by the union of simple ions and molecules. Ions present in aqueous solutions are commonly hydrated and are complex ions. Thus, the hydronium ion, H_3O^+, is a complex ion formed by the combination of the proton with a water molecule. Such ions formed by the addition of molecules of the solvent are a special variety of complex ions, called solvated ions. In experimental

practice, a *complex ion* is one whose formation results in the more or less complete removal of the constituent simple ions from the solution. The stability of a complex ion is measured by the concentrations of its dissociation products required for equilibrium, the smaller the concentrations of the simple products tolerated by the complex ion, the greater the stability of the ion.

The combination of simple ions with other ions and molecules to form complex ions is not in accord with the oxidation numbers of the substances involved. Thus, the cupric ion may add four molecules of water or four molecules of ammonia without change in its electrovalence. In the formation of such products, a secondary valence relationship is involved. Werner called this the *coördination number*, which is equal to the number of atoms or radicals that tend to surround a central atom. In many of the more familiar complex ions, the coördination number is 4; and 6 is also very common. The number is always even and varies from 2 to 12; but a given ion tends to retain a constant coördination number. The cadmium ion, for example, tends to hold in combination four atoms or radicals to form complex ions, such as CdI_4^{--}, $CdCl_4^{--}$, $Cd(CN)_4^{--}$, $Cd(NH_3)_4^{++}$, and $Cd(H_2O)_4^{++}$.

Complex ions are formed by the sharing of electron pairs between the simple ion and the ions or molecules which become added to it. The bond is the coördinate type in which both electrons of the pair are from the same atom or ion. Molecules and ions which readily add in this manner to other substances contain atoms which have pairs of unshared electrons in the outermost shell. Electronic formulas representing several substances which react readily to form complex ions are:

H:Ö: H	H:Ö:	H:N:H H	:S:	:Cl:	:C:::N:
H_2O	OH^-	NH_3	S^{--}	Cl^-	CN^-

In each of the molecules and ions, the oxidation numbers are satisfied; but there are pairs of unshared electrons which may become shared in the formation of complex ions. A number of the cations readily form complex cations by adding neutral molecules, and complex anions by adding simple negative ions. This property is particularly prominent for the metals of the transition series of the periodic system: *i.e.*, the elements whose uncombined atoms

have an incomplete electron shell containing from 9 to 17 electrons beneath the valence shell; but it is by no means limited to these transition elements. Even numbers of electrons, particularly 2 and 8, appear to give stability to the electron structure. Ions possessing some other number in the outer shell may add molecules or other ions to acquire this structure. These added pairs of electrons may enter an incomplete existing shell or may build up a new shell outside of the kernel of the atom. Thus, the copper atom, having an atomic number of 29, loses two electrons to form the cupric ion, Cu^{++}. The remaining 27 electrons are assumed to be distributed in three shells, having 2, 8, and 17 electrons, respectively. If the cupric ion adds four molecules of ammonia, four coördinate bonds are formed and the complex ion, $Cu(NH_3)_4^{++}$, still has the same electrovalence as the simple cupric ion, Cu^{++}. The electron formula for this complex ion is shown in Fig. 96. The electron distribution about the copper nucleus is now 2, 8, 17, 8. The cuprous ion has an electrovalence of 1 +; and the electron distribution, 2, 8, 18. This simple ion may add two cyanide ions to form the complex cuprocyanide ion, $Cu(CN)_2^-$. The electron distribution about the nucleus of the copper atom is 2, 8, 18, 4.

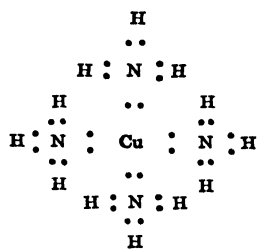

FIG. 96. — Diagram of the Cupric Ammonia Ion.

The formation of complex ions may cause ionic reactions to go practically to completion because, like other slightly dissociated products, they permit only low concentrations of simple ions in equilibrium. Complex ion formation is one of the methods used in analytical chemistry to dissolve certain precipitates or to prevent their formation.

Ammonia Complex Ions. A number of the metal ions yield complex ions with ammonia: *e.g.*, $Ag(NH_3)_2^+$; $Cu(NH_3)_4^{++}$; $Cu(NH_3)_2^+$; $Cd(NH_3)_4^{++}$; $Zn(NH_3)_4^{++}$; $Ni(NH_3)_6^{++}$; $Co(NH_3)_6^{++}$. These ions are fairly stable in the presence of an excess of ammonia, but are decomposed by acids. The formation of the complex ions reduces the concentration of the simple metal ions so greatly that the hydroxides of these metals do not precipitate from solutions containing an excess of ammonia. This principle is applied in the separation of iron, aluminum,

and chromium, which do yield hydroxide precipitates with a solution of ammonia, from a solution which contains the ions of zinc, nickel, and cobalt.

$$Zn^{++} + 4\ NH_3 \rightleftharpoons Zn(NH_3)_4{}^{++}.$$

Since the complex ion is stable,

$$\frac{[Zn^{++}] \times [NH_3]^4}{[Zn(NH_3)_4{}^{++}]} = K.$$

The concentration of the zinc ion is so small that the hydroxide does not precipitate.

$$[Zn^{++}] \times [OH^-]^2 < S_{Zn(OH)_2},\ 4 \times 10^{-17}.$$

Aluminum hydroxide is much less soluble and does precipitate from this solution.

$$[Al^{+++}] \times [OH^-]^3 > S_{Al(OH)_3},\ 1.9 \times 10^{-33}.$$
$$Al^{+++} + 3\ OH^- \rightleftharpoons Al(OH)_3\downarrow.$$

Silver, lead, and mercurous chlorides are so slightly soluble that they are precipitated as the *silver group* by the addition of hydrochloric acid to a solution containing these ions. Lead chloride is much more soluble at high than at low temperatures, so that it may be removed from the group precipitate by prolonged washing with hot water. The separation of silver and mercurous chlorides may be effected by the use of a solution of ammonia. Slightly soluble silver chloride suspended in water produces a saturated solution.

$$AgCl\downarrow \rightleftharpoons Ag^+ + Cl^-.$$
$$[Ag^+] \times [Cl^-] = S_{AgCl} = 1 \times 10^{-10}.$$

Ammonia combines with free silver ions, thus reducing their concentration in the solution and causing the precipitate to dissolve.

$$Ag^+ + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2{}^+.$$
$$[Ag^+] \times [Cl^-] < 1 \times 10^{-10}.$$

Mercurous chloride, however, reacts with ammonia to form the white ammono-chloride, $HgNH_2Cl$, and free mercury. The presence of free mercury in this mixture causes it to appear black. This serves as an identifying test for the presence of the mercurous ion.

$$Hg_2Cl_2 + 2\ NH_3 \longrightarrow HgNH_2Cl\downarrow + Hg + NH_4{}^+ + Cl^-.$$

Since metal-ammonia ions are decomposed by acids, the addition of an excess of nitric acid to a solution containing the silver ammonia complex ions and chloride ions causes the reprecipitation of silver chloride.

$$Ag(NH_3)_2^+ + 2\,H_3O^+ \longrightarrow Ag^+ + 2\,NH_4^+ + 2\,H_2O.$$
$$Ag^+ + Cl^- \rightleftharpoons AgCl\downarrow.$$

Sulfide Complex Ions. Arsenic trisulfide precipitates when hydrogen sulfide is passed into an acidic solution of an arsenious compound.

$$2\,AsCl_3 + 3\,H_2S + 6\,H_2O \rightleftharpoons As_2S_3\downarrow + 6\,H_3O^+ + 6\,Cl^-.$$

The sulfide is slightly soluble so that it is easily precipitated and the concentration of arsenious ions in the suspension is very small.

$$As_2S_3\downarrow \rightleftharpoons 2\,As^{+++} + 3\,S^{--}.$$
$$[As^{+++}]^2 \times [S^{--}]^3 = S_{As_2S_3}.$$

The arsenious ion reacts with a high concentration of sulfide ions to form the complex thioarsenite ion.

$$As^{+++} + 3\,S^{--} \rightleftharpoons AsS_3^{---}.$$

The formation of the complex ion reduces the concentration of the arsenious ions enough to cause the precipitate to dissolve. When an excess of free sulfur is added to the basic sulfide solution, the disulfide is formed, and arsenic trisulfide reacts with the solution of the disulfide to produce the thioarsenate.

$$S^{--} + S \rightleftharpoons S_2^{--}$$
$$As^{+++} + 2\,S^{--} + S_2^{--} \rightleftharpoons AsS_4^{---}.$$

Antimony and stannic sulfides react in a similar manner with the ordinary sodium or ammonium sulfide, but stannous sulfide does not. Stannous sulfide is converted into the complex thiostannate by reaction with ammonium polysulfide,

$$SnS + S_2^{--} \rightleftharpoons SnS_3^{--}.$$

Ammonium polysulfide is an ammonium sulfide solution containing additional amounts of sulfur. The sulfide ion has four pairs of unshared electrons, while the sulfur atom has three such pairs. When sulfur is added to the basic sulfide solution, the atom and the ion combine to form a complex sulfide ion. The simplest of

these complex ions is the disulfide ion formed by the following reaction:

$$:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}}: + :\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}}: \longrightarrow :\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}}:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}}:$$

This addition of particles may continue with the formation of ions of greater complexity. All of these complex ions, built up in this manner by the addition of atoms of sulfur to sulfide ions, have the simple electrovalence of the sulfide ion, 2 −.

A number of the metal sulfides may be precipitated under the same experimental conditions as the sulfides of arsenic, antimony, and tin. Among the other familiar metal ions which yield sulfide precipitates under these conditions are mercuric, cupric, lead, bismuth, and cadmium. The ions of this latter group, known as the copper group of cations, do not readily yield thio-salts. Consequently, the ions of the tin group may be separated from those of the copper group by the action of ammonium polysulfide.

When hydrochloric acid is added to solutions containing the thio-salts of arsenic, antimony, and tin until they are slightly acidic, the simple sulfides are reprecipitated. The addition of an acid reduces the concentration of the sulfide ions enough to cause the decomposition of the complex ion, thus liberating the simple ions in high enough concentration to cause precipitation.

$$2\ AsS_4^{---} + 6\ H_3O^+ \longrightarrow As_2S_5\downarrow + 3\ H_2S + 6\ H_2O.$$

Cyanide Complex Ions. Several of the metals yield cyanide complex ions. As in the formation of the other complex ions, this causes a reduction in the concentration of the free metal ions and leads to the solution of the simple cyanides, if the complex cyanide is soluble and sufficiently stable. Potassium cyanide reacts with a solution of a ferrous salt with the precipitation of ferrous cyanide.

$$Fe^{++} + 2\ CN^- \rightleftharpoons Fe(CN)_2\downarrow.$$

With a high concentration of cyanide ions, ferrous ions yield the complex ferrocyanide ion.

$$Fe^{++} + 6\ CN^- \rightleftharpoons Fe(CN)_6^{----}.$$

The concentration of simple ferrous ions permitted by this complex ion is so low that ferrous cyanide is dissolved.

$$[Fe^{++}] \times [CN^-]^2 < S_{Fe(CN)_2}.$$

A deep blue precipitate of ferric ferrocyanide, Prussian blue, is formed by the reaction of the ferrocyanide ion with ferric ions.

$$4\,Fe^{+++} + 3\,Fe(CN)_6^{----} \longrightarrow Fe_4[Fe(CN)_6]_3\downarrow.$$

The presence of cyanides may be detected by first forming the ferrocyanide and then precipitating Prussian blue.

Both cupric and cadmium ions yield complex ions with ammonia; but these ammonia complex ions are decomposed by the addition of soluble cyanides with the formation of cyanide complex ions. In the formation of the copper complex cyanide ion, cupric ions are reduced to the cuprous state with the oxidation of an equivalent amount of the cyanide to free cyanogen. Therefore, the complex cyanide ion of copper is the cuprocyanide ion.

$$Cd(NH_3)_4^{++} \rightleftharpoons Cd^{++} + 4\,NH_3.$$
$$Cd^{++} + 4\,CN^{--} \rightleftharpoons Cd(CN)_4^{--}.$$
$$Cu(NH_3)_4^{++} \rightleftharpoons Cu^{++} + 4\,NH_3.$$
$$2\,Cu^{++} + 6\,CN^{-} \longrightarrow 2\,Cu(CN)_2^{-} + C_2N_2\uparrow.$$

The stability of the cuprocyanide is so great that copper sulfide is not precipitated by the action of hydrogen sulfide; but the cadmium cyanide complex ion is less stable and a yellow precipitate of cadmium sulfide is formed with hydrogen sulfide.

EXERCISES

1. What are completed ionic reactions? What conditions are required to cause an ionic reaction to go virtually to completion?
2. Give examples of ionic reactions which are virtually complete because of the formation of precipitates. In each example, indicate the condition at the final state of equilibrium.
3. What is meant by the solubility product of a substance? What conditions affect the numerical value of the solubility product?
4. From the solubility data in Appendix IX, calculate the solubility product of lead sulfate, strontium sulfate, calcium carbonate, calcium fluoride, and magnesium hydroxide.
5. From the solubility product data in Appendix X, calculate the solubility, in grams per 100 g. of water, of silver chloride, barium carbonate, silver sulfate, lead chromate, and manganous sulfide.
6. In terms of the solubility product principle, what conditions are necessary for the precipitation of a substance?
7. Explain, in terms of the solubility product principle and the ionic equilibria by which the ion concentrations are regulated, the following separations:
   (*a*) The ions of chromium and magnesium by the use of an ammonia solution;

(*b*) The ions of barium and calcium by the use of a chromate solution;
(*c*) Cupric and ferrous ions by the use of hydrogen sulfide.

8. Explain the solution of the following slightly soluble substances:
   (*a*) Lead chloride in hot water;
   (*b*) Barium carbonate in low concentration of hydronium ions;
   (*c*) Barium carbonate in high concentration of hydronium ions;
   (*d*) Silver phosphate in hydronium ion solution;
   (*e*) Lead sulfate in a high concentration of acetate ions.
9. Show how the formation of weak electrolytes and gaseous products causes ionic reaction to go practically to completion.
10. How is the formation of complex ions interpreted in terms of electronic structures?
11. Show how the formation of complex ions may cause ionic reactions to go to completion.
12. Explain in terms of the equilibria involved:
   (*a*) The separation of ferric hydroxide and cupric hydroxide by the use of a solution of ammonia;
   (*b*) The separation of silver and mercurous chlorides by the use of ammonia;
   (*c*) The separation of cupric and stannous sulfides by the use of ammonium polysulfide;
   (*d*) The solution of ferrous cyanide by an excess of cyanide ions.

SUPPLEMENTARY READINGS

Hammett, *Solutions of Electrolytes*, Chapters II, III, and V.
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CHAPTER XIII

ACIDS. BASES. AMPHOLYTES

According to the Arrhenius theory, acids are hydrogen compounds which dissociate in aqueous solution to yield hydrogen ions, and acidity is due to the presence of hydrogen ions. Similarly, bases are the hydroxides of metals, which dissociate to give hydroxide ions. The solvent, water, is itself slightly ionized to give these same ions. In terms of this theory, neutrality is defined by the properties of this solvent; and acidic solutions are those which contain a higher concentration of hydrogen ions than pure water, while basic solutions contain a higher concentration of hydroxide ions. For many purposes, these definitions are clear and sufficient. There are, however, other solvents in which ions are formed; and there are reactions in each of these systems which are analogous to the reactions ascribed to hydrogen and hydroxide ions in aqueous solutions. In solutions in which liquid ammonia is the solvent, acidity is ascribed to the ammonium ion, NH_4^+, and basicity to the amide ion, NH_2^-. There are also substances, in addition to those historically called acids and bases, which in aqueous solutions exhibit reactions of the same nature as those of the acids and the metal hydroxides. The reactions of acids and bases are fundamentally different from those of salts, in which the behavior can be accounted for by considerations based on the forces of attraction of oppositely charged ions. The Lowry and Brönsted definitions of acids and bases are important in general chemistry, chiefly because they give a more satisfactory view of acidity and basicity in aqueous solutions than the hydrogen and hydroxide ion definitions. They are also applicable to solutions in other solvents than water; but such solutions are ordinarily of minor importance in the study of the reactions in inorganic chemistry.

Acids and Bases. According to the Brönsted definitions, *acids are substances which may give up protons, the charged nuclei of*

hydrogen atoms, and bases are substances which may combine with protons. The removal of a proton from an acid molecule is a reversible reaction. Consequently, the negative ions of the acids show basic properties. The relation of the acid to the base in the loss and gain of protons is defined by the equation,

$$\text{Acid} \rightleftharpoons \text{Proton} + \text{Base}.$$

This change does not occur spontaneously, yielding any measurable concentration of free protons. It occurs only in the presence of some other substance which can combine with the proton. When the acid is dissolved in water, molecules of water combine with the proton, splitting it off from the acid molecule, as discussed in a preceding chapter. In this reaction, water is a base and protons are transferred between molecules of the acid and water. In its simplest form, the acid-base reaction involves the following changes:

$$\text{Acid}^1 + \text{Base}^2 \rightleftharpoons \text{Acid}^2 + \text{Base}^1.$$
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-.$$

The reaction is called *protolysis.* In the competition for the proton pictured in this reaction, the equilibrium concentrations are determined by the strengths of the acids and bases involved.

Acids. The substances which are acids, according to the definition just given, may be grouped into three classes: *viz.,* neutral acids, anion acids, and cation acids. *The neutral acids* are the uncharged molecules of the familiar acids. The strong acids are those which readily give up protons to water molecules, so that they are almost entirely in the ionic state in dilute solutions. The weak acids are those in which the hydrogen is held so firmly in the acid molecules that only a relatively small per cent of the material is in the ionic state at equilibrium. Water is a very weak acid since it gives low concentrations of the hydronium and hydroxide ions.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-.$$

Only the uncharged molecules which lose protons more readily than water molecules exhibit acid properties in aqueous solutions.

The anion acids are ions such as the hydrogen sulfate, HSO_4^-, the hydrogen carbonate, HCO_3^-, and the dihydrogen phosphate,

$H_2PO_4^-$, ions. These ions give up protons in aqueous solution, producing hydronium ion.

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{--}.$$

The anion acids are formed from neutral acid molecules which contain two or more replaceable atoms of hydrogen. Such neutral acid molecules may split off protons successively with different degrees of activity. In its primary ionization, sulfuric acid is strong,

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-.$$

The ionization of the hydrogen sulfate ion is only moderately strong.

The cation acids are positive ions which may give up protons. The most important of these is the hydronium ion itself. This ion readily gives up a proton to a stronger base, such as the hydroxide ion,

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O.$$

The ammonium ion, NH_4^+, also shows important acidic properties. It reacts to a small extent with water, but much more completely with hydroxide ions.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3.$$
$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3.$$

When salts dissolve in water, the ions become surrounded by groups of water molecules to form hydrated ions. The number of water molecules associated with each ion is definite and depends on the coördination number of the ion. In many of these hydrated ions, the attraction of the central atom for the water molecules is so weak that the water of hydration is not held in the solids formed by the combination of the ions. The water molecule is held in combination by the formation of a coördinate bond involving pairs of electrons in the oxygen atom which are not already shared by protons. In some of these ions the attraction for the oxygen of the water molecule is so slight that there is no evidence of any distortion of the molecule. The hydrated sodium and barium ions, for example, exhibit neither acidic nor basic properties. There are many hydrated ions, however, in which the oxygen of the water molecule is held so strongly by the kernel of the

central atom of the cluster that these water molecules are distorted, so as to weaken the forces binding the proton to the oxygen atom. Hydrated cations in which the protons are repelled by the charge of the metal cation so strongly that they interact with water to form hydronium ions are cation acids. The hydrated cupric ions, $Cu(H_2O)_4^{++}$, and aluminum ions, $Al(H_2O)_6^{+++}$, are examples of such acids. They give low concentrations of hydronium ions in solution.

$$Cu(H_2O)_4^{++} + H_2O \rightleftharpoons H_3O^+ + Cu(OH)(H_2O)_3^+.$$

Substances containing anion acids or cation acids must contain also enough ions of the opposite sign to neutralize the electric charges which they bear. A solution of a cation acid must contain anions such as chloride or sulfate; *e.g.*, NH_4Cl, $Al(H_2O)_6Cl_3$. Although, strictly speaking, it is the ion which shows the acid property, the salt which contains the cation acid may be included in the general grouping of acidic substances.

Bases. The definition of bases as substances which combine with protons places emphasis on the most important and characteristic reaction which they exhibit rather than on the composition. The hydroxides of the metals, formerly considered to be the only true bases, are now regarded as one of the classes of bases. The bases fall into two important groups: *viz.*, the anion bases, and the neutral or molecular bases.

Anion bases are the negative ions of the molecular acids, including water among these acids. The negative ions of the strong acids are very weak bases, for they show little tendency to take up protons and form molecular acids. The anions of the weak acids are more effective in removing hydronium ions from solution than the ions of the strong acids. These ions are introduced into solution along with an equivalent concentration of cations. Consequently, it is customary to extend the definition of the base to include the substances which contain the anion bases. The hydroxide ion is an active base, and sodium and potassium hydroxides are commonly called bases.

The hydroxide ion is the strongest of the bases in aqueous solution, because its reaction with hydronium ions yields water as a product, and the reaction is exothermic.

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O + 13{,}200 \text{ cal.}$$

At 20°, the equilibrium concentrations of these ions is shown by the constant,

$$[H_3O^+] \times [OH^-] = 1 \times 10^{-14}.$$

This constant is smaller than that of most of the weak acids. Even the weak acids, such as hydrogen sulfide and the ammonium ion, which yield very low concentrations of the hydronium ion, react readily with solutions which contain high concentrations of the hydroxide ion.

$$H_2S + OH^- \rightleftharpoons H_2O + HS^-.$$
$$HS^- + OH^- \rightleftharpoons H_2O + S^{--}.$$
$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3.$$

All of the metal hydroxides which are appreciably soluble in water furnish hydroxide ions and exhibit basic properties.

The acetate ion is the anion of the weak acid, acetic acid. The ionization constant of this acid at 20° is,

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K = 1.8 \times 10^{-5}.$$

The addition of sodium acetate to a solution of a strong acid causes a decrease in the concentration of the hydronium ions in a ratio already considered in terms of the common ion effect. If 0.1 mole of sodium acetate is added to a liter of 0.1 molar solution of hydrochloric acid, the ion concentrations at equilibrium will be approximately those in a 0.1 molar solution of acetic acid.

$$H_3O^+ + Cl^- + Na^+ + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2 + H_2O + Na^+ + Cl^-.$$
$$H_3O^+ + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2 + H_2O.$$

This causes a decrease in the hydronium ion concentration from approximately 0.1 to 0.00136 molar. If another 0.1 mole of sodium acetate is added, the hydronium ion concentration is further decreased to 0.0000186 molar.

The soluble carbonates cause the removal of hydronium ions from solution, because the carbonate ion readily adds a proton to form the bicarbonate ion.

$$H_3O^+ + CO_3^{--} \rightleftharpoons HCO_3^- + H_2O.$$

The ionization constant for this ion is,

$$\frac{[H_3O^+] \times [CO_3^{--}]}{[HCO_3^-]} = K = 4.7 \times 10^{-11}.$$

Bicarbonate ions are also basic for they react with hydronium ions to form water and carbon dioxide,

$$H_3O^+ + HCO_3^- \rightleftharpoons 2\,H_2O + CO_2.$$

The ionization constant is,

$$\frac{[H_3O^+] \times [HCO_3^-]}{[CO_2]} = K = 4.3 \times 10^{-7}.$$

The bicarbonate ion is not so strongly basic as the carbonate ion.

The sulfide, cyanide, borate, and phosphate ions also take protons from the hydronium ions and are basic anions.

$$H_3O^+ + PO_4^{---} \rightleftharpoons H_2O + HPO_4^{--}.$$
$$H_3O^+ + HPO_4^{--} \rightleftharpoons H_2O + H_2PO_4^-.$$
$$H_3O^+ + H_2PO_4^- \rightleftharpoons H_2O + H_3PO_4.$$

Consequently, salts which furnish these ions react with acids which are stronger than those formed by gaining the protons.

Ammonia and water are molecular bases. Ammonia reacts to some extent with water, but more actively with the stronger acids, to form ammonium ions,

$$NH_3 + H_3O^+ \rightleftharpoons H_2O + NH_4^+.$$

The combination of water with protons has already been discussed as the reaction which causes the decomposition of acid molecules to produce ionic solutions. The *oxides* of some of the metals have molecular structure in the solid state. These oxides react with hydronium ions to form water and the free ions of the metal. The oxides of the active metals, however, have an ionic structure. The basic properties of these oxides are due in part to their combination with water to form hydroxide ions, and in part to the direct reaction of the oxide ion at the surface of the solid with the hydronium ions in the solution.

$$Ca^{++}O^{--} + H_2O \longrightarrow Ca^{++} + 2\,OH^-.$$
$$Ca^{++}O^{--} + 2\,H_3O^+ \longrightarrow Ca^{++} + 3\,H_2O.$$

Ampholytes. There are a number of substances which are both acids and bases, *i.e.*, they may give up protons and they may also combine with protons. These substances are known as *ampholytes or amphoteric electrolytes.* It has been observed that water exhibits both of these properties.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-.$$

The bicarbonate ion is also both basic and acidic.

$$HCO_3^- + H_3O^+ \rightleftharpoons 2\,H_2O + CO_2.$$
$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{--}.$$

A number of the hydroxides are ampholytes. Some of these are discussed further as amphoteric hydroxides in a subsequent paragraph in this chapter.

Corresponding Acids and Bases. It has been shown in preceding paragraphs that acids and bases are related to each other as shown by the equation,

$$\text{Acid} \rightleftharpoons \text{Base} + \text{Proton.}$$

The acid and base which bear this relation are called *corresponding or conjugate acids and bases*. If the acid is strong, actively giving up protons, the corresponding base is weak, showing little tendency to take on protons. In Table 21, a number of pairs of corresponding acids and bases are listed.

TABLE 21

CORRESPONDING ACIDS AND BASES

Acid		*Base*	
Name	*Formula*	*Name*	*Formula*
Hydrochloric acid	HCl	Chloride ion	Cl^-
Hydronium ion	H_3O^+	Water	H_2O
Hydrosulfate ion	HSO_4^-	Sulfate ion	SO_4^{--}
Acetic acid	$HC_2H_3O_2$	Acetate ion	$C_2H_3O_2^-$
Ammonium ion	NH_4^+	Ammonia	NH_3
Zinc hydroxide	$Zn(OH)_2$	Zincate ion	$Zn(OH)_4^{--}$
Hydrated cupric ion	$Cu(H_2O)_4^{++}$	Cupric hydroxy ion	$Cu(H_2O)_3(OH)^+$
Water	H_2O	Hydroxide ion	OH^-
Hydroxide ion	OH^-	Oxide ion	O^{--}

Since hydrochloric acid is a strong acid, the basic properties of the chloride ion in dilute aqueous solution are insignificantly small. The hydronium ion is somewhat less active than hydrogen chloride in giving up the proton, and water is more actively basic than the chloride ion, as shown by the fact that water takes up protons from hydrogen chloride molecules. The ammonium ion is a much weaker acid and the corresponding base, ammonia, is active toward the strong acids. Water is a very weak acid and

the corresponding base, the hydroxide ion, is a strong base. The hydroxide ion may also behave as an acid and suffer the loss of a proton; but it does not exhibit this reaction in aqueous solution because the corresponding base, the oxide ion, is so strongly basic that it cannot exist in aqueous solution except in extremely low concentrations.

Aqueous Solutions of Acids and Bases. The concentrations of the hydronium and hydroxide ions in aqueous solutions are so related to each other as to satisfy the equilibrium conditions for water.

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O.$$

The concentrations of hydronium and hydroxide ions required for this equilibrium in pure water are low. At 20°, the concentration of each ion is 1×10^{-7} molar; and the ionization constant for water is

$$\frac{[H_3O^+] \times [OH^-]}{[H_2O]^2} = K.$$

The molar concentration of water in dilute solutions is practically constant. Hence, the product of the molar concentrations of the ions of water is equal to a constant which is usually called the *ionization constant of water.*

$$[H_3O^+] \times [OH^-] = 1 \times 10^{-14}, \text{ at } 20°.$$

Solutions which contain a higher concentration of the hydronium ion than water, as in solutions of hydrochloric acid, contain a correspondingly lower concentration of the hydroxide ion; and, conversely, if the concentration of the hydroxide ion is greater than in water, as in a solution of sodium hydroxide, the concentration of the hydronium ion is less.

$$[OH^-] = \frac{K}{[H_3O^+]}; \quad [H_3O^+] = \frac{K}{[OH^-]}.$$

In common practice, a solution which contains the same concentration of hydronium and hydroxide ions is called a *neutral solution.* This definition is purely arbitrary, and some other concentration of one of these ions could have been selected as the point of neutrality. Nevertheless, since water is the common solvent, it has been found convenient to use it as the basis for comparisons of basicity and acidity.

Neutralization. Since a neutral aqueous solution is arbitrarily defined as one in which the concentrations of the hydronium and hydroxide ions are the same, the process of neutralization involves the removal of any excess of either variety of these ions. Strong acids may be neutralized by the addition of equivalent proportions of strong basic hydroxides; and basic solutions, by the addition of acids. Unless the cation of the basic hydroxide and the anion of the acid also unite, the same reaction takes place in the reaction of any strong acid with any strong basic hydroxide, provided that they are present in dilute solution. This conclusion is confirmed by the fact that the same amount of heat is evolved in the neutralization of equivalent quantities of any strong basic hydroxide by any strong acid. The number of calories of heat given out during the neutralization of one gram ion of hydronium ions by one gram ion of hydroxide ions, *the heat of neutralization*, is equal to 13,200 calories.

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O + 13{,}200 \text{ cal.}$$

The Hydrolysis of Ions. The ions furnished by many of the salts in aqueous solution react with water. Anions which have active basic properties take up protons from water molecules; and cations which are actively acidic give up protons to water molecules. These two reactions are reversible and a state of equilibrium results unless insoluble or inactive molecular products are formed. The reactions of the ions of the salt with water take place independently; and the anion, the cation, or both varieties of ions may enter into such changes. Whether the solution is more acidic or less acidic than pure water depends on the relative acidity or basicity of the ions of the salt. The reaction involves the transfer of protons from one substance to another, a reaction called *protolysis*. The particular reaction in which water is one of the active reactants entering into the proton exchange is called *hydrolysis*.

Salts which contain the anions of weak acids undergo hydrolysis to form basic solutions if the cations are neutral in aqueous solution. These anions are bases and they combine with protons. Acetates hydrolyze to form weakly ionized acetic acid and free hydroxide ions.

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-.$$

Since both hydroxide and acetate ions combine with protons, the reaction is reversible and a state of equilibrium is established when the concentrations of the ions have become adjusted so that the velocity of each of the reactions is the same. The solution, however, contains a greater concentration of hydroxide than hydronium ions.

Salts containing the cations of weakly ionized basic substances and the anions of strong acids interact with water to form acidic solutions, because such cations are acids. Ammonium ions and many of the hydrated metal ions hydrolyze to form hydronium ions and slightly ionized molecular products or hydroxide complex ions. These reactions also result in a state of equilibrium because, in addition to hydronium ions, they yield the conjugate bases.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3.$$
$$Al(H_2O)_6^{+++} + H_2O \rightleftharpoons H_3O^+ + Al(OH)(H_2O)_5^{++}.$$

This latter reaction may then proceed to the secondary stage to some extent, but water is not basic enough to remove protons from the hydrated ion to a further degree.

$$Al(OH)(H_2O)_5^{++} + H_2O \rightleftharpoons H_3O^+ + Al(OH)_2(H_2O)_4^+.$$

In these reactions it is observed that the coördination number of the aluminum ion remains constant at 6. As molecules of water of hydration break up to form hydronium ions, the residual hydroxide ions remain associated with the aluminum ion in the form of hydrated hydroxide complexes.

The hydrolysis of salts which furnish both anion bases and cation acids, active enough to react with water, combines the two effects described separately in the preceding paragraphs. The hydrolysis of ammonium acetate in aqueous solution involves the following reactions.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3.$$
$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-.$$
$$C_2H_3O_2^- + H_3O^+ \rightleftharpoons HC_2H_3O_2 + H_2O.$$
$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O.$$

Consideration of these reactions shows that a single equation may be written to summarize the changes which occur during the hydrolysis of the ions of ammonium acetate.

$$NH_4^+ + C_2H_3O_2^- \rightleftharpoons NH_3 + HC_2H_3O_2.$$

In the presence of water as the solvent, a proton transfer takes place between the acidic ammonium ion and the basic acetate ion to form the molecular acid, acetic acid, and the molecular base, ammonia.

There are a number of types of substances which undergo hydrolysis. The extent of the reaction and the effects of changing conditions on the concentrations of ions are discussed more fully for a number of these reactions in the following chapter.

The Significance of *p*H. The molar concentrations of the hydronium and hydroxide ions in any aqueous solution are expressed by stating the concentration of one of them, because the product of the two concentrations is equal to the constant, 1×10^{-14}, at 20°. In an acidic solution having an effective concentration of the hydronium ion equal to 1 M., the concentration of the hydroxide ion is equal to 1×10^{-14} M. The unit of concentration changes is so small that a range from 1 to 1×10^{-14} is required to express the change from a one-molar hydronium ion solution to a one-molar hydroxide ion solution.

For many purposes a more compact scale is desired, and it is more convenient to use the logarithm of the reciprocal of the hydronium ion concentration as proposed by Sörensen in 1909. This is designated ***p*H.**

$$p\text{H} = \log \frac{1}{[\text{H}_3\text{O}^+]} = -\log [\text{H}_3\text{O}^+].$$

The range from 1 to 1×10^{-14} on the scale of the hydronium ion concentrations is covered by numbers from 0 to 14 on this scale. In a solution in which the concentration of the hydronium ion is 1 M., the *p*H is equal to 0. With decreasing concentration of the hydronium ion, the *p*H increases one unit for each unit in the negative exponent of ten, *i.e.*, for each ten-fold decrease in the hydronium ion concentration. In pure water, the concentration of the hydronium ion is 1×10^{-7} and the *p*H, 7. In a basic solution in which the concentration of the hydronium ion is 1×10^{-14}, the *p*H is 14. For unit changes in the negative exponent of the hydronium ion concentration, the *p*H may be determined by inspection. For intermediate values, it is necessary to use a table of logarithms. It is important to remember that the logarithm as commonly written consists of the sum of a characteristic which

may be either positive or negative and a mantissa which is always positive. The *p*H is a number in which both parts have the same sign. The following examples will illustrate the calculation of *p*H from the concentration of the hydronium ion, and of the concentration of the hydronium ion from the *p*H. Suppose that the molar concentration of the hydronium ion in a solution is 5.2×10^{-6}.

$$p\mathrm{H} = \log \frac{1}{[H_3O^+]} = -\log [H_3O^+] = -(\bar{6}.72) = 5.28.$$

Suppose that the *p*H in a second solution is 3.64.

$$p\mathrm{H} = 3.64 = \log \frac{1}{[H_3O^+]}$$
$$\log [H_3O^+] = -3.64 = \bar{4}.36$$
$$[H_3O^+] = 2.3 \times 10^{-4}.$$

Indicators. There are a number of substances, known as indicators, which are affected reversibly by varying concentrations of the hydronium ion. An indicator is a conjugate acid-base system in which the acid has a different color from that of the base. The reaction of hydronium ions in solution converts a system such as this into the acid. When the hydronium ion concentration is low the indicator base is formed. The concentrations at which these changes occur are characteristic of each indicator. The changes are not abrupt; but a mixture of the two forms of the indicator may exist together over a certain range of *p*H values.

TABLE 22

INDICATORS

Indicator	*p*H *Range*	*Color*	
		Acid	*Base*
Thymol blue	1.2–2.8	red	yellow
Brom phenol blue	3.0–4.6	yellow	blue
Methyl orange	3.1–4.4	red	yellow
Methyl red	4.2–6.3	red	yellow
Brom thymol blue	6.0–7.6	yellow	blue
Neutral red	6.8–8.0	red	yellow
Litmus	4.5–8.3	red	blue
Thymol blue (base)	8.0–9.6	yellow	red
Phenolphthalein	8.3–10.0	colorless	red

By the selection of indicators which give a sharp color change in the proper *p*H range, the acidity of the solution may be determined directly by observing the color effects produced. In Table 22, several indicators are listed with the characteristic *p*H range and the color change characteristic of each.

Indicators are also used for the determination of the end point in the reaction of an acid with a base. For this purpose, an indicator should be chosen which shows the color change when equivalent amounts of the acid and base have reacted. The end point shown by the indicator should be at the same *p*H as a solution prepared by dissolving approximately the same weight of the salt which is formed during the reaction of the acid and base. Such solutions may or may not be neutral as defined by the properties of pure water. The nature of the salt which is present in the solution determines the *p*H of the solution at the end point. An ammonium salt gives an acidic solution on account of the presence of ammonium ions; a salt such as sodium chloride gives a neutral solution; and sodium acetate, a basic solution.

Titration of Acids and Bases. The experimental determination of the concentration or quantity of an acid in a solution is known as *acidimetry;* and of a base, *alkalimetry*. This is accomplished by measuring accurately the volume of a solution of known concentration, a standard solution, required to react with a definite volume of the acidic or basic solution of unknown concentration. The procedure is called *titration*. The solutions may be placed in the burettes, Fig. 97, from which the volumes required for the reaction are measured into the beaker below. The indicator should be chosen which will show a color change at the *p*H resulting from the reaction of equivalent amounts of the acid and base.

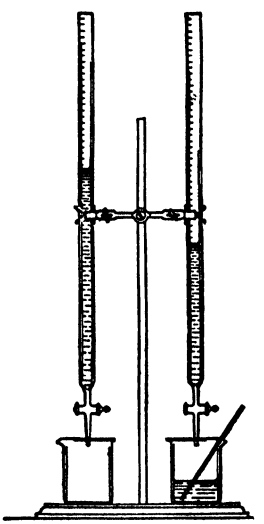

FIG. 97. — Burettes.

If the concentration of one of the solutions is known, the concentration of the other is easily calculated from the volumes which have been found to be equivalent. Suppose that it is found by experiment that 25.5 ml. of a 0.1 N. solution of a base neutralize

25.0 ml. of an acidic solution whose concentration is to be determined. The acidic solution is the more concentrated and the normalities of the two solutions vary inversely with the volumes required for the reaction. Using the subscripts, A and B, to represent the acid and base, respectively, N to represent the normality, and V the volume,

$$\frac{N_A}{N_B} = \frac{V_B}{V_A};$$

or,

$$N_A V_A = N_B V_B.$$

$$N_A = \frac{25.5 \times 0.1}{25.0} = 0.102.$$

Suppose that it is desired further to calculate the dilution of the acid that would be required to make it 0.1 N. Since the volumes vary inversely with the normalities, the product of the normality multiplied by the volume is constant.

$$N_1 V_1 = N_2 V_2.$$

$$0.102\ V_1 = 1000 \times 0.1$$

$$V_1 = 980.4 \text{ ml.}$$

That is, 980.4 ml. of this acid are required for each liter of exactly 0.1 N. solution.

The weight of an acid or base in a solution may be determined by measuring the volume of a standard solution which is equivalent to it. Suppose that 31.56 ml. of 0.2 M. hydrochloric acid solution are required to neutralize the sodium hydroxide in an unknown solution.

$$H_3O^+ + OH^- \rightleftharpoons 2\ H_2O.$$

One mole of hydrochloric acid reacts with one mole of sodium hydroxide. One mole of hydrochloric acid is contained in 5 liters of the 0.2 M. solution; and 5 liters of this solution react with 40.0 g. of sodium hydroxide. Therefore, the weight of sodium hydroxide in the solution is equal to $40 \times 31.56/5000$, or 0.252 g.

Buffer Solutions. The addition of the salt of a weak acid to the acid decreases the concentration of the hydronium ion; and the addition of the salt of a weak base to a solution of the base decreases the concentration of the hydroxide ions. This effect is most readily understood by the consideration of the acid-base equilibria. When sodium acetate is added to a solution of acetic

acid, the concentration of the anion base is made large. Therefore, the equilibrium between this ion and the hydronium ion is disturbed so that a lower concentration of the hydronium ion remains in solution than in the absence of the salt.

$$H_3O^+ + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2 + H_2O.$$

If small additional quantities of hydronium ions are introduced into this solution, a further reaction with acetate ions takes place and the concentration of hydronium ions remains practically constant. If hydronium ions are removed from the solution by reaction with some stronger base, the molecular acetic acid serves as a reservoir to keep the concentration at practically its former value. Consequently, such solutions resist changes in the concentration of the hydronium ion. Solutions containing a regulated low concentration of the hydronium ion, together with molecular substances and ions which prevent significant changes in the concentration of the hydronium ion, are known as *buffer solutions*. By varying the concentrations of the acid and salt and by selecting different weak acids and their salts, it is possible to prepare solutions which are buffered at different *p*H values.

Amphoteric Hydroxides. The amphoteric hydroxides are a special class of *ampholytes*, substances which are capable both of giving up and of taking on protons. The acid-base properties of the hydroxides of the elements vary greatly. This may be illustrated by considering the hydroxides of the elements of the third period of the periodic system. Sodium hydroxide is strongly basic. The bond between the metal ion and the hydroxide ion is electrovalent.

$$Na^+OH^- \longrightarrow Na^+ + OH^-.$$

Magnesium hydroxide is less actively basic than sodium hydroxide; and the basic character of the hydroxides becomes progressively weaker from element to element through the period. The hydroxides of silicon, phosphorus, sulfur, and chlorine are acidic. In its low positive oxidation state, chlorine yields an hydroxide which is weakly acidic.

$$ClOH + H_2O \rightleftharpoons H_3O^+ + ClO^-.$$

The acidity of the hydroxide of an element commonly increases with the oxidation number; and perchloric acid, the hydroxy-

compound of chlorine in its highest oxidation state, is a strong acid.

$$ClO_3OH + H_2O \rightleftharpoons H_3O^+ + ClO_4^-.$$

Phosphoric and silicic acids are weaker than sulfuric and perchloric acids, and aluminum hydroxide shows the properties of both a base and an acid.

It has been observed previously that the acidity or basicity of the hydroxide of an element depends on the relative force of attraction between oxygen and hydrogen in the hydroxide radical, and that between oxygen and the kernel of the atom to which the hydroxide group is attached. The force with which the oxygen atom is bound increases with the charge of the kernel, but decreases as the radius of the kernel becomes greater. The radii of the atomic kernels in a period of elements having similar electronic structures decrease with increase in atomic number. Just as the oxygen atom is held more firmly as the distance between the atoms decreases and the charge increases, so the proton, being positive, is held less firmly.

From a consideration of the general relationships shown in the periodic system, it is apparent that a number of the elements should yield amphoteric hydroxides. Among the common amphoteric hydroxides are the hydroxides of the zinc, aluminum, stannous, lead, chromic, and antimony ions. These cations are all highly hydrated in solution and the amphoteric hydroxides are hydrated hydroxides in which the coördination number of the metal ion tends to remain constant. Aluminum hydroxide may be represented by the formula, $Al(OH)_3(H_2O)_3$, and zinc hydroxide by the formula, $Zn(OH)_2(H_2O)_4$. Some of the metal hydroxides lose water of hydration when they separate from the solution, and these substances are frequently represented by formulas in which the water of hydration is not indicated.

Preparation and Reactions of the Amphoteric Hydroxides. The hydrated ions of a number of the metals interact with water to form hydronium ions and hydroxide complex ions.

$$Al(H_2O)_6^{+++} + H_2O \rightleftharpoons H_3O^+ + Al(OH)(H_2O)_5^{++}.$$

With stronger bases, such as the hydroxide ion, this reaction proceeds further and the hydrated hydroxide is precipitated.

$$Al(H_2O)_6^{+++} + 3\ OH^- \rightleftharpoons 3\ H_2O + Al(OH)_3(H_2O)_3\downarrow.$$

This hydroxide is amphoteric, so that it reacts as both a base and an acid. However, its solubility is small and its acidity is not great enough to produce a significant concentration of hydronium ions in solution. The hydroxide reacts with hydroxide ions to form water and soluble hydroxide complex ions.

$$Al(OH)_3(H_2O)_3\downarrow + OH^- \rightleftharpoons H_2O + Al(OH)_4(H_2O)_2^-.$$

With an excess of hydroxide ions, this weakly acidic anion may react further to form the hydroxide complex ion.

$$Al(OH)_4(H_2O)_2^- + 2\ OH^- \rightleftharpoons 2\ H_2O + Al(OH)_6^{---}.$$

Since the amphoteric hydroxide reacts with an excess of a strong base, the preparation of these substances may be accomplished by the reaction of salts which furnish the necessary cations with either a weak base or a limited proportion of a strong base.

The amphoteric hydroxides may also be prepared by the reaction of an acid with a salt containing the hydroxide complex ions. The hydroxide complex ions are anion bases. The reaction of hydronium ions with the hydroxide complex ions of aluminum, known as aluminate ions, produces the molecular hydroxide as the precipitate.

$$Al(OH)_6^{---} + 3\ H_3O^+ \rightleftharpoons 3\ H_2O + Al(OH)_3(H_2O)_3\downarrow.$$

The hydroxide is a molecular base which reacts with an excess of hydronium ions to form a series of hydroxide complex cations and finally the free hydrated aluminum ions.

$$Al(OH)_3(H_2O)_3 + 3\ H_3O^+ \rightleftharpoons 3\ H_2O + Al(H_2O)_6^{+++}.$$

The total concentration of aluminum compounds in an aqueous solution is equal to the sum of the concentrations of the various anions and cations containing this element. In an acidic solution the hydrated aluminum ions predominate. As the concentration of hydroxide ions is increased through the addition of sodium hydroxide, aluminum ions become converted successively into hydroxide complex cations and aluminum hydroxide as a precipitate. The concentration of the aluminum cations decreases during the precipitation reaction and the total solubility likewise decreases. There is little change in the concentration of the complex anions so long as the solution does not contain an excess of

hydroxide ions. The concentration of the aluminum cations is very low when the solution is slightly basic. With further increases in the concentration of the hydroxide ion, increasingly large proportions of the aluminum hydroxide are converted into the complex anions and taken into solution. The effect of changes in the hydroxide ion concentration on the total solubility of aluminum compounds is shown in Fig. 98. The point *B* represents the concentration of the hydroxide ion at which precipitation is most nearly complete. This point is known as the *isoelectric point*, at which the acidic ionization of the amphoteric hydroxide is equal to its basic ionization. Along the branch of the curve *AB*, the solute is primarily in the form of aluminum ions; and along the curve *BC*, the complex anions. The concentration of the hydroxide ion at the isoelectric point is that which is most favorable for the precipitation of the hydroxide from solution. In the analytical procedure, ferric, aluminum, and chromium ions are separated together from solution as the hydroxide precipitate by the use of a solution of ammonia containing ammonium hydroxide, because this solution gives a concentration of the hydroxide ion which is near the isoelectric point for each of these hydroxides.

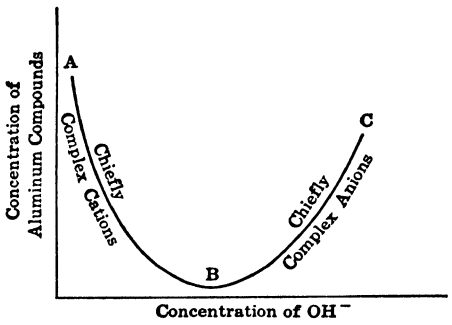

FIG. 98

The equations in which the water of hydration of the reactants is represented are frequently confusing and cumbersome. A simplification may be introduced through the omission of the molecules of water from these formulas. The explanations based on these simplified reactions, however, are incomplete. Shown in this manner, the precipitation of aluminum hydroxide from an aluminum salt may be represented by the equation,

$$Al^{+++} + 3\ OH^- \rightleftharpoons Al(OH)_3\downarrow .$$

This precipitate is also in equilibrium with a low concentration of hydronium ions.

$$Al(OH)_3\downarrow + 2\ H_2O \rightleftharpoons H_3O^+ + Al(OH)_4^-.$$

The addition of an excess of hydroxide ions causes the removal of the hydronium ions sufficiently to cause the reaction to continue with the conversion of the hydroxide into the complex aluminate ions.

$$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-.$$

The amphoteric nature of zinc hydroxide may be applied analytically in the separation of zinc and manganous ions. Both zinc and manganous ions react with hydroxide ions to form the hydroxide precipitates.

$$Zn^{++} + 2\ OH^- \rightleftharpoons Zn(OH)_2\downarrow.$$
$$Mn^{++} + 2\ OH^- \rightleftharpoons Mn(OH)_2\downarrow.$$

Zinc hydroxide reacts with an excess of hydroxide ions to form the zincate ion; but manganous hydroxide is not amphoteric and remains as an insoluble precipitate when a mixture of the two hydroxides is digested with sodium hydroxide.

$$Zn(OH)_2\downarrow + 2\ OH^- \rightleftharpoons Zn(OH)_4^{--}.$$

EXERCISES

1. In terms of the Brönsted definitions, what is the significance of acid and base?
2. Name three classes of acids and give examples of each. Write equations to show the acidic nature of a member of each class.
3. Name the classes of bases and give examples of each class. Write equations to show how they react as bases.
4. What is meant by corresponding acids and bases? Give examples to illustrate. How does the strength of the base vary with the strength of the corresponding acid?
5. What is meant by a neutral aqueous solution? What is the essential reaction of neutralization? What is meant by the heat of neutralization?
6. Show how the hydrolysis of ions leads to the formation of acidic and basic solutions.
7. What is meant by the *p*H of a solution? What advantage does the definition of the acidity of a solution in terms of *p*H offer over that in terms of the concentration of the hydronium ion?
8. What are the indicators? How do they indicate the end point of a titration?
9. How is the amount of an acid or a base in solution determined?
10. What is a buffer solution? How are changes in the hydronium ion concentration prevented in such solutions?
11. What are amphoteric hydroxides? Illustrate by equations two reactions which may be used for the preparation of an amphoteric hydroxide, and two reactions which are characteristic of these hydroxides.

12. Why is a solution of ammonia containing ammonium chloride the most satisfactory reagent for the precipitation of aluminum hydroxide?
13. Calculate the *p*H of a solution in which the concentration of the hydronium ion is 2.7×10^{-9}, and the concentration of the hydronium ion in a solution having a *p*H of 4.73.
14. If 35.7 ml. of an acidic solution are neutralized by 33.5 ml. of a 0.32 N. solution of a base, what is the normality of the acid?
15. Calculate the volume of 0.25 M. sulfuric acid required for reaction with 5.3 g. of sodium carbonate.

SUPPLEMENTARY READINGS

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CHAPTER XIV

HYDROLYSIS

A large number of reactions occur in aqueous solution. In many of these reactions it is possible to disregard the action of water and to assume that the changes which occur are due solely to the properties of the dissolved substances. It is recognized, of course, that water plays a useful rôle in these reactions, serving as a liquid medium in which the solutes are dispersed into molecules and ions. There are also reactions in aqueous solution into which water enters as a reactant. In many of these reactions the substances are decomposed, more or less completely, when water is added; and the reactions of the solutions may be due to the products formed by the interaction of the solute and solvent.

The Cause of Hydrolysis. All aqueous solutions contain hydronium and hydroxide ions due to the slight ionization of water. The concentration of these ions in pure water is low at equilibrium. In the ionization of water, as in all other reversible reactions, the presence of any substance which affects the concentration of one of the varieties of ions disturbs the equilibrium in the direction of the change which tends to counteract the effect. If the substance added combines with the hydronium ions or with the hydroxide ions, forming molecular products, the ionization of water proceeds further until equilibrium is established. *Hydrolysis involves the interaction of the ions of water with other substances* to which it is added, with the formation of acids and bases. Hydrolytic reactions are expressed in terms of the same laws of chemical equilibrium as other reversible reactions.

Types of Hydrolysis. The reactions of hydrolysis fall into several classes. Some of these reactions are complete and irreversible, while others normally lead to an equilibrium. *The hydrolysis is irreversible* if both of the products formed by the reaction of the solute with water are of the same chemical nature; *i.e.*, if both products are acidic or both products are basic. The

reaction is irreversible also if one of the products is either acidic or basic and the other is neither basic nor acidic. The hydrolysis of binary compounds composed of two non-metals, such as non-metal halides, illustrates the first of these types; and the hydrolysis of some of the binary compounds of metals and non-metals, such as the carbides and phosphides, illustrates the second group of completed reactions. The hydrolysis of molecular substances is usually complete and irreversible. The hydrolysis of ions is usually reversible, although there are some instances in which this reaction may be caused to proceed virtually to completion.

Hydrolysis of Molecular Substances. *The hydrolysis of the non-metal halides is complete and irreversible* because both of the products of the reaction are acids which do not react with each other. Phosphorus trichloride, for example, reacts with water to produce highly ionized hydrochloric acid and the weak acid, phosphorous acid, which is largely in the molecular state. In this reaction, the hydroxide ions of the water react to produce the hydroxide of a non-metal, which is an acidic substance. Therefore, the hydroxide ion concentration cannot remain large enough for equilibrium with the hydronium ions of water at the surface of the trichloride. The reaction goes to completion even in the presence of an excess of the hydrohalogen acid.

$$PCl_3 + 6\,H_2O \longrightarrow 3\,H_3O^+ + 3\,Cl^- + H_3PO_3.$$

Since phosphorus trihydroxide is a weak acid, it is represented by the molecular formula. This reaction is typical of many of the non-metal halides, such as those of boron, silicon, sulfur, phosphorus, etc. There are, however, some non-metal halides which are not decomposed by water. Carbon tetrachloride and nitrogen iodide are insoluble in water, and the nature of the electron bond is such as to prevent the splitting of the molecule by the action of water. The formation of acidic products in the hydrolysis of the halide is characteristic of the non-metallic elements.

The distinction between metals and non-metals is not always sharp, and the borderline elements exhibit amphoteric properties. The hydrolysis of the halides of such elements is reversible in the presence of an excess of the hydrohalogen acid, so that these halides are salts in so far as their behavior with water is concerned.

Some of the non-metallic elements undergo hydrolysis. The

halogens are hydrolyzed with the formation of acidic products, the highly ionized hydrohalic acid and the weakly ionized hypohalous acid.

$$Cl_2 + 2\,H_2O \rightleftharpoons H_3O^+ + Cl^- + ClOH.$$

The reversibility of this reaction is not due to acid-base equilibria, since the hydroxide of chlorine is acidic, but to the oxidation-reduction equilibria of chlorine and water with hypochlorous acid and chloride ions. Elementary phosphorus is also hydrolyzed, with the formation of phosphine, PH_3, and the weak acid, hypophosphorous acid, H_3PO_2.

$$4\,P + 6\,H_2O \longrightarrow PH_3 + 3\,H_3PO_2.$$

The velocity is greatly increased by the addition of a basic hydroxide, and the hypophosphite is produced instead of the acid.

$$4\,P + 3\,H_2O + 3\,OH^- \longrightarrow PH_3 + 3\,H_2PO_2^-.$$

The hydrolysis of the phosphides, carbides, and silicides of the metals is also irreversible. The reaction of water with each of these types of compounds yields the non-acidic hydride of the non-metal and the hydroxide of the metal. Calcium phosphide, Ca_3P_2, yields phosphine and calcium hydroxide in solution. In this reaction, the hydrogen nucleus is split away from the water molecules, or the hydronium ions, forming phosphine in an irreversible reaction.

$$Ca_3P_2 + 6\,H_2O \longrightarrow 2\,PH_3 + 3\,Ca^{++} + 6\,OH^-.$$

Equilibrium between molecular water and its ions is not possible in contact with the surface of the phosphide. After the decomposition of the phosphide is complete, the hydronium ion concentration may become adjusted to the increased hydroxide ion concentration to establish the water equilibrium.

$$[H_3O^+] \times [OH^-] = 1 \times 10^{-14}.$$

The hydrolysis of calcium carbide, CaC_2, is complete because acetylene, C_2H_2, is not appreciably ionized; and its formation reduces the hydronium ion concentration so greatly that the equilibrium of water with its ions is destroyed and can be reestablished only after the decomposition of the carbide is complete.

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca^{++} + 2\,OH^-.$$

Carborundum, SiC, and carbon disulfide, CS_2, are not hydrolyzed.

The silicides of many of the metals are decomposed by water with the formation of silicon hydride, a non-acidic gas. Magnesium silicide, Mg_2Si, reacting with water, yields also the slightly soluble magnesium hydroxide on the surface of the silicide. This material prevents the contact of the silicide with water and the presence of an acid is necessary to remove the hydroxide and permit the reaction of hydrolysis to proceed.

$$Mg_2Si + 4\,H_2O \longrightarrow SiH_4 + 2\,Mg(OH)_2\downarrow.$$
$$Mg(OH)_2 + 2\,H_3O^+ \longrightarrow Mg^{++} + 4\,H_2O.$$

The hydrolysis of metal nitrides is also irreversible. This reaction is similar to those discussed in preceding paragraphs. The only notable difference is that the hydride of nitrogen is the basic substance ammonia. Therefore, the formation of ammonia leads to the removal of hydronium ions from solution.

$$Ca_3N_2 + 6\,H_2O \longrightarrow 2\,NH_3 + 3\,Ca^{++} + 6\,OH^-.$$

Since one of the varieties of ions furnished by the water is removed in an irreversible process to form a molecular product, the hydrolysis of the nitride is complete.

The Hydrolysis of Ions. The hydrolysis of ions differs fundamentally from the reactions just discussed. The change leading to the withdrawal of ions from solution is a reversible process. The presence of the ions of the solute disturbs, but does not destroy, the equilibrium between water and its ions. A new equilibrium with a modified concentration of hydronium ions is established in the presence of the ions of the solute. In the preceding chapter, the types of ions which undergo hydrolysis have been discussed briefly. The anion bases react with hydronium ions to form the molecular acids, so that the solution is basic. The cation acids react with water molecules, forming hydronium ions in solution. The ions of strong acids and strong bases show no significant tendency either to form hydronium ions or to react with hydronium ions in solution. Consequently, solutions of salts which furnish ions of these types are neutral.

Hydrolysis of Anion Bases. The equilibria involved in this type of reaction may be illustrated by the interaction of water and the cyanide ion in a solution of potassium cyanide. The salt is completely ionized in dilute solution.

$$K^+CN^- \longrightarrow K^+ + CN^-.$$

The cyanide ion is an anion base. Its reaction with hydronium ions yields hydrocyanic acid.

$$H_3O^+ + CN^- \rightleftharpoons HCN + H_2O.$$

This decreases the concentration of the hydronium ions and disturbs the equilibrium of these ions with hydroxide ions.

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O.$$

Consequently, additional molecules of water break up to form ions and the changes continue until the concentrations of hydronium and cyanide ions have decreased and the concentration of the hydroxide ions has increased, so that both equilibria exist simultaneously. The hydrolysis of the cyanide is also shown by the equation,

$$H_2O + CN^- \rightleftharpoons HCN + OH^-.$$

The equilibrium concentrations of the substances involved in this reaction are represented according to the law of molecular concentrations by the ratio:

$$\frac{[HCN] \times [OH^-]}{[CN^-]} = K_{\text{hydrolysis}}. \tag{1}$$

In order that this relationship may exist, the concentrations of the ions must become adjusted so that the hydronium ion can be simultaneously in equilibrium with both the hydroxide and the cyanide ions.

$$[H_3O^+] \times [OH^-] = K_{\text{water}}. \tag{2}$$

$$[H_3O^+] = \frac{K_{\text{water}}}{[OH^-]}.$$

$$\frac{[H_3O^+] \times [CN^-]}{[HCN]} = K_{HCN}. \tag{3}$$

$$[H_3O^+] = \frac{K_{HCN} \times [HCN]}{[CN^-]}.$$

That is,
$$\frac{K_{HCN} \times [HCN]}{[CN^-]} = \frac{K_{\text{water}}}{[OH^-]} = [H_3O^+],$$

or
$$\frac{[HCN] \times [OH^-]}{[CN^-]} = \frac{K_{\text{water}}}{K_{HCN}}. \tag{4}$$

That is,
$$\frac{K_{\text{water}}}{K_{HCN}} = K_{\text{hydrolysis}}. \tag{5}$$

The extent of hydrolysis depends on the ratio of the ionization constant of water to the ionization constant of the weak acid whose formation causes the hydrolysis to occur. If the ionization of water is small compared to that of the acid formed, the hydrolysis is slight; but if relatively large, the extent of hydrolysis is great.

The calculation of the degree of hydrolysis may be made in the following manner. Let C equal the concentration of the cyanide in gram equivalent weights per liter of solution, and X equal the fraction of the ionic material which is hydrolyzed. From the equation which represents the hydrolysis, if the change in the hydroxide ion concentration on account of the water equilibrium be neglected,

$$[HCN] = [OH^-] = CX,$$
$$[CN^-] = (1 - X)C.$$

Substituting these numbers in equation (4),

$$\frac{(CX)(CX)}{C(1-X)} = \frac{CX^2}{1-X} = \frac{K_{water}}{K_{HCN}} = K_{hydrolysis}. \qquad (6)$$

If only a small per cent of the solute is hydrolyzed, $1 - X$ is so near 1 that little error is introduced if the difference is ignored.

$$CX^2 = \frac{K_{water}}{K_{HCN}}; \quad X = \sqrt{\frac{K_{water}}{CK_{HCN}}}. \qquad (7)$$

Suppose that a solution of potassium cyanide is 0.1 M. $C = 0.1$, $K_{water} = 1 \times 10^{-14}$, and $K_{HCN} = 7 \times 10^{-10}$, at 20°. Substituting these values in equation (7),

$$X = \sqrt{\frac{1 \times 10^{-14}}{0.1(7 \times 10^{-10})}} = 0.012.$$

In this reaction, the extent of hydrolysis is 1.2%.

$$[OH^-] = 0.1 \times 0.012 = 1.2 \times 10^{-3}.$$
$$[H_3O^+] = \frac{1 \times 10^{-14}}{1.2 \times 10^{-3}} = 8 \times 10^{-12}.$$

The hydrolysis of sodium carbonate also yields a basic solution. Carbonic acid is a weak acid and the secondary stage of its ionization is much less than the primary stage. The concentration of hydronium ions from water is too low to form more than an inap-

preciable trace of carbonic acid; but it is high enough to cause the formation of bicarbonate ions, producing a strongly basic solution.

$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^-.$$

The extent of the hydrolysis of sodium carbonate in 0.1 M. solution at 20° is 4% and the concentration of the hydroxide ion is equal to 4×10^{-3}. Similar results are obtained in the hydrolysis of the sodium and potassium salts of other weak acids, such as phosphoric, boric, and silicic acids, hydrogen sulfide, and the amphoteric hydroxides.

Hydrolysis of Cation Acids. As considered in the preceding chapter, many of the hydrated cations react with water to form hydronium ions and complex hydroxide cations. This is due to the fact that the size of the unhydrated cation and the charge which it bears are of such a nature as to attract the oxygen of the water molecule strongly and to repel the proton. When zinc sulfate dissolves in water, the zinc ions undergo hydrolysis.

$$Zn(H_2O)_6^{++} + H_2O \rightleftharpoons H_3O^+ + Zn(OH)(H_2O)_5^+.$$

Because of the formation of hydronium ions in this solution, it is necessary for the hydroxide ion concentration to undergo a corresponding decrease in order to maintain the conditions for equilibrium between water and its ions. Equilibrium is established in the solution when the concentrations of the zinc ions and of the hydroxide ions have decreased and the concentration of the hydronium ion has increased, so that all of the equilibria exist simultaneously, and the solution is acidic. The chlorides, nitrates, and sulfates of the aluminum, ferric, cupric, zinc, and many other metal ions hydrolyze to yield acidic solutions. The ammonium salts of the strong acids also hydrolyze to give acidic solutions, because the ammonium ion is a cation acid.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3.$$

The concentration of the hydronium ion in a 0.1 M. solution of ammonium chloride at 20° is 7.5×10^{-6}.

Hydrolysis of Salts of Cation Acids with Anion Bases. Salts of this class are hydrolyzed to a greater extent than those in which either the cations show little tendency to give up protons, or the anions show little tendency to take up protons. The reac-

tion of the cations with water to produce hydronium ions demands an acidic solution to establish equilibrium. The hydronium ions formed in this manner react with the anion base to produce a molecular acid or a complex anion. Consequently, the conditions required for equilibrium cannot be maintained until the concentrations of the ions of the salt have become so low that all of the equilibria may exist simultaneously in the same solution. If the acidic character of the cation is equal to the basic character of the anion, the resulting solution is neutral. If the two are not of the same strength, the character of the solution depends on the relative strength of the conjugate base and acid. The hydrolysis of ammonium carbonate illustrates these equilibria.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3.$$
$$CO_3^{--} + H_3O^+ \rightleftharpoons HCO_3^- + H_2O.$$

The combined effect of water on the two ions is shown by the single equation,

$$NH_4^+ + CO_3^{--} \rightleftharpoons NH_3 + HCO_3^-.$$

Three simple ionic equilibria are involved.

$$[H_3O^+] \times [OH^-] = K_{water}.$$
$$\frac{[CO_3^{--}] \times [H_3O^+]}{[HCO_3^-]} = K_{HCO_3^-}.$$
$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = K_{NH_3}.$$

At equilibrium, the ionic concentrations are adjusted so that all of these constants are satisfied:

$$\frac{[NH_3] \times [HCO_3^-]}{[NH_4^+] \times [CO_3^{--}]} = \frac{K_{water}}{K_{NH_3} \times K_{HCO_3^-}} = K_{hydrolysis}.$$

Since ammonia is more actively basic than the bicarbonate ion is acidic, the solution of ammonium carbonate is basic. This salt hydrolyzes to a greater extent than sodium carbonate because both the anion and the cation yield slightly ionized products. The concentration of the carbonate ion in 0.1 M. solution of sodium carbonate is 0.096 M.; and in 0.1 M. solution of ammonium carbonate, 0.024 M. Ammonium cyanide in 0.1 M. solution would be hydrolyzed to the extent of 99.3% at 20°.

Conditions Affecting the Extent of the Hydrolysis of Salts. In the preceding paragraphs it has been shown that the extent of hydrolysis of salts is normally small and that *it is dependent on the properties of the ions of the solute and of the molecular products which they form* by their reaction with water. The more weakly ionized the base or acid whose formation in the molecular state leads to hydrolysis, the greater the extent of hydrolysis. If both the acid and the base formed are weak, hydrolysis is more extensive than if one is strong. The solubility of the molecular product also plays a part in some of these reactions.

The hydrolysis of some salts is virtually complete but may be reversed. Bismuth trichloride contains the cation acid, hydrated bismuth ion. This ion is trivalent and the hydrolysis proceeds in stages, forming the $Bi(OH)^{++}$ ion in the primary stage, and the $Bi(OH)_2^+$ ion in the secondary stage. For simplicity the water of hydration is omitted from these formulas. The solubility of the chloride of the ion formed at the secondary stage of the hydrolysis is so slight that precipitation occurs, and the hydrolysis goes virtually to completion with the precipitation of bismuth oxychloride.

$$Bi^{+++} + 4\,H_2O \rightleftharpoons Bi(OH)_2^+ + 2\,H_3O^+.$$
$$Bi(OH)_2^+ + Cl^- \rightleftharpoons BiOCl\downarrow + H_2O.$$

Antimony trichloride, $SbCl_3$, exhibits a similar reaction. During the reaction hydronium ions accumulate in the solution. The hydrolysis is reversible and the addition of an excess of a strong acid, such as hydrochloric acid, dissolves the precipitate. The hydrolysis proceeds virtually to completion if one of the products of the reaction is very slightly soluble under the conditions of the experiment. If the other product which might form is a highly soluble strong electrolyte, the reaction is reversible.

There are also salts which are completely hydrolyzed in an irreversible reaction. Aluminum sulfide is a slightly soluble salt which yields the cation of the weak base, aluminum hydroxide, and the anion of the weak acid, hydrogen sulfide. Aluminum hydroxide is also slightly soluble and the solubility of hydrogen sulfide is low.

$$Al_2S_3\downarrow \rightleftharpoons 2\,Al^{+++} + 3\,S^{--}.$$
$$Al^{+++} + 6\,H_2O \rightleftharpoons Al(OH)_3 + 3\,H_3O^+.$$
$$S^{--} + 2\,H_3O^+ \rightleftharpoons H_2S + 2\,H_2O.$$

Neither the hydronium nor the hydroxide ions may remain in the water in contact with the solid in high enough concentrations to satisfy the requirements for their equilibrium with water. The hydrolysis of a salt is complete and irreversible if both of the products formed are not only weak, but are also slightly soluble. The sulfides and carbonates of the aluminum, ferric, and chromium ions are not obtained by precipitation from aqueous solution. The sulfides of the calcium, barium, strontium, and magnesium ions hydrolyze to form the hydrosulfide ion and molecular hydrogen sulfide, and the reaction is so nearly complete that these sulfides are not precipitated by the passage of hydrogen sulfide into solutions of their salts.

The extent of hydrolysis is increased by dilution if the reaction is due to the formation of a single weak electrolyte, either acidic or basic. Changes in concentration have no effect on the ionization constants of the substances involved; but they do affect the ratio between the concentrations of the materials, which in turn affects the extent of hydrolysis. If, however, both the acid and the base formed are weak, the ratio of the product of the concentrations of the acid and base produced to the product of the concentrations of the ions is not changed by dilution; and there is no effect on the extent of hydrolysis.

Changing the concentration of one of the ions involved, by the addition of an electrolyte which furnishes an ion in common, affects the extent of hydrolysis. The addition of ammonium chloride to a solution of ammonium carbonate increases the degree of hydrolysis of the carbonate, and the addition of ammonia decreases it.

The extent of hydrolysis is affected also by changes in temperature. This is due to the increased ionization of water at the higher temperatures. The ionization constant of water at 20° is 1×10^{-14}, but it is 49×10^{-14} at 100°. The increased concentration of the ions of water naturally increases the effects caused by these ions. The extent of hydrolysis in which molecular gases are formed is increased by a rise in the temperature because the solubilities of the gases are decreased. This change in solubility causes the completion of some hydrolytic reactions which normally yield an equilibrium mixture of products.

Applications of Hydrolysis. Solutions of sodium carbonate contain hydroxide and carbonate ions. Consequently, the use of

sodium carbonate as a precipitant may lead to the precipitation of insoluble carbonates or of insoluble hydroxides. The product actually obtained in any specific instance is determined by the relative solubility of these compounds. The addition of a sodium carbonate solution to a solution of a barium salt yields a precipitate of barium carbonate, because the carbonate is much less soluble than the hydroxide.

$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^-.$$
$$Ba^{++} + CO_3^{--} \rightleftharpoons BaCO_3\downarrow.$$

Magnesium salts, however, yield a precipitate of the hydroxycarbonate.

$$4\,Mg^{++} + 3\,CO_3^{--} + 2\,OH^- \rightleftharpoons Mg_4(OH)_2(CO_3)_3\downarrow.$$

Aluminum salts yield the hydroxide.

$$Al^{+++} + 3\,OH^- \rightleftharpoons Al(OH)_3\downarrow.$$

Calcium and strontium ions also yield the carbonate; copper and lead, the hydroxycarbonate; and chromium and ferric iron the hydroxides or hydrated oxides.

The precipitation of the calcium group of cations, free from magnesium carbonate, requires a regulated concentration of the hydroxide and carbonate ions. The precipitation must take place in basic solution, because the concentration of the carbonate ions is too low in acidic solutions. The concentrations of the carbonate and hydroxide ions must be low enough to avoid the precipitation of magnesium hydroxide or of the hydroxycarbonate. The solubility products of the carbonates of barium, calcium, and strontium are low enough to permit this condition to be established. The hydrolysis of ammonium carbonate is much more extensive than that of sodium carbonate, as discussed in a preceding paragraph. Furthermore, the concentration of hydroxide ions may be controlled by the addition of a solution of ammonium chloride in ammoniacal solution. Consequently, the concentration of both the carbonate and hydroxide ions may be regulated so as to obtain the desired separation through the use of ammonium carbonate as the precipitant in an ammoniacal solution containing ammonium chloride.

The hydroxides of the members of the iron group may be precipitated by hydrolysis from weakly acidic solutions. This is desirable

in analysis if the solution contains phosphate ions. In the presence of phosphate ions, the precipitation of the iron group hydroxides in the regular manner by the use of ammonia and ammonium chloride may cause the precipitation also of the phosphates of some of the ions of subsequent groups, such as barium and calcium phosphates. The phosphates may be removed along with the hydroxides of iron, aluminum, and chromium in weakly acidic solution if an excess of ferric ions is present. In order to bring about the precipitation, sodium or ammonium acetate is added to the weakly acidic solution. The solution is then heated to boiling and the ions of ferric iron, aluminum, and chromium are hydrolyzed through successive stages, yielding finally the hydrated oxides, which for simplicity may be represented as hydroxides.

$$C_2H_3O_2^- + H_3O^+ \rightleftharpoons HC_2H_3O_2 + H_2O.$$
$$Fe^{+++} + PO_4^{---} \rightleftharpoons FePO_4\downarrow.$$
$$Fe^{+++} + 2\,H_2O \rightleftharpoons Fe(OH)^{++} + H_3O^+.$$
$$Fe(OH)^{++} + 2\,H_2O \rightleftharpoons Fe(OH)_2^+ + H_3O^+.$$
$$Fe(OH)_2^+ + 2\,H_2O \rightleftharpoons Fe(OH)_3\downarrow + H_3O^+.$$

The complete precipitation of these ions as their hydroxides from the weakly acidic solution depends on the slight solubility of the hydroxides, and on the excess of acetate ions which prevent an increase in the concentration of the hydronium ions, as the water molecules are decomposed to maintain the supply of hydroxide ions.

EXERCISES

1. What is meant by hydrolysis? What is the cause of hydrolysis?
2. Under what conditions is the reaction of hydrolysis complete and irreversible?
3. Explain the completed hydrolysis of non-metal hydrides, free non-metals, calcium phosphide, calcium carbide, magnesium silicide, and magnesium nitride.
4. Under what conditions is the reaction of hydrolysis reversible, leading to a state of equilibrium?
5. Explain the presence of an excess of hydroxide ions in a solution of sodium sulfide.
6. What factors determine the extent of the hydrolysis of the anion bases?
7. What explanation may be advanced to account for the acidity of solutions of cupric sulfate, ferric chloride, aluminum chloride, and ammonium chloride?

8. Explain the fact that the extent of the hydrolysis of ammonium carbonate is greater than that of sodium carbonate. What analytical application is made of this difference? Explain.
9. Under what conditions is salt hydrolysis virtually complete? Select an example and explain the fact that hydrolysis is nearly complete. Tell how the reaction may be reversed and explain the reversal of the reaction.
10. Give an example of the complete and irreversible hydrolysis of a salt and explain in terms of the equilibria involved.
11. Explain the completed hydrolysis of a solution of an aluminum salt in the presence of an excess of an acetate at the boiling temperature of the solution.

SUPPLEMENTARY READINGS

Hammett, *Solutions of Electrolytes*, Chapter IV.

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Meldrum and Gucker, *Introduction to Theoretical Chemistry*, pp. 222–226; 271–276.

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CHAPTER XV

THE HYDROACIDS

Solutions of acids contain in common the hydronium ion and, on this account, exhibit a series of common reactions due to this ion. These general acid reactions are illustrated in the discussion of the hydrohalic acids. In addition, each acidic solution contains a specific anion and exhibits a second series of reactions characteristic of this ion. The reactions of the solution of an acid are additive, some of the reactions being due to the hydronium ions and others to the specific anions.

The hydroacids are molecular acids which give up protons, forming hydronium ions, when they dissolve in water. In the pure state they are the hydrides of certain of the non-metals. Not all non-metal hydrides are acidic; but the hydrides of the halogens, sulfur, and the cyanide radical yield hydronium ions in aqueous solution.

The Hydroacids of the Halogens. The most important of the hydroacids of the halogens is hydrochloric acid. These acids do not occur naturally in industrially important quantities. Gaseous hydrogen chloride is a component of some volcanic gases; and a small per cent of this substance is present as an important component of the gastric juices of animals. The preparation of the substances requires their formation from the naturally occurring salts.

Preparation of the Hydrohalic Acids. The preparation of these substances usually involves preparing first the gaseous hydrogen halides, which are then absorbed in water to form the acidic solutions. The hydrogen halides may be prepared by the reaction of an acid of high boiling point with the salts of these acids. In this reaction, concentrated sulfuric acid may be used for the preparation of hydrogen fluoride and hydrogen chloride, but is not suitable for hydrogen bromide and hydrogen iodide. The sulfuric acid must be concentrated because the hydrohalide gases are highly

soluble in water. Hence, no reaction occurs when dilute solutions of the salt and an acid are mixed because all of the materials may remain together in solution in the ionic state. The hydrohalides are not soluble in hot concentrated sulfuric acid; and the evolution of the gas causes the completion of the reaction. The reaction of sodium chloride with sulfuric acid occurs in two stages,

$$NaCl + H_2SO_4 \longrightarrow HCl\uparrow + NaHSO_4.$$
$$NaCl + NaHSO_4 \longrightarrow HCl\uparrow + Na_2SO_4.$$

In industrial practice, both stages of the reaction are employed; and a mixture of the salt and acid is warmed gently until the first stage of the reaction is completed, and is then heated more strongly. The complete reaction is represented by the equation,

$$2\,NaCl + H_2SO_4 \longrightarrow 2\,HCl\uparrow + Na_2SO_4.$$

The gas is absorbed in water to form hydrochloric acid solution. In the laboratory preparation, the gas may be collected by the upward displacement of air, as in the preparation of chlorine.

For the preparation of hydrogen fluoride, a mixture of calcium fluoride and concentrated sulfuric acid is heated in a retort made of platinum or lead, because hydrofluoric acid attacks glass.

$$CaF_2 + H_2SO_4 \longrightarrow 2\,HF\uparrow + CaSO_4.$$

The product may be condensed to a liquid which has a boiling point of 20°, or it may be absorbed in water to form a solution of the acid. The acid is usually stored in bottles made of rubber or of paraffin.

Bromine and iodine are less active than fluorine and chlorine; and their salts are less stable and are more easily oxidized to the free halogens. Hot concentrated sulfuric acid is active enough as an oxidizing agent to cause this change. Consequently, the reaction of concentrated sulfuric acid with a bromide yields a gaseous mixture containing some hydrogen bromide gas, bromine, and sulfur dioxide; and the per cent of hydrogen bromide in the mixture decreases as the temperature rises. A similar result is obtained in the reaction of hot, concentrated sulfuric acid with an iodide, except that the sulfuric acid is reduced in part to hydrogen sulfide.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr\uparrow.$$
$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI\uparrow.$$
$$2\,HBr + H_2SO_4 \longrightarrow 2\,H_2O + Br_2\uparrow + SO_2\uparrow.$$
$$8\,HI + H_2SO_4 \longrightarrow 4\,H_2O + 4\,I_2\uparrow + H_2S\uparrow.$$

In order to apply the general method for the preparation of volatile acids to the production of hydrobromic and hydriodic acids, an acid of high boiling point, but lower oxidizing activity than sulfuric acid, must be used. Phosphoric acid is suitable, and hydrogen bromide and hydrogen iodide may be prepared by warming the appropriate salt with phosphoric acid.

$$NaBr + H_3PO_4 \longrightarrow HBr\uparrow + NaH_2PO_4.$$
$$KI + H_3PO_4 \longrightarrow HI\uparrow + KH_2PO_4.$$

The hydrogen halides may be prepared by the direct union of the elements. This reaction is not an important source of hydrofluoric acid, but may be used for the other hydrohalic acids. Chlorine burns readily in an atmosphere of hydrogen, producing hydrogen chloride.

$$H_2 + Cl_2 \longrightarrow 2\,HCl.$$

The cost of hydrochloric acid by this method is prohibitive unless very cheap sources of hydrogen and chlorine are available. The electrolysis of solutions of sodium chloride yields chlorine, hydrogen, and sodium hydroxide. If the demand for sodium hydroxide is so great as to lead to the production of a greater amount of chlorine than the market will consume directly, the excess may be converted into hydrochloric acid. The direct union of hydrogen and bromine is the most important method of preparing hydrobromic acid. The velocity of the reaction is low; but very porous charcoal and platinum gauze are effective catalysts, so that the reaction takes place at a suitable rate when a mixture of hydrogen and bromine is passed in contact with the catalyst at a temperature of approximately 200°. The direct union of hydrogen and iodine takes place in the presence of a heated catalyst, and produces an equilibrium mixture of hydrogen iodide with free hydrogen and iodine. In commercial practice, the reaction is carried out at a temperature of 150°–200°, under a pressure of 200 pounds per square inch, with chromic oxide as a catalyst, and in the presence of water. Hydrogen iodide dissolves in the water, disturbing the equilibrium so as to increase the total yield of the acid.

The hydrohalic acids may be formed in solution by the hydrolysis of the halides of several of the non-metallic elements, such as phosphorus, sulfur, and arsenic.

$$2\,S_2Cl_2 + 6\,H_2O \longrightarrow 4\,H_3O^+ + 4\,Cl^- + SO_2\uparrow + 3\,S\downarrow.$$
$$AsBr_3 + 6\,H_2O \longrightarrow 3\,H_3O^+ + 3\,Br^- + H_3AsO_3.$$
$$PI_3 + 6\,H_2O \longrightarrow 3\,H_3O^+ + 3\,I^- + H_3PO_3.$$

The reaction is of practical importance only in the production of hydrobromic acid in limited amounts for laboratory use. In practice the preparation of the tribromide and its reaction with water are carried out in one process. Liquid bromine is allowed to drop into a suspension of red phosphorus in a small amount of water. The laboratory apparatus is represented in Fig. 99. Hydrogen bromide is very soluble and the volume of water in the reacting vessel must be kept very small, because this water must be saturated before the gaseous product can be obtained. Some bromine is carried along by the gas. This is absorbed by passing the gaseous mixture through a U-tube filled with glass beads which are coated with red phosphorus. Hydrogen bromide may be dissolved in water, thus forming a solution, or the gas may be collected by the upward displacement of air.

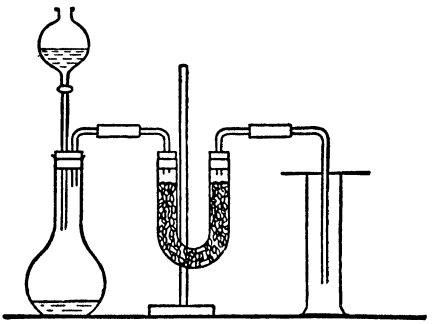

FIG. 99. — Laboratory Preparation of Hydrobromic Acid.

$$2\,P + 3\,Br_2 \longrightarrow 2\,PBr_3.$$
$$PBr_3 + 6\,H_2O \longrightarrow H_3PO_3 + 3\,H_3O^+ + 3\,Br^-.$$

Phosphorous acid remains dissolved in the water in the flask.

Solutions of the hydrohalic acids result from the displacement of less active non-metals from their hydroacids by reaction with the halogens. The applications of this reaction are limited. Hydriodic acid is the only one of the hydrohalic acids prepared by the displacement reaction. When hydrogen sulfide is passed into a suspension of pulverized iodine, sulfide ions are displaced by the iodine with the formation of a solution of hydriodic acid.

Properties of the Hydrogen Halides. These substances are colorless gases at room temperature, with the exception of hydrogen fluoride which has a boiling point of 20°. They are highly soluble in water and the gases fume strongly in moist air on account of

the condensation of water vapor in the air to form a fog of minute droplets of the acidic solutions. The gases possess disagreeable, pungent odors and produce an irritating effect on the nose and throat. In the pure liquid state the substances are poor conductors of the electric current; and the aqueous solutions are good conductors. Molecular weight determinations indicate that the substances exist in the gaseous state as single molecules, with the exception of hydrogen fluoride. Hydrogen fluoride also exists as single molecules at 100°; but it is partially in the form of complex molecules, H_6F_6, at lower temperatures. Approximately 80% of the gas is in this form at 20°. Each of these substances forms a constant boiling solution with water. In Table 23, the numerical values of several of the properties of the substances are listed.

TABLE 23

PROPERTIES OF THE HYDROGEN HALIDES

	HF	HCl	HBr	HI
Boiling point	20°	− 85°	− 67°	− 36°
Melting point	− 83°	− 114°	− 87°	− 51°
Critical temperature	—	51.4°	90°	151°
Solubility, g. per 100 g. H_2O (20° and 1 Atm.)	35.3	42	49	57
Constant boiling solution				
a. Boiling point	120°	110°	126°	127°
b. Wt. per cent of acid	35.4	20.24	47	57
Heat of formation of gas, cal. per mole	64,000	22,000	8,600	− 6,400

Reactions of the Hydrohalic Acids. The hydrogen halides decompose in aqueous solution with the formation of ions. Hydrochloric, hydrobromic, and hydriodic acids are completely ionized in dilute solution; but the reaction is reversible in concentrated solution.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-.$$

Hydrofluoric acid is a moderately weak acid, standing between acetic and phosphoric acids in strength.

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-.$$

The ionization constant at 20° is 7.2×10^{-4}. In concentrated solution, the acid yields the complex hydrogen fluoride ion, HF_2^-.

$$HF + F^- \rightleftharpoons HF_2^-.$$

The formula $:\ddot{F}:H:\ddot{F}:$ represents the electronic constitution of this complex ion. The reactions of the solutions of the highly ionized acids are due entirely to the ions, but hydrofluoric acid solution also exhibits reactions due to the molecular material.

All of these acids in aqueous solutions show the reactions of hydronium ions. They react with active metals and with basic substances, such as metallic oxides and hydroxides, ammonia, and the salts of weak acids.

$$Mg + 2\,H_3O^+ \longrightarrow Mg^{++} + H_2\uparrow + 2\,H_2O.$$
$$ZnO + 2\,H_3O^+ \longrightarrow Zn^{++} + 3\,H_2O.$$
$$OH^- + H_3O^+ \rightleftharpoons 2\,H_2O.$$
$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O.$$
$$CO_3^{--} + 2\,H_3O^+ \rightleftharpoons CO_2\uparrow + 3\,H_2O.$$
$$FeS + 2\,H_3O^+ \longrightarrow Fe^{++} + H_2S\uparrow + 2\,H_2O.$$

Most of these reactions are reversible to some extent; but with strong acids they go virtually to completion. The activity of hydrofluoric acid in these general acid reactions is lower than that of the other three hydrohalic acids, because it is not highly ionized.

The hydrohalic acids also exhibit reactions which are due to their anions. The anions of these acids have an electrovalence of 1 −. Consequently, the loss of an electron converts each ion into an electrically neutral atom. The process is *the oxidation of anions.* The oxidation of hydrofluoric acid cannot be carried out in aqueous solution because the stability of the ion is too great. This acid may be decomposed by the passage of an electric current through the anhydrous liquid containing dissolved potassium hydrogen fluoride. Fluorine is discharged at the anode.

$$2\,F^- - 2\,\epsilon \longrightarrow F_2.$$

The chloride, bromide, and iodide ions may be oxidized by the electrolysis of aqueous solutions.

At the anode, $2\,Cl^- - 2\,\epsilon \longrightarrow Cl_2.$
At the cathode, $2\,H_3O^+ + 2\,\epsilon \longrightarrow H_2 + 2\,H_2O.$

They may also be oxidized in acidic solutions by oxidizing agents such as manganese dioxide.

$$MnO_2 + 4\,H_3O^+ + 2\,Cl^- \longrightarrow Mn^{++} + Cl_2\uparrow + 6\,H_2O.$$

A second anion reaction of these acids is *the precipitation of slightly soluble halides.* The chlorides, bromides, and iodides of the silver, mercurous, and lead ions are slightly soluble. Mercuric iodide is also slightly soluble. The chlorides, bromides, and iodides of the other common cations are at least moderately soluble. Most of the fluorides have low solubility. Potassium and silver fluorides are highly soluble and sodium fluoride is only moderately soluble.

In accord with this summary of solubilities, one may select examples to illustrate the reactions of the hydrohalic acids involving precipitation caused by their anions.

$$Ba^{++} + 2\,F^- \rightleftharpoons BaF_2\downarrow.$$
$$Hg_2^{++} + 2\,Cl^- \rightleftharpoons Hg_2Cl_2\downarrow.$$
$$Pb^{++} + 2\,Br^- \rightleftharpoons PbBr_2\downarrow.$$
$$Hg^{++} + 2\,I^- \rightleftharpoons HgI_2\downarrow.$$

In each instance precipitation is brought about by adding the one solution to the other in such quantities that the product of the molar concentrations of the ions would exceed the solubility product if all of the ions could remain together in the solution. Since this condition cannot exist at equilibrium, precipitation occurs as demanded by the equilibrium in the saturated solution,

$$[Ba^{++}] \times [F^-]^2 = S_{BaF_2}.$$

In the presence of a trace of moisture, the gaseous halides of hydrogen unite with ammonia to form a white smoke consisting of solid particles of the ammonium halide.

$$NH_3 + HCl \longrightarrow NH_4Cl.$$

The most important of the reactions of hydrofluoric acid is that with silica and the complex silicates to form the gaseous product, silicon fluoride. This reaction is not due to the hydronium ions, but to the stability of silicon fluoride. Common glass is composed of sodium and calcium silicates together with an excess of silicon dioxide. The reactions of these substances with hydrofluoric acid cause the etching of glass.

$$SiO_2 + 4\,HF \longrightarrow SiF_4\uparrow + 2\,H_2O.$$
$$Na_2SiO_3 + 6\,HF \longrightarrow SiF_4\uparrow + 3\,H_2O + 2\,NaF.$$
$$CaSiO_3 + 6\,HF \longrightarrow SiF_4\uparrow + 3\,H_2O + CaF_2.$$

The markings on thermometer stems and on graduated cylinders and flasks may be etched by coating the glass with paraffin and cutting through this layer to uncover the glass at the desired points. When the object is then exposed to the action of the acid, the glass is attacked at the unprotected areas.

Stability of the Hydroacids of the Halogens. In the preceding paragraphs, the similarities in the properties and reactions of the hydrohalic acids, both in the gaseous condition and in solution, have been discussed. The similarities in behavior are especially close for hydrochloric, hydrobromic, and hydriodic acids. These substances exhibit similar reactions, not only because they contain replaceable atoms of hydrogen, but also because the properties of the chloride, bromide, and iodide radicals are very much alike. The most important difference in properties among these substances is in their stability. In Chapter VII, the relative activity of the halogens was discussed, and it was shown that the heat of formation of hydrogen fluoride is the greatest and of hydrogen iodide the least among the four hydrides. This means, of course, that hydrofluoric acid is the most stable and hydriodic acid the least stable of the hydrohalic acids. Neither hydrochloric nor hydrofluoric acid is oxidized by hot, concentrated sulfuric acid; but hydrochloric acid is oxidized by manganese dioxide, whereas hydrofluoric acid is not oxidized by this substance. Both hydrobromic and hydriodic acids are oxidized by hot concentrated sulfuric acid and also by manganese dioxide; and hydriodic acid is oxidized slowly by atmospheric oxygen.

Uses of the Hydrohalic Acids. Hydrochloric acid is the only one of these acids having extensive uses due to its general acidic reactions. It is used in the laboratory as a convenient strong acid and as a source of chloride ions and of chlorine. Commercially, it is used in the preparation of ammonium chloride for the manufacture of dry cells, for dissolving the mineral matter in bone ash to prepare bone-black for use in clarifying sugar solutions, in cleaning rust from the surface of metals to be enameled, in the preparation of the chlorides of many of the metals, and in the manufacture of certain fine chemicals, glue, dyes, soap, textiles, and many other products.

The uses of hydrofluoric acid are based on its reactions with silica and the silicates. In addition to its use in the etching of

glass, it is used in cleaning metal castings, polishing cut glass, and in the decomposition of complex silicates for analysis.

Hydrobromic acid and hydriodic acid find limited use in the laboratory in the preparation of some of their salts. Hydriodic acid has some uses as a reducing agent. There are, however, no extensive uses of these acids.

Hydrocyanic Acid. HCN. This acid is similar in some of its reactions to the hydrohalic acids. Cyanide ions exhibit many properties similar to those of the halide ions; and both the acid and its salts bear names similar to those of binary compounds. The acid is weak and volatile and, consequently, may be displaced from its salts by the action of a number of other acids.

$$CN^- + H_3O^+ \rightleftharpoons HCN\uparrow + H_2O.$$

The pure acid is a colorless liquid with a normal boiling point at 26°. The acid is very poisonous so that great care must be exercised to avoid inhaling the vapors from acidified solutions of cyanides. Hydrocyanic acid is used as an insecticide in the citrus fruit groves, and is also used in the fumigation of ships. It is a weak acid, the ionization constant being equal to 4×10^{-10} at 20°. Therefore, its reactions due to hydronium ions are not prominent and the cyanide ion is basic. A number of the cyanides have low solubility and are, consequently, easily precipitated. Silver cyanide may be obtained as a white precipitate.

$$Ag^+ + CN^- \rightleftharpoons AgCN\downarrow.$$

This salt is soluble in the presence of an excess of cyanide ions, due to the formation of the complex silver cyanide ion.

$$Ag^+ + 2\,CN^- \rightleftharpoons Ag(CN)_2^-.$$
$$[Ag^+] \times [CN^-] < S_{AgCN}.$$

Many of the metal ions react with cyanide ions to produce complex ions of varying degrees of complexity.

Hydrogen Sulfide. Hydrosulfuric Acid. H_2S. This substance occurs free in nature in the water of sulfur springs and in volcanic gases. It is formed also in natural processes by the decay of organic matter in the absence of a sufficiently large supply of air to cause complete oxidation. The odor of rotten eggs is due in part to the presence of hydrogen sulfide.

Preparation of Hydrogen Sulfide. Although hydrogen sulfide results from the direct union of hydrogen and sulfur, it is commonly prepared by the action of acids which do not possess active oxidizing properties on the sulfides of metals, such as ferrous sulfide. Since the reaction proceeds readily at ordinary temperatures, it may be controlled by regulating the rate of the admission of the acid to the sulfide. For this purpose, the Kipp generator, Fig. 100, is convenient.

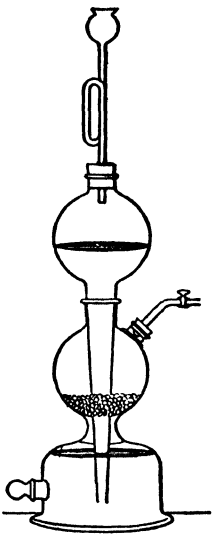

FIG. 100. — Kipp Generator.

$$FeS + 2\,H_3O^+ \longrightarrow H_2S\uparrow + Fe^{++} + 2\,H_2O.$$

Hydrochloric acid and dilute sulfuric acid are suitable for this reaction; but concentrated sulfuric acid and nitric acid are not suitable because of their strong oxidizing properties.

Properties of Hydrogen Sulfide. Hydrogen sulfide is a gas which has a very disagreeable odor. It is somewhat more dense than air and is moderately soluble in water, about three volumes of the gas in one of water at room temperatures and atmospheric pressure. Liquid hydrogen sulfide has a boiling point of $-60.3°$, a freezing point of $-85.5°$, and a critical temperature of 100.4°. The gas is very poisonous, one part in two hundred parts of air being likely to prove fatal if breathed for any considerable length of time.

Chemical Reactions of Hydrogen Sulfide. The gas burns in air with the formation of water and sulfur dioxide if the combustion is complete.

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2.$$

Water and free sulfur are the products of the incomplete combustion with a limited proportion of air.

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S.$$

Hydrogen sulfide in solution is a weak acid which contains two replaceable hydrogen atoms per molecule. It is ionized to the extent of only 0.07% in a 0.1 N. solution, producing hydronium and hydrosulfide ions.

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-.$$

The hydrosulfide is only slightly dissociated by water.

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{--}.$$

The acid reactions of hydrogen sulfide are not important except for the preparation of some of the soluble sulfides. Sodium hydrosulfide is formed when sodium hydroxide solutions are saturated with hydrogen sulfide.

$$H_2S + OH^- \rightleftharpoons HS^- + H_2O.$$

The normal salt is prepared by the addition of an equivalent amount of sodium hydroxide to the hydrosulfide.

$$HS^- + OH^- \rightleftharpoons S^{--} + H_2O.$$

Due to the sulfide ions present in its solution, hydrogen sulfide reacts with dissolved salts which furnish the metal ions of slightly soluble sulfides. The passage of hydrogen sulfide into a solution of cupric sulfate causes the precipitation of the black cupric sulfide.

$$Cu^{++} + H_2S + 2\,H_2O \longrightarrow CuS\downarrow + 2\,H_3O^+.$$

The sulfides of most of the metal ions except the members of the alkali and alkaline earth families are slightly soluble. Nevertheless, on account of the hydrolysis of the sulfide ion, the concentrations of the ions are not great enough to precipitate the sulfides of aluminum, ferric iron, and chromium in addition to those of the alkali and alkaline earth metals. The concentration of the sulfide ions is greatly affected by changes in the concentration of the hydronium ion. This effect and the resulting differences in the precipitation conditions for different metal sulfides are applied extensively in analysis.

A simple test for the presence of hydrogen sulfide is based on the formation of insoluble lead sulfide. A piece of filter paper moistened with a solution of lead acetate or lead nitrate is held in contact with the gas to be tested, and the formation of a black deposit of lead sulfide is observed if hydrogen sulfide is present.

$$Pb^{++} + H_2S + 2\,H_2O \longrightarrow PbS\downarrow + 2\,H_3O^+.$$

Solutions of hydrogen sulfide also have mild reducing properties on account of the presence of sulfide ions in low concentration. The passage of hydrogen sulfide into an acidic solution of a ferric salt causes its reduction to the ferrous ion.

$$2\,Fe^{+++} + H_2S + 2\,H_2O \longrightarrow 2\,Fe^{++} + S\downarrow + 2\,H_3O^+.$$

Analytical Uses of Hydrogen Sulfide. Hydrogen sulfide is a weak electrolyte which is only slightly soluble. The concentrations of the hydrogen and sulfide ions are related as shown by the constant,

$$\frac{[H_3O^+]^2 \times [S^{--}]}{[H_2S]} = 1 \times 10^{-22}.$$

The concentration of molecular hydrogen sulfide in its saturated solution at 20° is approximately 0.1 M. Therefore, the equilibrium concentrations of the ions in the saturated solution are shown by the constant,

$$[H_3O^+]^2 \times [S^{--}] = 1 \times 10^{-22} \times 1 \times 10^{-1} = 1 \times 10^{-23}.$$

Two points in connection with this constant are significant to this discussion: the constant is a small number, which represents the fact that only small concentrations of hydronium and sulfide ions can exist in equilibrium with each other; and the molar concentration of the sulfide ions varies inversely with the square of the concentration of the hydronium ion. The concentration of the hydronium ion may be increased by the addition of stronger acids. If the molar concentration of the hydronium ion is increased one thousandfold, the concentration of the sulfide ions is automatically decreased one millionfold. Similarly, the addition of an excess of a base increases the concentration of the hydroxide ion. This decreases the concentration of hydronium ions and permits an increase in the concentration of sulfide ions. Therefore, the concentration of the sulfide ions may be varied from large to small values and may be regulated within very narrow limits by controlling the concentrations of the hydronium ion.

The metal sulfides differ greatly in solubility, and hydrogen sulfide is used extensively in analysis to produce separations between the metal ions. The sulfides of the ions of the *tin group*, Sn^{++}, Sn^{++++}, Sb^{+++}, As^{+++}, and of the *copper group*, Cu^{++}, Hg^{++}, Pb^{++}, Bi^{+++}, Cd^{++}, are so slightly soluble that they may be precipitated by the action of hydrogen sulfide, even in the presence of the concentration of hydronium ions furnished by dilute, 0.3 N., solutions of strong acids such as hydrochloric acid. The solubility products of these sulfides are very small. The solubility product of lead sulfide is estimated to be 1×10^{-29}, and of the sulfides of most of the other ions in these groups even

smaller. The concentration of the sulfide ions in the dilute acidic solution, even though it is very small, is still great enough to cause the precipitation of these sulfides.

$$[Pb^{++}] \times [S^{--}] > S_{PbS},\ 1 \times 10^{-29}.$$

The ions of the tin and copper groups are also called the ions of the *acid hydrogen sulfide group*.

In solutions which contain an hydronium ion concentration equal to 0.3 M., the sulfide concentration is so low that zinc sulfide, solubility product 4.5×10^{-24}, manganous sulfide, 5.6×10^{-16}, and the alpha forms of the sulfides of nickel and cobalt, solubility products 3×10^{-21} and 7×10^{-23}, respectively, do not precipitate, unless the concentrations of the metal ions are high.

$$[Mn^{++}] \times [S^{--}] < S_{MnS},\ 5.6 \times 10^{-16}.$$

In the presence of the hydroxide ions of a basic solution, the concentration of the hydronium ions is very small

$$[H_3O^+] \times [OH^-] = 1 \times 10^{-14}.$$

The concentration of sulfide ions which may be obtained by the passage of hydrogen sulfide into a basic solution is relatively great. Under these conditions the sulfides of the ions of the *nickel group*, Ni^{++}, Co^{++}, Mn^{++}, Zn^{++}, may be precipitated.

$$[Mn^{++}] \times [S^{--}] > 5.6 \times 10^{-16}.$$

Ferrous sulfide is also formed by the action of hydrogen sulfide in basic solution; but the ferrous ions may be removed from the solution before the precipitation of the nickel group.

Slightly soluble sulfides may be dissolved by decreasing the concentration of sulfide ions. Many of the sulfides are dissolved readily by the action of dilute hydrochloric acid, *e.g.*, ferrous, manganous, and zinc sulfides.

$$ZnS\downarrow \rightleftharpoons Zn^{++} + S^{--}.$$
$$[Zn^{++}] \times [S^{--}] = S_{ZnS},\ 4.5 \times 10^{-24}.$$

When hydrochloric acid is added,

$$S^{--} + 2\,H_3O^+ \rightleftharpoons H_2S + 2\,H_2O.$$
$$[S^{--}] \times [H_3O^+]^2 = 1 \times 10^{-23}.$$

The concentration of the sulfide ion is thus reduced; and

$$[Zn^{++}] \times [S^{--}] < 4.5 \times 10^{-24}.$$

Therefore, the precipitate dissolves,

$$ZnS + 2\,H_3O^+ \longrightarrow Zn^{++} + H_2S\uparrow + 2\,H_2O.$$

Nickel and cobalt sulfides are not precipitated from acidic solutions, but the sulfides dissolve only very slowly in dilute acidic solutions. These sulfides are assumed to exist in two forms. The less stable forms, NiSα and CoSα, which are first formed by precipitation in ammoniacal solution, are more soluble than the second modifications, into which they quickly change. Precipitation, therefore, demands conditions which will bring down the more soluble form; and dissolving the sulfide requires that the more slightly soluble and more slowly dissolving variety be taken into solution. This may be applied analytically in dissolving zinc and manganous sulfides from the nickel cation group sulfide precipitate by the action of dilute hydrochloric acid, leaving a residue of the sulfides of nickel and cobalt.

There are also many sulfides which are not dissolved by hydrochloric acid but are dissolved by nitric acid, because its oxidizing action leads to a great decrease in the concentration of sulfide ions. The sulfides of copper, lead, bismuth, and cadmium are dissolved by dilute nitric acid; but mercuric sulfide is so slightly soluble that the combined action of nitric acid and hydrochloric acid is required to cause it to go into solution. Mercuric ions yield a chloride complex ion, $HgCl_4^{--}$, and cannot accumulate in the solution in the presence of the high concentration of chloride ions furnished by hydrochloric acid, so that the concentration of simple mercuric ions is kept low. Under these conditions, the oxidizing action of nitric acid is great enough to dissolve mercuric sulfide.

The separation of the ions of the elements of the tin group from each other may be accomplished by the regulation of the concentration of the sulfide ion. The properly prepared precipitate containing the sulfides of all three elements is digested with concentrated, 12 N., hydrochloric acid. The sulfides of antimony and tin dissolve; but the sulfide of arsenic is so slightly soluble that it is not affected by concentrated hydrochloric acid. If the hot solution containing the antimony and tin salts is diluted to make the hydronium ion concentration 2 – 2.5 N. and the solution is saturated with hydrogen sulfide, only antimony sulfide precipitates.

EXERCISES

1. What are the hydroacids?
2. What general method is used for the preparation of the acids of low boiling point? In the preparation of hydrogen chloride and hydrogen fluoride by this method, why is concentrated sulfuric acid used instead of dilute sulfuric acid?
3. Why is the reaction of concentrated sulfuric acid with the salt not suitable for the preparation of hydrogen bromide and hydrogen iodide? Could dilute sulfuric acid be used for this purpose? Explain.
4. What methods are used for the preparation of hydrogen bromide and hydrogen iodide?
5. What is a constant boiling solution? Explain the fact that the hydrogen halides give constant boiling solutions with water.
6. Illustrate by equations four reactions of the hydrohalic acids which are due to the hydronium ions present in their solutions.
7. Illustrate by equations reactions of hydrochloric, hydrobromic, and hydriodic acids which are due to the halide ions.
8. Explain the fact that silver chloride dissolves in an excess of a solution of ammonia, but silver iodide does not do so.
9. Explain the solution of silver cyanide in the presence of an excess of cyanide ions.
10. Account for the fact that hydrogen cyanide and hydrogen sulfide may be prepared by the action of a dilute and weak acid on solutions of the salts of these acids.
11. The sulfide and cyanide ions are anion bases. Explain.
12. Discuss the equilibria in aqueous solution of hydrogen sulfide, and account for the effect of adding an excess of an acid, a base, or an oxidizing agent.
13. Account for the separation of the ions of the tin and copper analytical groups from the ions of the nickel group by the use of hydrogen sulfide.
14. Explain the precipitation of the sulfides of the nickel group ions in basic, but not in acidic, solutions.
15. Account for the fact that the sulfides of nickel and cobalt are not precipitated by the passage of hydrogen sulfide into dilute acidic solutions of these ions, but the solid sulfides do not dissolve readily in dilute acids.

CHAPTER XVI

THE OXIDES AND HYDROXIDES OF THE METALS

The oxides and hydroxides of the metals possess in common the property of reacting with acids to produce water and salts. In such reactions, the acids are neutralized by the reaction of the hydronium ions with the oxide radical of the metal oxide and with the hydroxide radical of the metal hydroxide. Since, strictly speaking, the bases are substances which combine with protons, these oxides and hydroxides are not themselves bases; but they contain the basic oxide and hydroxide radicals, respectively. However, a logical extension of the classification includes among the bases the compounds which contain bases in the free or ionic state.

THE OXIDES OF THE METALS

The general reactions of these oxides with acids and with water have been discussed in Chapters IV and XIII. Many of the metal oxides unite directly with certain non-metal oxides to form salts. Most of the metal oxides react with active reducing agents, such as carbon, to liberate the free metal.

The Preparation of the Oxides of the Metals. Many of these oxides may be formed by the direct union of the metals with oxygen. The noble metals, gold, silver, and platinum, do not combine directly with oxygen under ordinary conditions; and the combustion of sodium yields the peroxide, Na_2O_2, while the combustion of potassium yields the oxide, KO_2. The hydroxides and the hydrated oxides of the common metals, except sodium, potassium, and barium, decompose at moderate temperatures to form the oxide and water.

$$Cu(OH)_2 \longrightarrow CuO + H_2O.$$
$$Al_2O_3(H_2O)_3 \longrightarrow Al_2O_3 + 3\ H_2O.$$

The nitrates and carbonates of most of the metals decompose when they are heated. Some of the metal oxides are themselves

unstable at the temperature required to decompose the other compounds, so that they yield the free metal instead of the oxide.

$$2\ Pb(NO_3)_2 \longrightarrow 2\ PbO + 4\ NO_2 + O_2.$$
$$ZnCO_3 \longrightarrow ZnO + CO_2.$$
$$Hg(NO_3)_2 \longrightarrow Hg + 2\ NO_2 + O_2.$$

The carbonates of sodium and potassium are stable and the nitrates decompose to yield the nitrite and oxygen.

$$2\ NaNO_3 \longrightarrow 2\ NaNO_2 + O_2.$$

By heating metallic sodium or potassium with its own nitrate or hydroxide, the simple oxide may be obtained.

$$2\ NaNO_3 + 10\ Na \longrightarrow 6\ Na_2O + N_2.$$
$$2\ KOH + 2\ K \longrightarrow 2\ K_2O + H_2.$$

The oxides of some of the metals are produced by the combustion of the sulfides in air.

$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2.$$

This reaction is important as a step in the production of the metals from their sulfide ores.

Calcium Oxide. Quicklime. CaO. This oxide is always prepared industrially by the decomposition of *limestone*, $CaCO_3$. The decomposition of limestone is an endothermic reaction which is reversible.

$$CaCO_3 \rightleftharpoons CaO + CO_2 - 42{,}900\ cal.$$

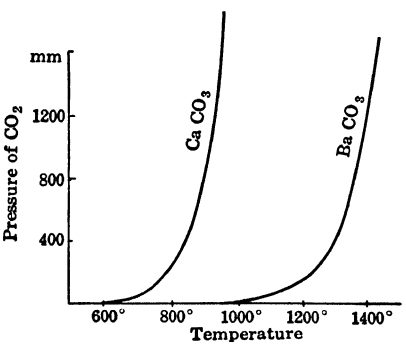

FIG. 101. — Pressures of Carbon Dioxide in Equilibrium with Calcium and Barium Carbonates.

The pressure of carbon dioxide in equilibrium with the oxide is about 2.3 mm. at 600°; 168 mm. at 800°; and 760 mm. at 910°, Fig. 101. Consequently, temperatures above 900° are necessary to complete the conversion of limestone into quicklime by heating the material in a retort. The same change may be brought about at much lower temperatures by blowing a current of a gas over the heated limestone to

sweep away the carbon dioxide, thus keeping its partial pressure below the equilibrium pressure.

The modern lime kiln is a large tower about 100 feet in height and 10 feet in diameter, Figs. 102 and 103. The upper portion is a storage hopper into which the limestone is fed. The heated portion of the kiln is approximately 50 feet in height. The flame of the burning fuel sweeps in from the side of the kiln. For the use of solid fuels, furnaces are built at the side of the kiln to prevent the mixing of the ash with the lime. A current of air rises through the kiln, sweeping out the carbon dioxide. Rotary kilns are also employed in the production of quicklime. The limestone gradually works its way down through the hottest part of the rotating kiln where complete decomposition takes place.

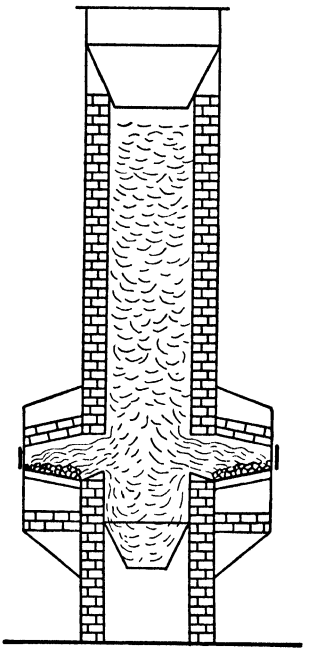

FIG. 102. — Vertical Section of Shaft Lime Kiln.

Properties and Reactions of Calcium Oxide. Calcium oxide is a white solid which melts at about 2700°. It becomes incandescent when it is strongly heated and emits a brilliant white light, the

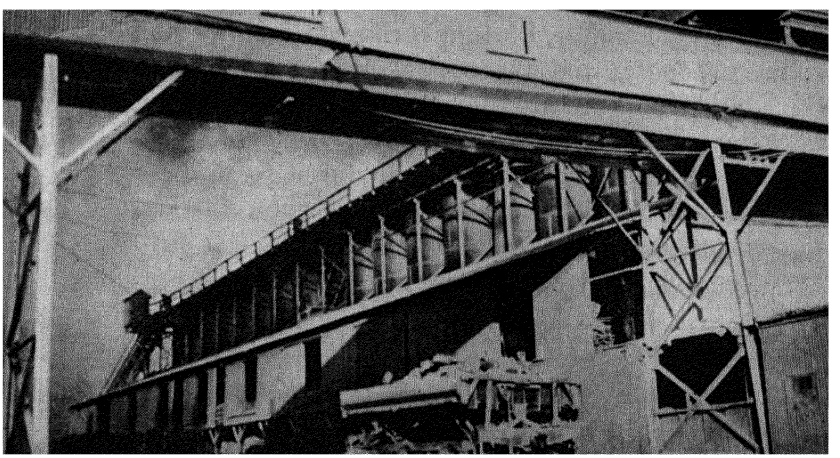

FIG. 103. — Shaft Kiln Lime Plant. (Courtesy of National Lime Association.)

limelight. The oxide is very stable and does not decompose at the temperature of the electric arc. It enters into the usual reaction of the oxides of the metals with water, with acidic oxides, and with acids.

$$CaO + H_2O \longrightarrow Ca(OH)_2.$$
$$CaO + SiO_2 \longrightarrow CaSiO_3.$$
$$CaO + 2\,H_3O^+ \longrightarrow Ca^{++} + 3\,H_2O.$$

The oxide becomes air-slaked when it is exposed for some time to air, combining with water and carbon dioxide. Calcium oxide yields the carbide when it is strongly heated with carbon.

$$CaO + 3\,C \longrightarrow CaC_2 + CO.$$

Industrial Importance of Calcium Oxide. The production of lime in the United States in 1939 was approximately 4,255,000 tons. Large quantities of this substance are consumed in making slaked lime used in plaster and mortar in building operations. It also has extensive uses in agriculture for the treatment of acid soils; and it is used in water treatment and in the refining of sugar. In the chemical industries, lime is important in the manufacture of glass, calcium carbide, bleaching powder, the hydroxides of sodium and potassium, and many other important substances.

Barium Oxide. BaO. Barium Peroxide. BaO_2. Barium oxide is also prepared by the decomposition of the naturally occurring carbonate. Barium carbonate is more stable than calcium carbonate; and the partial pressure of carbon dioxide in the equilibrium mixture at each temperature is lower than in the limestone decomposition, Fig. 101. By mixing coke with the carbonate, the carbon dioxide is reduced to the monoxide, thus lowering the partial pressure of the carbon dioxide and largely preventing the reverse reaction.

$$BaCO_3 \longrightarrow BaO + CO_2.$$
$$CO_2 + C \longrightarrow 2\,CO.$$

When barium oxide is heated moderately in air under pressure, it combines with oxygen to form the peroxide,

$$2\,BaO + O_2 \longrightarrow 2\,BaO_2.$$

Barium peroxide is a salt of the weak acid, hydrogen peroxide. Consequently, it reacts with stronger acids, such as sulfuric acid, with the formation of hydrogen peroxide.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2.$$

Magnesium Oxide. MgO. This oxide also is prepared by the decomposition of the carbonate. The oxide is stable toward heat and is highly infusible. On account of these properties it is used in the manufacture of firebrick for the lining of furnaces. It is used, mixed with asbestos, for the insulation of hot water and steam pipes. Magnesium oxide is used in the vulcanization of rubber and as an absorbent in the production of dynamite. As a basic oxide, it is used in steel furnaces for the removal of acidic substances, such as silicon dioxide and phosphorus pentoxide, through the formation of a slag.

$$MgO + SiO_2 \longrightarrow MgSiO_3.$$

A mixture of magnesium and calcium oxides, prepared by heating dolomite, $MgCO_3 \cdot CaCO_3$, has extensive uses in steel furnaces instead of magnesium oxide alone.

Zinc Oxide. ZnO. The oxide occurs naturally as an ore of zinc. It is also prepared by the decomposition of the carbonate and by the combustion of the sulfide. When prepared in this way, the oxide is important as a source of the metal; but it contains impurities and is not suitable for the direct uses of the oxide. Zinc oxide is prepared industrially by the combustion of the metal. It is used extensively as a filler in rubber for the manufacture of automobile tires and as a white pigment in paint and enamels, in the manufacture of oilcloth and linoleum, and in the preparation of zinc oxide ointments. A mixture of zinc oxide, gutta-percha, and Venice turpentine is used in making adhesive plaster.

Other Metal Oxides. Oxides of most of the metals may be prepared by one or more of the general methods illustrated in the preceding paragraphs. Some of these oxides will be discussed later in connection with the metals. Several of the oxides occur naturally and are important ores of the metals, *e.g.*, the oxides of iron and aluminum. Other oxides are prepared as intermediates in the production of metals from their sulfide and carbonate ores.

THE HYDROXIDES OF THE METALS

The hydroxides of the metals are basic in reaction because they contain the hydroxide radical which combines with hydronium ions. The soluble metal hydroxides yield the hydroxide ion in solution and they, consequently, possess in common the properties of this ion. They produce characteristic colors with indicators; *e.g.*, they cause litmus to turn blue, and phenolphthalein to turn red. They react with acids, with non-metal oxides, and with solutions containing ions which yield insoluble hydroxides or hydrated oxides.

$$OH^- + H_3O^+ \rightleftharpoons 2\ H_2O.$$
$$2\ OH^- + CO_2 \rightleftharpoons H_2O + CO_3^{--}.$$
$$2\ OH^- + Zn^{++} \rightleftharpoons Zn(OH)_2 \downarrow.$$

The metal hydroxides of low solubility react with the acids and with some of the non-metal oxides. There are great differences in the solubilities of the metal hydroxides; but, with the exception of the hydroxides of sodium, potassium, barium, strontium, and calcium, the hydroxides of the common metals have low solubility and may easily be precipitated. Ammonia is a highly soluble, weak base.

Preparation of the Hydroxides of the Metals. The soluble metal hydroxides may be prepared by several methods. They result from the reaction of the active metals with water, the union of the metal oxides with water, the electrolysis of salt solutions, and the precipitation of a slightly soluble salt, leaving the metal and hydroxide ions in solution. The first of these reactions is not of practical importance. The other methods will be illustrated in the following discussion of some of the important compounds. The hydroxides of low solubility are precipitated directly from solution.

The Hydroxides of Sodium and Potassium. These substances are strong, highly soluble, basic hydroxides. They are prepared by the same methods, and are so similar in properties that they may be used interchangeably for many purposes, except for the preparation of specific sodium and potassium compounds. Since sodium hydroxide is the cheaper of the two, it is the more extensively prepared and used.

Preparation of Sodium Hydroxide. The preparation of this compound by the *lime-soda method* depends on the slight solubility of calcium carbonate. Sodium carbonate solutions are boiled in iron vessels with a suspension of calcium hydroxide. As calcium carbonate precipitates, moderately soluble calcium hydroxide continues to dissolve, keeping the solution saturated with this substance.

$$2\,Na^{++} + CO_3^{--} + Ca^{++} + 2\,OH^- \longrightarrow CaCO_3\downarrow + 2\,Na^+ + 2\,OH^-.$$

After the reaction is complete the solids are allowed to settle. The clear liquid containing sodium and hydroxide ions and a low concentration of calcium ions is drawn off and evaporated.

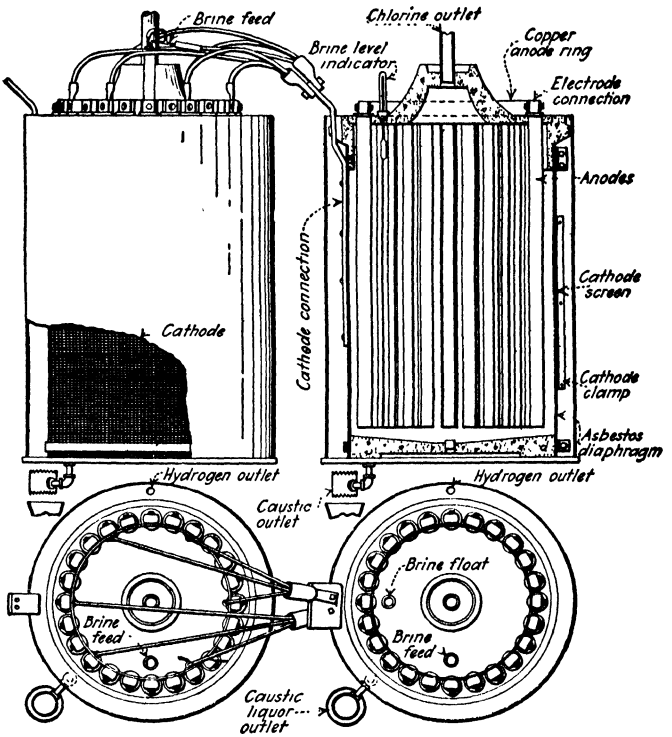

FIG. 104. — Cross Section of Vorce Cylindrical Cell. (Courtesy of Westvaco Chlorine Products Corporation.)

The electrolysis of saturated solutions of sodium chloride is an important industrial source of sodium hydroxide. Hydrogen is discharged at the cathode, leaving a basic solution; and chlorine

is discharged at the anode. The necessity for a special type of cell to prevent the mixing of the chlorine with the basic solution is discussed in Chapter VII, in connection with the preparation of chlorine. Among the cells for the production of sodium hydroxide and of chlorine in addition to the Nelson cell, the Vorce cell, Figs. 104 and 105, is extensively used. This cell

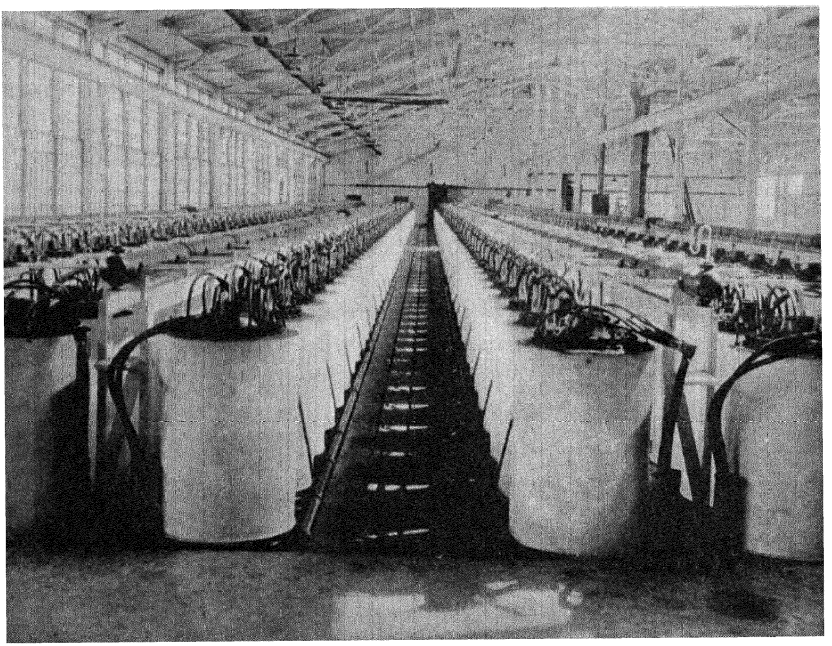

FIG. 105. — Vorce Cells. (Courtesy of Westvaco Chlorine Products Corporation)

is cylindrical and is very compact. It employs a current of 1000 amperes. The solution emerging from the cathode compartment of the electrolytic cell contains 8–10% of sodium hydroxide and 14–16% of sodium chloride. The solution is partially evaporated to remove most of the sodium chloride, which is much less soluble than the sodium hydroxide. After the removal of the salt, the evaporation of the water is completed and the molten residue is allowed to cool and solidify. The solid contains a small per cent of sodium chloride, so that it must be further purified for those uses which require a highly pure product. For most of its uses, the presence of a small per cent of salt may be tolerated.

The production of sodium hydroxide in the United States in 1940 was estimated to be approximately 1,095,000 tons, with 54 per cent from the electrolytic processes.

Properties of Sodium and Potassium Hydroxides. These substances are white solids which are highly soluble in water and absorb moisture from the air. The solids melt at moderate temperatures, sodium hydroxide at 322° and potassium hydroxide at 360°. In the preparation of the solid bases, the process of evaporation is carried on until a molten residue free from water is obtained. This material is poured into molds and allowed to solidify. The substances frequently appear on the market in the form of sticks of sodium or potassium hydroxide.

Chemical Reactions of Sodium and Potassium Hydroxides. These compounds are the hydroxides of active metals, and are highly soluble and highly ionized. They show to a high degree the reactions which are characteristic of solutions containing a high concentration of hydroxide ions. In solution they react with the active non-metals, such as the halogens, with acids, and with soluble salts of metals whose hydroxides are insoluble. They react slowly with the components of glass, so that bottles which contain solutions of these bases become etched. Since they react readily with non-metal oxides, sodium and potassium hydroxides must be protected from the air, which contains carbon dioxide. Both of these substances react with animal matter such as wool. They are known as *caustic alkalies*, the name alkali being applied to the soluble and active bases.

Uses of Sodium and Potassium Hydroxides. Sodium hydroxide is the cheapest of the strong, highly soluble basic hydroxides. It is extensively used in making soap, rayon, paper, and leather, and in the refining of petroleum, the reclaiming of rubber, and a number of other industries. The estimated consumption of sodium hydroxide in the United States for the production of valuable products is shown in Table 24, p. 320.

Calcium Hydroxide. Slaked Lime. $Ca(OH)_2$. The direct reaction of calcium oxide with water is the most suitable method for the preparation of calcium hydroxide. A large amount of heat is evolved in this reaction, which is known as the slaking of lime.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 15{,}100 \text{ cal.}$$

TABLE 24

CONSUMPTION OF SODIUM HYDROXIDE [1]

(Thousands of tons)

Industry	*1938*	*1939*	*1940*
Soap	95	100	95
Chemicals	138	195	220
Petroleum refining	80	84	88
Rayon and cellulose film	156	196	230
Lye	40	44	48
Textile	36	44	48
Rubber reclaiming	11	18	20
Vegetable oils	21	17	16
Pulp and paper	37	47	50
Exports	101	130	105
Miscellaneous	150	150	175
Totals	865	1,025	1,095

The reaction is reversible, so that calcium hydroxide may be decomposed by heating it strongly; but at ordinary temperatures calcium hydroxide is stable. This substance is a white powder which is soluble in water to the extent of only 0.165 g. in 100 g. of water at 20°; and its solubility decreases with rise in temperature. The dissolved portion of the base is highly ionized and the substance is a strong base.

$$Ca(OH)_2 \longrightarrow Ca^{++} + 2\ OH^-.$$

Since calcium hydroxide is a cheap base, it finds extensive application in industry. In many of the uses of calcium oxide it is first slaked to form the hydroxide. This substance is employed in the preparation of the alkalies and ammonia, in the purification of water, in the removal of hair from hides in preparation for tanning, in making mortar and plaster, and in agriculture to neutralize the acids which some soils contain. Calcium hydroxide is used in the refining of sugar because it reacts with sucrose to form an insoluble saccharate. After the separation of this compound from the solution, it is suspended in water and decomposed by the action of carbon dioxide, with the formation of a precipitate of calcium carbonate and a solution of the sugar. Solutions of calcium hydroxide, known as limewater, are used

[1] *Chem. Met. Eng.* **48**, number 2, 93 (1941).

medicinally to counteract too great acidity of the contents of the stomach. Limewater is used in the laboratory in testing for the presence of carbon dioxide. The gas is absorbed by solutions of calcium hydroxide with the formation of a white precipitate.

$$2\,OH^- + CO_2 \longrightarrow H_2O + CO_3^{--}.$$
$$Ca^{++} + CO_3^{--} \longrightarrow CaCO_3\downarrow.$$

Mortar is a mixture of slaked lime, sand, and water. As the mixture dries, the lime crystallizes and cements the particles of sand together and to the brick or stone. When exposed to air, there is also some combination with carbon dioxide; but this seems to be of minor importance in the setting of mortar, for it is only a superficial change even after the mortar has stood for years.

Hydroxides of Strontium and Barium. *Strontium hydroxide* is prepared by heating the carbonate in a current of steam.

$$SrCO_3 + H_2O \longrightarrow Sr(OH)_2 + CO_2\uparrow.$$

This is equivalent to the decomposition of the carbonate into the oxide and the subsequent union of the oxide with water. The direct reaction of the carbonate with water takes place at a lower temperature than the decomposition into the oxide and carbon dioxide, due to the low pressure of carbon dioxide and the large amount of energy evolved in the union of the oxide with water. Strontium hydroxide is used in the refining of sugar.

Barium hydroxide, like calcium hydroxide, is prepared by the hydration of the oxide.

$$BaO + H_2O \longrightarrow Ba(OH)_2 + 22{,}300 \text{ cal.}$$

This hydroxide is more stable than either strontium hydroxide or calcium hydroxide and may be melted without decomposition. It is used to a limited extent in the refining of sugar and has laboratory uses in the preparation of standard solutions.

Ammonia. The gas is highly soluble in water, with which it reacts to form a solution containing a low concentration of hydroxide ions. This solution is commonly called *ammonium hydroxide.* When solutions of ammonia are left exposed to air, the gas slowly evaporates but it may be driven out more quickly by boiling the solutions.

Industrial Sources of Ammonia. The synthesis of ammonia under high pressure, moderately high temperature, and in the

presence of a catalyst is discussed in Chapter VIII, in connection with the application of the principle of Le Chatelier to chemical equilibrium. The production of synthetic ammonia now serves as the chief source of supply, not only of ammonia and its salts, but also of a great many other compounds produced from atmospheric nitrogen through the intermediate formation of ammonia. The estimated production of synthetic ammonia in the United States in 1940 amounted to 247,500 tons of fixed nitrogen.

Ammonia from Coal. Bituminous coal contains 1–2½% of nitrogen in the form of complex compounds. When this coal is destructively distilled, these compounds decompose and approximately one half of the nitrogen is evolved as ammonia. Ammonia is separated from the other gases driven out in this process by absorbing it in dilute sulfuric acid, with the formation of ammonium sulfate. Large quantities of ammonia and other valuable materials have been wasted by the production of coke, for use in the metal industries, in bee-hive coke ovens and by the direct combustion of bituminous coal as a fuel. Through the production of coke in by-product coke ovens, these important products may be separated and conserved. Ammonium sulfate is used as a plant fertilizer and as a source of ammonia gas.

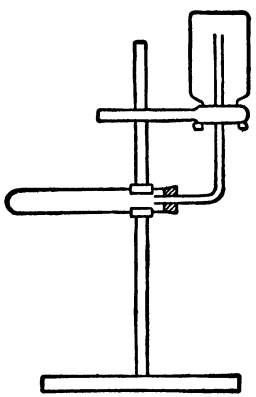

FIG. 106

Preparation of Ammonia from Ammonium Salts. Ammonia is liberated from ammonium salts by the action of strong bases. Ammonium sulfate and calcium hydroxide are commonly used; but other ammonium salts and other bases will also serve. When a mixture of the solid substances is warmed, ammonia is evolved.

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2\,NH_3\uparrow + 2\,H_2O.$$

A convenient laboratory method for the preparation and collection of ammonia may be based on this reaction. A sketch of the apparatus, Fig. 106, indicates that the gas is collected by the downward displacement of air. This is due to the fact that ammonia is soluble in water and is less dense than air.

Properties of Ammonia. Ammonia is a colorless gas which has a suffocating effect when it is inhaled. Its density is about one half that of air. The gas is so soluble that an ammonia fountain may be constructed as indicated in Fig. 107. The flask is filled with ammonia gas and a drop or two of water is forced into the flask by the use of the dropping tube. Ammonia dissolves, reducing the pressure in the flask and causing water to be forced up rapidly through the jet tube. A solution saturated with the gas at 20° and an ammonia gas pressure of one atmosphere contains 36% of ammonia. The critical temperature of ammonia is 133°; and ammonia gas is easily liquefied at room temperature by the application of pressure. Liquid ammonia boils at − 33.5° and exerts a pressure of 4.2 atmospheres at 0°. The heat of vaporization of ammonia is 330 calories.

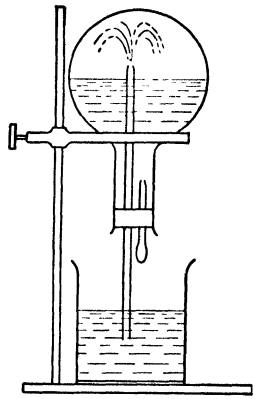

FIG. 107. — Ammonia Fountain.

Chemical Reactions of Ammonia. Ammonia is a molecular base which combines readily with protons to form ammonium ions. Reacting with water, ammonia yields a weakly basic solution in a reversible reaction.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-.$$

$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = K = 1.8 \times 10^{-5}.$$

The presence of an ammonium salt decreases the concentration of the hydroxide ion, so that basic solutions which are much more weakly basic than ammonia may be obtained in this manner.

Ammonia also unites with acids to form ammonium salts.

$$NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O.$$

The formation of a white smoke with gaseous hydrogen chloride and the odor of the gas serve as a test for the presence of ammonia.

Ammonia also exhibits acid properties and its hydrogen atoms may be displaced by metals. The nitride is formed when magnesium is heated in ammonia gas.

$$2\,NH_3 + 3\,Mg \longrightarrow 3\,H_2\uparrow + Mg_3N_2.$$

Sodium and potassium react to displace one of the three atoms of hydrogen per molecule forming the amide.

$$2\ Na + 2\ NH_3 \longrightarrow H_2\uparrow + 2\ NaNH_2.$$

The acid ionization of ammonia is insignificantly small and these compounds are decomposed by water.

$$Mg_3N_2 + 6\ H_2O \longrightarrow 2\ NH_3\uparrow + 3\ Mg(OH)_2\downarrow.$$
$$NaNH_2 + H_2O \longrightarrow Na^+ + OH^- + NH_3\uparrow.$$

Ammonia is unstable toward heat, being almost entirely decomposed at temperatures above 700°. When the gas is passed over hot cupric oxide, water and free nitrogen are obtained.

$$3\ CuO + 2\ NH_3 \longrightarrow 3\ Cu + N_2 + 3\ H_2O.$$

The gas burns in air and in oxygen producing nitrogen and water.

$$4\ NH_3 + 3\ O_2 \longrightarrow 2\ N_2 + 6\ H_2O.$$

At temperatures of approximately 1000° and in the presence of platinum as a catalyst, ammonia is selectively oxidized so that the main products are nitric oxide and water.

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O.$$

The industrial method for the conversion of ammonia into nitric acid employs this reaction as the first step.

Ammonia adds directly to a number of the metal ions to form complex ions. This reaction is attributed to the unshared pair of electrons in the ammonia molecule which yields a coördinate bond with the metal ions involved.

$$Cu^{++} + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4{}^{++}.$$

Uses of Ammonia. Since ammonia may be liquefied at room temperature by the application of moderate pressures, 9.9 atmospheres at 25°, and has a moderately low normal boiling point and a high heat of vaporization, it is extensively used in refrigeration and in the production of ice. Large quantities of ammonia are converted into ammonium sulfate for use in fertilizer, and additional large quantities are converted into nitric acid. Aqueous solutions of ammonia are sold as household ammonia for use as a cleansing agent. Ammonia is also used in the Solvay process for the production of sodium carbonate.

The Ammonium Radical. The ammonium ion exhibits a number of properties similar to those of the ions of the alkali metals. An oxide, $(NH_4)_2O$, may be prepared at $-79°$. The free ammonium radical in a solution in mercury, known as an amalgam, may be produced by the reaction of sodium amalgam with a solution of ammonium chloride.

$$Na + NH_4^+ \longrightarrow NH_4 + Na^+.$$

At ordinary temperatures the amalgam is a spongy mass, because of the rapid decomposition of the ammonium radical into gaseous ammonia and hydrogen; but at low temperatures a stable crystalline solid is produced.

Slightly Soluble Metal Hydroxides. These hydroxides are commonly prepared by precipitating them from solution. A solution of a soluble hydroxide is added to a solution containing the ions of the metal. Ammonia is not a suitable base for the precipitation of some of the metal hydroxides because the metal ions form complex ions with ammonia. An excess of a solution of a strong base must be avoided in the production of the amphoteric hydroxides. The hydroxides of mercury, silver, and cuprous copper are unstable at room temperatures, decomposing into the metal oxide and water. Consequently, the addition of a solution of sodium hydroxide to solutions of the ions of these metals yields a precipitate of the oxide.

$$Hg^{++} + 2\ OH^- \longrightarrow HgO\downarrow + H_2O.$$
$$Hg_2^{++} + 2\ OH^- \longrightarrow Hg_2O\downarrow + H_2O.$$

A suspension of silver oxide in water is strongly basic.

$$2\ Ag^+ + 2\ OH^- \rightleftharpoons Ag_2O\downarrow + H_2O.$$

The gelatinous precipitates formed when a solution of a soluble hydroxide is added to solutions of some of the metal ions contain indefinite and varying proportions of water. These compounds do not have the exact composition of the hydrate or of the hydroxide, and they do not decompose in the manner of true compounds. Such gelatinous precipitates are known as *hydrous oxides.* Some of the products are both hydrated and hydrous. The precipitates formed when a solution of hydroxide ions is added to solutions containing ferric, aluminum, chromium, tin, and lead ions are hydrous oxides. They may be represented by formulas such as

$Fe_2O_3(H_2O)_x$, in which x does not represent any specific, fixed number. For the sake of simplicity in writing formulas, a specific number is usually assigned, as $Fe_2O_3(H_2O)_3$, and $SnO(H_2O)$. These precipitates adsorb dissolved salts and suspended matter, so that they are useful in the clarification of muddy water in municipal water supplies. Some of the substances are used as mordants in dyeing.

Reactions of the Slightly Soluble Metal Hydroxides. These hydroxides furnish only low concentrations of the hydroxide ions; and the reaction with acids is the only one of the general reactions of the basic hydroxides into which they enter readily.

$$Mg(OH)_2 + 2\,H_3O^+ \longrightarrow Mg^{++} + 4\,H_2O.$$
$$[Mg^{++}] \times [OH^-]^2 < S_{Mg(OH)_2}.$$

The slightly soluble hydroxides which are amphoteric react with concentrated hydroxide ion solutions to form complex hydroxide ions and to cause the precipitate to dissolve.

$$Zn(OH)_2 + 2\,OH^- \rightleftharpoons Zn(OH)_4^-.$$
$$[Zn^{++}] \times [OH^-]^2 < S_{Zn(OH)_2}.$$

When the hydroxides are heated, water is driven out, leaving the metal oxide. Some of the metals yield oxides in more than one oxidation state. The hydroxides of such metals in the lower state may be oxidized by atmospheric oxygen when they are suspended in basic solution. Pure ferrous hydroxide is white; but the precipitate usually observed, when a solution containing hydroxide ions is added to a solution of a ferrous salt, is green or black. This is due to the presence of some ferric iron and the formation of an intermediate product. If the suspension stands it becomes converted to the ferric state of oxidation.

$$4\,Fe(OH)_2 + O_2 + 2\,H_2O \longrightarrow 2\,Fe_2O_3(H_2O)_3.$$

Analytical Separations in Basic Solutions. It has been observed in preceding paragraphs that a number of differences exist in the behavior of the ions which yield slightly soluble hydroxides. Through the use of a regulated low concentration of hydroxide ions, it is possible to precipitate hydrous oxides of iron, aluminum, and chromium without precipitating the hydroxides of manganese and magnesium. A second property leading to

the failure of certain ions to yield a precipitate in basic solution is the formation of ammonia complex ions. The ions of nickel, cobalt, and zinc yield such complex ions, and they also escape precipitation in the iron group. A third group of ions fail to form hydroxide precipitates in the presence of an excess of hydroxide ions because the hydroxides are amphoteric and yield hydroxide complex ions. The separation of aluminum from iron and of manganese from zinc may be based on the formation of the hydroxide complex ions of aluminum and zinc; but the hydroxides of ferric iron and manganese do not yield such complex ions.

EXERCISES

1. What general methods may be used for the preparation of the oxides of the metals? Illustrate by equations.
2. Explain in terms of the principles relating to equilibrium why lime kilns are so designed that a current of air must pass through the kiln.
3. Illustrate by equations reactions which are typical of the basic oxides.
4. Describe the production of sodium hydroxide by the lime-soda method and by the electrolytic method.
5. Represent by equations the chemical reactions of sodium hydroxide.
6. What are the two chief industrial sources of ammonia?
7. Explain the liberation of ammonia from ammonium salts by the action of sodium hydroxide.
8. Write equations to represent the reactions of ammonia.
9. How do hydrous oxides differ from hydrated oxides? How are the slightly soluble hydroxides and hydrous oxides commonly prepared?
10. Discuss three instances in which slightly soluble metal hydroxides fail to precipitate from basic solution.

SUPPLEMENTARY READINGS

Badger and Baker, *Inorganic Chemical Technology*, Chapter VII.
Rogers, *Manual of Industrial Chemistry*, Chapters X and XIV.
Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Volumes II and III.
Hammett, *Solutions of Electrolytes.*

CHAPTER XVII

OXIDATION-REDUCTION

Oxidation-reduction is a chemical reaction in which the oxidation number of one element or radical is increased while that of another is decreased. In *electrovalent compounds*, the oxidation numbers are equal to the electronic differences between the ions and the elementary substances. Consequently, oxidation-reduction reactions between ionic substances involve the transfer of electrons; and oxidation is due to the loss of electrons, while reduction is due to the gain of electrons. In *covalent compounds*, substances which are molecular in structure, the electron bonds are attributed to pairs of shared electrons. Hence, the complete transfer of electrons does not occur during the formation and decomposition of the substances. In this type of compound, oxidation numbers are assigned and oxidation-reduction involves changes in these oxidation numbers.

Oxidizing Agents. Substances which cause the oxidation of other materials are oxidizing agents. Such substances contain atoms or ions which are capable of gaining or of sharing additional electrons. They cause an increase in the oxidation numbers of atoms in the substances from which the electrons are taken. *Metal ions and hydronium ions* gain electrons to neutralize their electric charges. Consequently, these ions are oxidizing agents. The oxidizing activity of the ions of metals places them in an order which is the reverse of the arrangement on the basis of the activities of the metals.

Elementary non-metals which form simple negative ions gain electrons in these reactions and are oxidizing agents. The oxidizing activity of such non-metals is the same as their activity in the formation of anions.

The oxyacids and oxysalts of nitrogen, the halogens, sulfur, manganese, chromium, and a number of other elements are active oxidizing agents under the proper experimental conditions. In

some of these reactions the changes are essentially non-ionic in nature, while others are ionic and involve the transference of electrons.

Reducing Agents. Substances which readily give up electrons are reducing agents. *Elementary metals* lose electrons to form positive ions. The more active metals are the better reducing agents. Some metals yield ions in more than one oxidation state. In such instances, *metal ions* in a low state of oxidation may serve as reducing agents. *Simple negative ions*, such as chloride, bromide, and iodide ions, give up electrons when they are oxidized to the elementary condition. *The less active non-metals* are oxidized to form molecules and radicals in which they exhibit covalent bonds. These non-metals are assigned positive oxidation numbers in their products.

The Activity of Oxidation and Reduction. Some oxidizing and reducing substances react vigorously with each other, evolving relatively large amounts of heat. The intensity of an oxidation-reduction depends on the activity of both the oxidizing agent and the reducing agent. The activity of these substances is affected by the temperature and by the concentration. In many of these reactions, particularly those involving the formation and decomposition of oxyions, the activity is affected by the concentration of hydronium ions. In general, the oxyions are more stable in basic solutions than in acidic solutions. Hence, the presence of an acid increases the oxidizing activity of such substances; and, conversely, the presence of a base is a favorable condition for the formation of the oxyions.

In the following paragraphs, the typical reactions involving different classes of oxidizing and reducing agents are discussed to illustrate the general principles applied. The effect of changing conditions of acidity and basicity on the activity of the reagents and the nature of the reduction products is shown. Numerous examples applying these principles are found in subsequent chapters dealing with the specific substances.

The Formation of Ions from Elementary Substances. The reactions of elementary substances with each other to form binary compounds are commonly called reactions of direct union. These reactions involve either the transfer or the sharing of electrons. When active metals react with active non-metals,

electrons are transferred from the atoms of the metal to the atoms of the non-metal. The reaction of calcium with chlorine produces calcium and chloride ions.

$$Ca + Cl_2 \longrightarrow Ca^{++} + 2\ Cl^-.$$

In this reaction, each calcium atom gives up the two electrons in its valence shell and each chlorine atom in the molecule gains one electron to complete its valence shell. The two changes may be represented separately by ion-electron equations.

$$Ca \longrightarrow Ca^{++} + 2\ \epsilon.$$
$$Cl_2 + 2\ \epsilon \longrightarrow 2\ Cl^-.$$

The calcium is oxidized and the chlorine is reduced in this reaction.

Phosphorus combines vigorously with chlorine to produce the trichloride as the first product. In this reaction, there is no evidence of a transfer of electrons, for the product is composed of molecules in which the electron bonds are of the covalent type. The molecules are polar and the chlorine atoms are negative toward the phosphorus atoms in the molecule. Therefore, the chlorine is arbitrarily assigned an oxidation number of 1 − and the phosphorus an oxidation number of 3 +. For each molecule of chlorine which enters into this reaction, the change in the oxidation number is 2 and for each atom of phosphorus 3. The smallest common multiple of these numbers is 6, so that the reacting ratio is two atoms of phosphorus to three molecules of chlorine.

$$2\ P + 3\ Cl_2 \longrightarrow 2\ PCl_3.$$

The Displacement of Ions. The metals of higher activity readily displace the ions of the metals of lower activity from solution, unless these metals are active enough to displace hydronium ions from water. This follows as a direct consequence of the fact that the activity of a metal is dependent on the intensity of the reaction in which its atoms lose electrons. Zinc reacts with acidic solutions, displacing hydronium ions, and with solutions of cupric salts and of silver salts, displacing cupric and silver ions, respectively.

$$Zn + 2\ H_3O^+ \longrightarrow Zn^{++} + H_2\uparrow + 2\ H_2O.$$
$$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu\downarrow.$$
$$Zn + 2\ Ag^+ \longrightarrow Zn^{++} + 2\ Ag\downarrow.$$

In these reactions, atoms of zinc lose electrons and become oxidized to zinc ions. The electrons are gained by the ions which become reduced to the elementary state.

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon.$$
$$Cu^{++} + 2\,\epsilon \longrightarrow Cu.$$

The electronic nature of this reaction may be demonstrated by arranging the reacting materials in a *cell*, so that they are separated and the direct transfer of electrons cannot take place. To permit the transference of electrons under these conditions, the materials must be electrically connected through the use of suitable electrodes and ionic solutions. This arrangement is

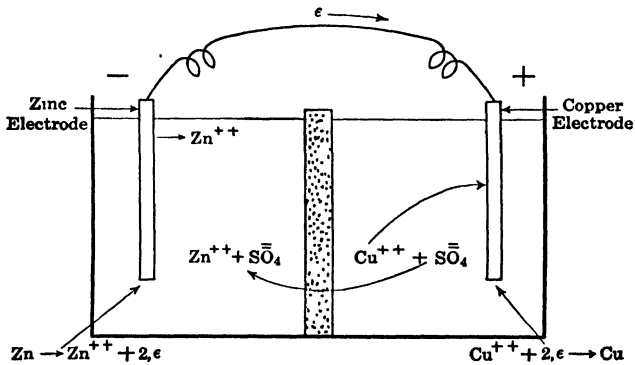

FIG. 108

shown diagrammatically in Fig. 108. The cell is divided into two compartments by a porous material; and a solid zinc rod is placed in a dilute solution of an electrolyte, such as zinc sulfate, in one compartment. This zinc rod serves as both the active metal and one of the electrodes. The solution containing the cupric ions is in the other compartment and an electrode of copper is used. A conducting wire with a galvanometer in the circuit is used to complete the external connections. It may now be observed that a current is flowing through the external circuit. The reactions of oxidation and reduction take place in different parts of the cell and electrons are transferred along the metallic conductor from the zinc to the copper ions. Ions migrate through the porous dividing wall between the two compartments to complete the circuit.

The Displacement of Simple Negative Ions. Simple negative ions are converted into the elementary substances by oxidation. There are many oxidizing agents which may take electrons from the simple negative ions. The activity of the elementary non-metals may be measured in terms of their tendency to gain electrons. Consequently, the more active non-metals displace the ions of the non-metals of lower activity. Chlorine displaces the bromide, iodide, and sulfide ions.

$$Cl_2 + 2\,Br^- \longrightarrow 2\,Cl^- + Br_2.$$
$$Cl_2 + 2\,I^- \longrightarrow 2\,Cl^- + I_2\downarrow.$$
$$Cl_2 + S^{--} \longrightarrow 2\,Cl^- + S\downarrow.$$

Electrons are transferred from the ions of the non-metals of lower activity to the atoms of chlorine.

$$Cl_2 + 2\,\epsilon \longrightarrow 2\,Cl^-.$$
$$2\,Br^- - 2\,\epsilon \longrightarrow Br_2.$$

The bromide ions are oxidized by free chlorine, which is itself reduced to form chloride ions.

Electrolysis. The electronic nature of the reactions which take place at the electrodes during the electrolysis of salt solutions has been discussed in Chapter XI. The reactions include the reduction of positive ions at the cathode and the oxidation of negative ions at the anode. Elementary products are usually obtained as the result of these reactions. There are, however, a number of instances in which other products are formed. The electrolytic preparation of sodium perchlorate from the chlorate results from the anode reaction,

$$ClO_3^- + 3\,H_2O \longrightarrow ClO_4^- + 2\,H_3O^+ + 2\,\epsilon.$$

The cathode reaction is

$$2\,H_3O^+ + 2\,\epsilon \longrightarrow H_2 + 2\,H_2O.$$

If the anode used during the electrolysis of a salt solution is of suitable activity, the anode reaction by which electrons are released is the conversion of the metal into its ions. This is applied in electroplating through the use of an anode of the same metal as that which is deposited by the discharge of its ions at the cathode. A copper anode and a solution of cupric sulfate are used

in electroplating with copper. The object to be plated is the cathode. The migration of ions takes place in the usual manner and copper is deposited on the cathode, Fig. 109.

$$Cu^{++} + 2\epsilon \longrightarrow Cu.$$

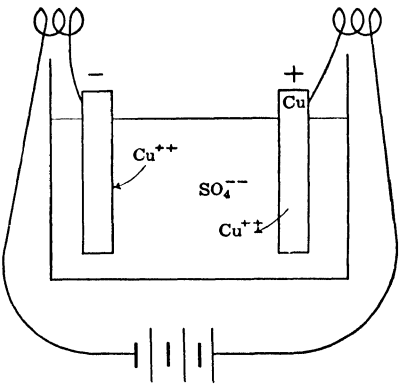

FIG. 109

At the anode, the formation of cupric ions from metallic copper takes place more readily than the discharge of hydroxide ions.

$$Cu - 2\epsilon \longrightarrow Cu^{++}.$$

The process involves the transfer of copper from the anode to the cathode, without significant change in the concentration of the ions in solution. The same principle is applied in the electrorefining of metals.

OXIDATION BY OXYACIDS AND OXYSALTS

Reactions in which simple ions are formed from the elementary substances and those in which simple ions are converted into the atoms of the elements, either by the displacement of ions or by electrolysis, involve the individual atoms and ions. During these changes a direct transfer of electrons takes place and no additional ions are affected in so far as their oxidation numbers are concerned.

The ionic reactions of the oxyions as oxidizing agents usually involve hydronium ions, hydroxide ions, or water molecules in addition to electrons. The materials entering into these reactions may be arranged so as to cause the oxidation and the reduction portions of the changes to take place in different parts of a cell and to observe the effects of the transfer of electrons. The equations for these reactions are most satisfactorily derived by the use of the ion-electron equations.

There are also many oxidation-reduction reactions which do not take place in aqueous solutions, so that the ion-electron equation is not a convenient mechanism for the interpretation of the changes which occur. Nevertheless, the changes in the oxida-

tion numbers may be considered to be equivalent to the gain or loss of electrons. This second type of oxidation-reduction, involving compound oxidizing agents in a non-ionic condition is most satisfactorily represented by equations based on changes in the oxidation numbers of atoms in the substances entering into reaction.

The Ion-Electron Method. This method of deriving equations for oxidation-reduction consists in writing two partial equations, the one to represent the behavior of the oxidizing agent and the other the behavior of the reducing agent. The partial equations are then added to secure the equation for the complete reaction. To illustrate the procedure, the oxidation of zinc by an acidic solution of permanganate ions will be considered. The permanganate ion, MnO_4^-, is decomposed during the reaction with the formation of the manganous ion, Mn^{++}. Oxygen is not produced as an elementary substance as the result of the decomposition of this complex ion; and the only reasonable conclusion is that the permanganate ion interacts with hydronium ions from the acid. The bound oxygen atoms in the permanganate ion combine with protons to form water molecules, and electrons are absorbed in the process.

In writing the equations for such oxidation-reduction reactions, the proton required in the partial equation will be represented by the use of the symbol, H^+. It must be understood, however, that the particle actually involved as one of the initial substances is not the free proton but some complex particle which furnishes the proton, such as the hydronium ion or some of the molecular acids. The apparent inconsistency in the symbolism to represent this ion is adopted in the interest of simplicity in order that emphasis may be placed properly on the formation of water by the interaction of protons with the complex anions, without the confusion arising from the additional molecules of water resulting from the removal of the proton from the hydronium ion. This simple particle will be called the hydrogen ion.

In order to apply this procedure to the equation for the reaction under consideration, it is necessary to represent eight hydrogen ions for each permanganate ion decomposed, in order to convert its four atoms of oxygen into water molecules.

$$MnO_4^- + 8\,H^+ \longrightarrow Mn^{++} + 4\,H_2O.$$

Although this expression is balanced with respect to the atoms involved, it is not balanced in the total number of electrical charges represented. An excess of seven units of positive charge is shown to the left of the reaction symbol, but only two to the right. Hence, five electrons are required on the left to reduce this surplus to two units and thus balance the equation for the half reaction.

$$MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O.$$

The source of the electrons in this reaction is the oxidation of metallic zinc.

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon.$$

The complete equation for the oxidation of zinc by permanganate ions in acidic solution is now secured by adding the partial equations, with the cancellation of the electrons which appear on opposite sides of the two half reactions; but, first, each of the partial equations must be multiplied by an integer so that the number of electrons in the one is equal to the number in the other. This requires that the first partial equation be multiplied by two and the second by five.

$$\begin{aligned} 2\,MnO_4^- + 16\,H^+ + 10\,\epsilon &\longrightarrow 2\,Mn^{++} + 8\,H_2O. \\ 5\,Zn &\longrightarrow 5\,Zn^{++} + 10\,\epsilon. \\ \hline 2\,MnO_4^- + 16\,H^+ + 5\,Zn &\longrightarrow 2\,Mn^{++} + 5\,Zn^{++} + 8\,H_2O. \end{aligned}$$

If now it is desired to represent an actual acid instead of the proton, sixteen hydronium ions may be substituted for the sixteen hydrogen ions or protons and the equation takes the form,

$$2\,MnO_4^- + 16\,H_3O^+ + 5\,Zn \longrightarrow 2\,Mn^{++} + 5\,Zn^{++} + 24\,H_2O.$$

It is customary to use molecular formulas to represent weak electrolytes. In this manner, it is possible to indicate the condition in which most of the material is present in the solution, even though the reaction may involve the intermediate formation of ions.

Compound Oxidizing Agents. There are a number of oxyacids and anions which are strong oxidizing agents under the proper experimental conditions. These complex substances are decomposed when they are reduced, with the formation of reduction products in which the non-metallic elements exhibit lower

oxidation numbers, as illustrated by the permanganate ion in the preceding paragraph. The oxidizing activity of such substances is increased by establishing conditions which decrease the stability of the oxycompound. The stability of the oxyions toward reduction is less in acidic solution than in basic solution, because protons from the hydronium ions of the acid enter into the reaction. Among the *anions* which are active oxidizing agents in acidic solution are the nitrate, chlorate, permanganate, perchlorate, and dichromate ions. *The molecular substances*, hypochlorous acid, hydrogen peroxide, nitrous acid, and concentrated sulfuric acid are also oxidizing agents of the same type.

The partial equations representing the reduction of oxidizing agents of this type may now be derived through the use of the electron to indicate the reducing agent and the simple hydrogen ion or proton to represent the acid. Equations representing the half reactions for the reduction of a number of oxidizing agents are shown in Appendix VII. It is necessary to know the products formed in these reactions, as in all reactions, in order to write partial equations for the half reactions. The principal reduction product of *nitric acid* in moderately concentrated solution, approximately 6 M., is nitric oxide, NO. In the formation of nitric oxide from the nitrate ion, two oxygen atoms must be removed. Four hydrogen ions are required and two molecules of water are also produced.

$$NO_3^- + 4\,H^+ \longrightarrow NO + 2\,H_2O.$$

Neutral molecular products are obtained, so that the net charge of the initial substances must also be equal to zero. Therefore, three electrons are required in the reduction of each nitrate ion.

$$NO_3^- + 4\,H^+ + 3\,\epsilon \longrightarrow NO + 2\,H_2O.$$

When silver is oxidized by nitric acid, each silver atom gives up one electron, so that three atoms of silver are required for each nitrate ion reduced.

$$3\,Ag \longrightarrow 3\,Ag^+ + 3\,\epsilon.$$

By adding the two partial equations, the following equation for the reaction is written.

$$NO_3^- + 4\,H^+ + 3\,Ag \longrightarrow NO\uparrow + 3\,Ag^+ + 2\,H_2O.$$

If the hydronium ion is the acid which furnishes the protons, the complete equation is,

$$NO_3^- + 4\,H_3O^+ + 3\,Ag \longrightarrow NO + 3\,Ag^+ + 6\,H_2O.$$

Other reduction products of the nitrate ion will be discussed in the following chapter.

The reduction of the *chlorate ion* produces the chloride ion. Three molecules of water are formed in the reduction of each chlorate ion. Six protons and six electrons are required to balance the partial equation for the half reaction.

$$6\,H^+ + ClO_3^- + 6\,\epsilon \longrightarrow Cl^- + 3\,H_2O.$$

The perchlorate ion also yields the chloride ion.

$$ClO_4^- + 8\,H^+ + 8\,\epsilon \longrightarrow Cl^- + 4\,H_2O.$$

Permanganates in acidic solution yield manganous salts when they are reduced, as already discussed. The reduction of *dichromates* in acidic solution produces chromic ions and water.

$$Cr_2O_7^{--} + 14\,H^+ + 6\,\epsilon \longrightarrow 2\,Cr^{+++} + 7\,H_2O.$$

The decomposition of the molecular acids which show oxidizing properties may be represented in a similar manner. *Hypochlorous acid* is reduced to the chloride.

$$HClO + H^+ + 2\,\epsilon \longrightarrow Cl^- + H_2O.$$

Hydrogen peroxide is reduced to water.

$$H_2O_2 + 2\,H^+ + 2\,\epsilon \longrightarrow 2\,H_2O.$$

The reduction of *hot concentrated sulfuric acid* yields sulfur dioxide and water.

$$H_2SO_4 + 2\,H^+ + 2\,\epsilon \longrightarrow SO_2 + 2\,H_2O.$$

Reducing Agents. The electrons represented in each of the partial equations showing the decomposition of the oxidizing agent are obtained from the reducing agents. The common reducing agents may be classified into five groups: *viz.*, metals, metal ions in a low electrovalent state, simple non-metal ions, elementary non-metals, and oxyions containing a non-metal in the lower of two oxidation states. The formation of the simple ions from elementary substances and the reduction of these ions

by displacement reactions and by electrolysis have been discussed. The electronic changes for the common reducing agents may be summarized by the following equations for the half reaction liberating electrons. *Metals* yield positive ions. The oxidation of zinc produces zinc ions.

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon.$$

Metal ions in low states of oxidation yield ions in higher states of oxidation if such ions exist. Mercurous salts are oxidized to form mercuric salts.

$$Hg_2^{++} \longrightarrow 2\,Hg^{++} + 2\,\epsilon.$$

Simple negative ions yield the free non-metal. Chloride ions are oxidized to free chlorine.

$$2\,Cl^- \longrightarrow Cl_2 + 2\,\epsilon.$$

Elementary non-metals yield the oxyions containing the non-metals in their higher states of oxidation. The molecular acid is the product if these anions yield weak acids; and the non-metal oxide is formed if the acid is unstable under the conditions of the experiment. The production of the oxy-radical requires the combination of atoms of the non-metal with atoms of oxygen. In aqueous solutions, two sources of combined oxygen are available, water molecules and hydroxide ions. The concentration of the hydroxide ion in acidic solutions is small, so that water is logically represented as the source of oxygen in setting up the equations for the half reactions. Additional protons are given up to other water molecules with the formation of hydronium ions. The oxidation product of phosphorus with acidic oxidizing agents is phosphoric acid, H_3PO_4. Hence, four molecules of water are required by each atom of phosphorus. Three protons are held in the molecules of the weak acid. Five additional protons and five electrons are liberated.

$$P + 4\,H_2O \longrightarrow H_3PO_4 + 5\,H^+ + 5\,\epsilon.$$

The oxyacid or ion containing the non-metal in a lower oxidation state yields the oxyradical which contains the same element in a higher state of oxidation.

$$H_2SO_3 + H_2O \longrightarrow SO_4^{--} + 4\,H^+ + 2\,\epsilon.$$

A number of additional examples of the half reactions of reducing agents are given in Appendix VIII.

The Oxidation of Metals. The derivation of the equations representing the oxidation of metals by acidic oxidizing agents has been illustrated in preceding paragraphs of this chapter. The oxidation of silver by hot concentrated sulfuric acid is now shown to summarize the procedure for the equation. The products are water, sulfur dioxide, and silver ions.

$$\begin{array}{r} H_2SO_4 + 2\,H^+ + 2\,\epsilon \longrightarrow 2\,H_2O + SO_2. \\ [Ag \longrightarrow Ag^+ + 1\,\epsilon.] \quad \times 2. \\ \hline H_2SO_4 + 2\,H^+ + 2\,Ag \longrightarrow 2\,H_2O + SO_2 + 2\,Ag^+. \end{array}$$

The protons come from other molecules of sulfuric acid and an equivalent number of anions is produced.

The Oxidation of Low Valent Metal Ions. The representation of the oxidation of these ions follows the pattern already considered. Mercurous salts are oxidized to the mercuric state by the action of nitric acid.

$$\begin{array}{r} [4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO.] \quad \times 2. \\ [Hg_2^{++} \longrightarrow 2\,Hg^{++} + 2\,\epsilon.] \quad \times 3. \\ \hline 8\,H^+ + 2\,NO_3^- + 3\,Hg_2^{++} \longrightarrow 4\,H_2O + 2\,NO + 6\,Hg^{++}. \end{array}$$

The Oxidation of Simple Non-Metal Ions. The oxidation of chloride ions in acidic solution by manganese dioxide is the basis of the laboratory preparation of chlorine.

$$\begin{array}{r} MnO_2 + 4\,H^+ + 2\,\epsilon \longrightarrow Mn^{++} + 2\,H_2O. \\ 2\,Cl^- \longrightarrow Cl_2 + 2\,\epsilon. \\ \hline MnO_2 + 4\,H^+ + 2\,Cl^- \longrightarrow Mn^{++} + 2\,H_2O + Cl_2. \end{array}$$

The reaction of hot concentrated sulfuric acid with hydrobromic acid produces free bromine.

$$\begin{array}{r} H_2SO_4 + 2\,H^+ + 2\,\epsilon \longrightarrow SO_2 + 2\,H_2O. \\ 2\,Br^- \longrightarrow Br_2 + 2\,\epsilon. \\ \hline H_2SO_4 + 2\,H^+ + 2\,Br^- \longrightarrow SO_2 + 2\,H_2O + Br_2. \end{array}$$

Hydrogen peroxide oxidizes iodides to form free iodine.

$$\begin{array}{r} H_2O_2 + 2\,H^+ + 2\,\epsilon \longrightarrow 2\,H_2O. \\ 2\,I^- \longrightarrow I_2 + 2\,\epsilon. \\ \hline H_2O_2 + 2\,H^+ + 2\,I^- \longrightarrow 2\,H_2O + I_2. \end{array}$$

The Oxidation of Elementary Non-Metals. The reaction of moderately concentrated nitric acid with phosphorus produces phosphoric acid.

$$[4\ H^+ + NO_3^- + 3\ \epsilon \longrightarrow 2\ H_2O + NO.] \quad \times 5.$$
$$[P + 4\ H_2O \longrightarrow H_3PO_4 + 5\ H^+ + 5\ \epsilon.] \quad \times 3.$$
$$5\ H^+ + 5\ NO_3^- + 2\ H_2O + 3\ P \longrightarrow 5\ NO + 3\ H_3PO_4.$$

Hypochlorous acid converts iodine into iodic acid.

$$[HClO + H^+ + 2\ \epsilon \longrightarrow H_2O + Cl^-.] \quad \times 5.$$
$$I_2 + 6\ H_2O \longrightarrow 2\ IO_3^- + 12\ H^+ + 10\ \epsilon.$$
$$5\ HClO + I_2 + H_2O \longrightarrow 5\ Cl^- + 2\ IO_3^- + 7\ H^+.$$

The Oxidation of Oxyacids. Most of the non-metals yield oxyacids in more than one oxidation state. Arsenious acid is oxidized to form arsenic acid by reaction with hypochlorous acid.

$$HClO + H^+ + 2\ \epsilon \longrightarrow Cl^- + H_2O.$$
$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2\ H^+ + 2\ \epsilon.$$
$$HClO + H_3AsO_3 \longrightarrow Cl^- + H^+ + H_3AsO_4.$$

Oxidation in Basic Solution. In preceding paragraphs it has been shown that some of the oxyanions are good oxidizing agents in acidic solutions, because they are unstable in the presence of reducing agents. The stability of these ions is much greater in neutral and basic solutions than in acidic solutions. The nitrate and sulfate ions do not exhibit active oxidizing properties under these conditions. Other anions, such as hypochlorite and peroxide, have active oxidizing properties even in basic solution. Since the stability of such ions is increased by lowering the concentration of hydronium ions, a basic solution is the most favorable condition for the formation of these oxyanions. It will be recalled that chlorine reacts with water to form a mixture of hydrochloric and hypochlorous acids at equilibrium, and that only low concentrations of these acids are tolerated by the equilibrium conditions. $Cl_2 + 2\ H_2O \rightleftharpoons H_3O^+ + Cl^- + HClO.$

The reaction is virtually complete in the presence of a base, and a mixture of the chloride and hypochlorite is produced.

$$Cl_2 + 2\ OH^- \longrightarrow H_2O + Cl^- + ClO^-.$$

When the hypochlorites react as oxidizing agents, chlorides are formed, and the oxidation number of chlorine is reduced from

1 + to 1 −. The hypochlorite ion is decomposed by the removal of the oxygen atom. Since the solution is basic, the concentration of hydronium ions is small, so that it may logically be assumed that water molecules interact with the hypochlorite ions forming the chloride and hydroxide ions. The equation for the half reaction is, $ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-$.

Similarly, the equation for the half reaction of sodium peroxide as an oxidizing agent is,

$$Na_2O_2 + 2\,H_2O + 2\,\epsilon \longrightarrow 2\,Na^+ + 4\,OH^-.$$

The reducing agents which are oxidized in basic solution usually produce oxyanions. The source of the oxygen for the half reaction might be shown as either water molecules or hydroxide ions. In basic solution, the use of the hydroxide ion for this purpose seems logical. The oxidation of the sulfite to the sulfate ion is readily accomplished in basic solution by the action of sodium hypochlorite.

$$\begin{array}{r} ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-. \\ SO_3^{--} + 2\,OH^- \longrightarrow SO_4^{--} + H_2O + 2\,\epsilon. \\ \hline ClO^- + SO_3^{--} \longrightarrow Cl^- + SO_4^{--}. \end{array}$$

The Oxidation Number Method. There are a number of oxidation-reduction reactions which take place in the anhydrous state at elevated temperatures. Some of these reactions appear to be non-ionic, while many others involve ionized substances in the fused state. Nevertheless, the equations for these reactions are most simply balanced from a consideration of the changes in the oxidation numbers of atoms in the reacting substances, because no simple half reactions in terms of ions and electrons are apparent. Sodium nitrate decomposes at high temperatures to produce oxygen and the nitrite.

$$2\,NaNO_3 \longrightarrow 2\,NaNO_2 + O_2.$$

The oxidation number of nitrogen is reduced from 5 + to 3 + while that of oxygen is increased from 2 − to 0. To consider the change in oxidation number in such decomposition reactions is helpful when these substances are used to oxidize other complex materials; but they offer no value in the balancing of the simple decomposition reaction equation. In the decomposition

of potassium chlorate, the change in the oxidation number of chlorine is from 5 + to 1 −, and for oxygen from 2 − to 0.

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2.$$

These substances are active oxidizing agents at elevated temperatures and are suitable for use in fusion reactions. Many such reactions require the use of a flux. The oxidation of non-metals and of slightly soluble non-metal oxides to form the oxysalts in the high oxidation state is often carried out by heating these substances with an oxidizing agent and a melted alkali hydroxide or carbonate. Sulfur may be oxidized to form the sulfate by heating it with sodium nitrate and sodium hydroxide. The skeleton equation may be written as the first step in deriving the complete equation.

$$NaNO_3 + S + NaOH \longrightarrow NaNO_2 + Na_2SO_4 + H_2O.$$

It is an aid in balancing the equation to write above the formula of the oxidizing agent and its reduction product the symbol and oxidation number of the element undergoing reduction. Similarly, the symbol and oxidation number of the element undergoing oxidation is written beneath the formulas of the substances which contain these atoms. These oxidation numbers are connected by a line, and a number is written to show the change in the oxidation number. When this is done, the incomplete equation takes the form,

$$\begin{array}{c} N^{5+}\text{———————}(-\,2)\text{——}N^{3+} \\ NaNO_3 + S + NaOH \longrightarrow NaNO_2 + Na_2SO_4 + H_2O. \\ S^{0}\text{———}(+\,6)\text{———————}S^{6+} \end{array}$$

The ratio of the oxidizing agent to the reducing agent is obtained from these oxidation number changes. The numbers are converted to the least common multiple by the use of the proper coefficients. Three moles of sodium nitrate are required for one gram atom of sulfur. The balancing of the equation is now completed by inspection.

$$\begin{array}{c} N^{5+}\text{———————}(-\,2)\text{——}N^{3+} \\ 3\,NaNO_3 + S + 2\,NaOH \longrightarrow 3\,NaNO_2 + Na_2SO_4 + H_2O. \\ S^{0}\text{———}(+\,6)\text{———————}S^{6+} \end{array}$$

It is not necessary to rewrite the equation for each step in the procedure for the required numbers may be introduced directly to fill out the original skeleton equation.

Arsenic trioxide may be oxidized by heating it with potassium chlorate and potassium carbonate. The skeleton equation is written as directed above and the oxidation numbers of arsenic and chlorine are introduced. Since the molecule of arsenic trioxide contains two atoms of arsenic, it is necessary to consider the change in oxidation number shown by arsenic in terms of two atoms, for the final equation must show an even number of atoms of arsenic. The equation is then balanced through the equalization of the loss and gain in oxidation numbers by the use of the proper coefficients.

$$\begin{array}{c} Cl^{5+}\text{———————}(-6)\text{——}Cl^{-} \\ 2\,KClO_3 + 3\,As_2O_3 + 9\,K_2CO_3 \longrightarrow 2\,KCl + 6\,K_3AsO_4 + 9\,CO_2. \\ 2\,As^{3+}\text{———————}(+4)\text{————}2\,As^{5+} \end{array}$$

There are some instances in which an acidic flux is employed. If the oxidation number of a basic substance is increased by the oxidation reaction, the presence of a non-metal oxide is a favorable condition. Manganese dioxide is employed to some extent in the glass industry to oxidize ferrous to ferric compounds. A small per cent of some ferrous compound, equivalent to ferrous oxide, may be present in the sand or limestone used in making glass. If ferrous silicate were present in the product, a green color would be imparted to the glass. Through the use of manganese dioxide, ferric and manganous silicates are formed. The colors of these compounds are complementary so that a colorless product may be obtained. The derivation of the equation for this reaction is indicated diagrammatically in the following equation.

$$\begin{array}{c} Mn^{4+}\text{———————}(-2)\text{——}Mn^{2+} \\ MnO_2 + 4\,SiO_2 + 2\,FeO \longrightarrow MnSiO_3 + Fe_2(SiO_3)_3. \\ 2\,Fe^{2+}\text{——}(+2)\text{————}2\,Fe^{3+} \end{array}$$

EXERCISES

1. What changes occur during oxidation-reduction involving electrovalent compounds? covalent compounds?
2. What are oxidizing agents? reducing agents? Into what groups is it convenient to classify oxidizing and reducing agents?

3. What electron changes occur during the displacement of ions? How may this be shown experimentally?
4. How does the action of an oxyion as an oxidizing agent differ from the action of a simple ion or atom? Give examples to illustrate the differences.
5. Write ion-electron equations to illustrate the reduction of several oxidizing agents.
6. Write ion-electron equations to illustrate the oxidation of a member of each of the common classes of reducing agents.
7. Derive by the ion-electron method the equations for the oxidation of a member of each of the common classes of reducing agents by each of the following oxidizing agents: nitric acid; hypochlorous acid; an acidic solution of potassium permanganate; an acidic solution of potassium dichromate.
8. Under what conditions is a basic medium favorable for an oxidation-reduction reaction? Illustrate by examples.
9. Under what conditions are fusion reactions used for oxidation-reduction? Derive equations to illustrate reactions under these conditions by the oxidation number method.

SUPPLEMENTARY READINGS

Hammett, *Solutions of Electrolytes*, Chapter VI.
Meldrum and Gucker, *Introduction to Theoretical Chemistry*, pp. 403–413.
Hildebrand, *Principles of Chemistry*, Chapter IV.
Kelsey and Dietrich, *Fundamentals of Semimicro Qualitative Analysis* (The Macmillan Company, 1940), Chapter VIII.

CHAPTER XVIII

NITROGEN. THE OXYACIDS AND OXIDES OF NITROGEN

Nitrogen is the element of lowest atomic number in Group V of the Periodic System. The element has five valence electrons and yields compounds in a number of oxidation states. Nitrogen differs notably from the other elements in Group V; and these other elements are discussed separately in Chapter XX. The familiar hydride of nitrogen, ammonia, is a basic substance which has been described in Chapter XVI with the other common bases.

Occurrence of Nitrogen. The atmosphere contains nearly constant proportions of the elementary gases: nitrogen, 75.4% by weight; oxygen, 23.2%; argon, 1.2%; and very small percentages of the other inert gases. Nitrogen occurs also in ammonium salts, the nitrates and nitrites present in all fertile soils, and is a constituent of all proteins. Deposits of sodium nitrate are found in Chile, Turkestan, and Egypt. The most important of these is in an arid region in Chile and the salt is called "Chile saltpeter." Bituminous coal contains from 1 to 2½% of combined nitrogen. The total amount of the element is only approximately 0.03% of the matter in the outer part of the earth.

Inert Gases of the Atmosphere. In addition to its principal components, nitrogen, oxygen, and argon, and varying proportions of water vapor and carbon dioxide, the atmosphere contains several other inert gases. In 1785, Cavendish noticed a small amount of a residual gas when oxygen and nitrogen had been removed from a sample of air. Lord Rayleigh, a British physicist, observed, 1895, that the residual nitrogen obtained from air by the removal of the other known atmospheric substances is more dense than nitrogen obtained by the decomposition of its compounds. Sir William Ramsay found that a residual gas, amounting to 0.933% by volume of the sample of air, resulted after the re-

moval of all of the gases known at that time. This material was found to enter into no chemical reactions and was named *argon.* Subsequently, this residual gas has been found to contain several other substances in very small proportions, mixed with argon. These substances comprise a group of inert gases, known as the helium family: *helium*, *neon*, *argon*, *krypton*, and *xenon*. *Radon*, a product of the disintegration of radium, also belongs to this family.

These elements have stable electronic structures, so that they show no important chemical reactions. A few unstable compounds have been reported, such as complex hydrogen-helium ions, hydrides of krypton, and compounds of argon with boron trifluoride. The other elements tend to gain or lose electrons so as to attain the electronic configuration of the inert gases.

When liquid air is allowed to evaporate, different components predominate in the fractions obtained at different temperatures. It is possible to arrange the apparatus so as to secure several of the atmospheric gases in high enough concentration for industrial use. When an electric discharge passes through tubes containing neon at low pressure, a brilliant red light is emitted. Mercury vapor tubes give different color effects, and still different colors are secured by the use of gas mixtures and of tubes made of glass having special composition. The use of these tubes in electric signs has become familiar. Argon is used to fill electric light bulbs having tungsten filaments, and thus prevent the rapid disintegration of the filament.

Helium. Examination of the spectrum of prominences of the sun during an eclipse in 1868 led Lockyer to the discovery in the sun of a substance then unknown in terrestrial matter. To this substance, the name *helium* was given. Hillebrand observed in 1889 the liberation of a small quantity of an inert gas, supposed to be nitrogen, during the reaction of certain uranium minerals with acids. Ramsay, searching for sources of argon, repeated these experiments in 1895 and isolated an inactive gas of low density. The spectrum of this gas showed it to be the same as that discovered by Lockyer in the sun. The amount of this gas obtained from the uranium minerals is not of practical importance, nor is the proportion in the air sufficient to furnish, at present, a useful source of helium.

Next to hydrogen, helium has the least density of all the known substances. During the World War, Ramsay suggested the use of helium for the inflation of balloons and dirigibles. Even though its buoyant effect is only about 90% that of hydrogen, it has the advantage that it is inactive, whereas hydrogen is combustible. At the time, the suggestion seemed fanciful for there were no sources of helium then known from which a sufficient supply could be secured. It was found, however, that the natural gas in the Texas and Kansas gas fields contains small proportions of helium, in some samples one or two per cent. Methods were developed for separating helium from this gas and the process was installed in Texas. The war ended before a supply sufficient for actual use had been obtained. The production has been continued and the methods of separation improved so that the cost has been greatly reduced. The great dirigibles of the United States Navy were inflated with helium and the known commercial supply is under the control of the United States Government.

At the high pressure under which air must be supplied to divers, an increased concentration of nitrogen is dissolved in the blood. If the pressure is reduced too quickly when the diver comes to the surface, bubbles of this gas form in the blood stream. To prevent this condition, known as "caisson disease" or "bends," the pressure must be decreased slowly in a pressure chamber, so that the dissolved nitrogen may gradually escape through the lungs. The solubility of helium in the blood is much less than that of nitrogen, so that the length of time which the diver must spend in the decompression chamber is greatly decreased if a mixture of oxygen and helium, in preference to air, has been supplied to the diver while he was at work beneath the surface of the water.

Importance of Nitrogen and Nitrogen Compounds. Elementary nitrogen has few direct uses of importance. It is used in gas-filled electric light bulbs having tungsten filaments, to decrease the rate at which the filament evaporates. The stems of mercury thermometers may be filled with nitrogen under pressure so as to raise the boiling temperature of the mercury and make possible the use of such thermometers at temperatures somewhat above the boiling point of mercury, 356.9°. Nitrogen compounds are of fundamental importance under the conditions of modern civilization. The harvesting of agricultural products containing

nitrogenous substances, thus removing them from the soil where they grew, upsets the balance between the amount of these compounds taken out of the soil and the amount returned to it by natural agencies, such as bacterial action, the decay of organic matter, and the combination of nitrogen and oxygen at the temperature of the electric discharge in thunderstorms. Hence, fertilizers containing soluble nitrogen compounds must be applied in order to maintain the fertility of the soil. Ammonium sulfate and sodium nitrate are the compounds employed most generally in the form of chemical fertilizers. Ammonia is used extensively as a refrigerant. Nitric acid is essential to the manufacture of high explosives and of a large number of dyes, drugs, and other commercial products.

Sources of Nitrogen Compounds. There are three important industrial sources of nitrogen compounds. The deposits of sodium nitrate in Chile contain enough of this salt to meet the world's needs for a number of years; but nitrate from this source must be transported to other countries to meet industrial demands. The destructive distillation of bituminous coal yields nitrogen compounds among the volatile products. The third source of nitrogen compounds, the elementary nitrogen of the air, is now the most important.

Preparation and Properties of Elementary Nitrogen. Nitrogen of sufficiently high purity for industrial use is usually obtained by the liquefaction and fractionation of air. Pure nitrogen in limited quantities may be secured by the decomposition of certain of its compounds. Thus, ammonia, passed over hot copper oxide, is oxidized to nitrogen and water.

$$2\ NH_3 + 3\ CuO \longrightarrow 3\ H_2O + N_2\uparrow + 3\ Cu.$$

Ammonium nitrite is unstable toward heat, decomposing to yield nitrogen and water. Due to the difficulty in preserving ammonium nitrite, sodium nitrite and ammonium chloride are used for the preparation of nitrogen. When a solution of these substances is heated, nitrogen gas is evolved and sodium chloride is left in solution.

$$NH_4 + Cl^- + Na^+ + NO_2^- \longrightarrow N_2\uparrow + 2\ H_2O + Na^+ + Cl^-.$$

Elementary nitrogen is a colorless, odorless, and tasteless gas. It is only slightly soluble in water. Its critical temperature,

− 146°, indicates the difficulty in liquefying the gas. Liquid nitrogen has a boiling point of − 195.8°.

Chemical Reactions of Nitrogen. The atomic number of nitrogen is seven and its atom has five valence electrons. It exhibits oxidation numbers ranging from 3 − to 5 +. The molecules of the elementary substance are diatomic and are very stable. Under ordinary conditions the element is inactive; but it may be activated by subjecting the gas to a high voltage electrical discharge. The activated material reacts with several substances with which nitrogen does not ordinarily react. At high temperatures, magnesium, aluminum, and a few other elements unite directly with nitrogen to form the nitride.

$$3\ Mg + N_2 \longrightarrow Mg_3N_2.$$

Nitrogen and oxygen unite at the temperature of the electric arc with the formation of nitric oxide. The reaction is incomplete, coming to a condition of equilibrium when the percentage of nitric oxide is small.

$$N_2 + O_2 \rightleftharpoons 2\ NO.$$

The most important reaction of elementary nitrogen is its combination with hydrogen to form ammonia. This reaction also is incomplete and requires high pressure and moderately high temperature for successful operation.

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3.$$

At a temperature of about 1000°, nitrogen reacts with calcium carbide to form calcium cyanamide, CaNCN, and carbon.

$$CaC_2 + N_2 \longrightarrow CaNCN + C.$$

The heating of a mixture of sodium carbonate and carbon containing iron as a catalyst in an atmosphere of nitrogen produces sodium cyanide.

$$Na_2CO_3 + 4\ C + N_2 \longrightarrow 2\ NaCN + 3\ CO.$$

The Fixation of Nitrogen. The production of nitrogen compounds from atmospheric nitrogen is called *nitrogen fixation.* Only two of the reactions described in the preceding paragraph are now important for the production of nitrogen compounds. The reaction of nitrogen with hydrogen, which is described in Chapter VIII, is applied in the synthesis of ammonia. This is the most extensively used of the reactions for the fixation of nitrogen.

The cyanamide process is based on the reaction of nitrogen with calcium carbide to form calcium cyanamide, CaNCN. The reaction was discovered in 1895 by the German chemists, Caro and Frank. Commercial production of calcium cyanamide was begun in Germany in 1906. Calcium carbide is produced by heating a mixture of lime and coke in an electric furnace at a temperature of approximately 3000°.

$$CaO + 3\,C \longrightarrow CaC_2 + CO.$$

The molten carbide is withdrawn from the furnace, cooled, and pulverized. Nitrogen from liquid air is then passed over the calcium carbide at a temperature of approximately 1100°.

$$CaC_2 + N_2 \longrightarrow CaNCN + C + 98{,}430 \text{ cal.}$$

Since the reaction is highly exothermic, it is necessary to heat only a portion of the charge to start the reaction.

Ammonia may be produced from calcium cyanamide by reaction with steam under a pressure of 3–4 atmospheres.

$$CaNCN + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3.$$

Nevertheless, the chief source of ammonia is the direct synthetic process. The cyanamide process is important primarily for the production of cyanides, urea, and many other organic nitrogen compounds.

The union of nitrogen and oxygen at the temperature of the electric arc, to form nitric oxide from which nitric acid may be prepared, is historically important as the first industrial process for the fixation of nitrogen. Bradley and Lovejoy, Americans, worked out a process for the manufacture of nitric acid using the combination of nitrogen with oxygen as the initial step. They attempted in 1902 to develop it on an industrial scale at Niagara Falls. Birkeland and Eyde, Norwegians, developed a process, called the *arc process*, which began commercial operation in 1905. This process is no longer important, since the synthesis of ammonia is a more efficient process for the fixation of nitrogen.

The production of sodium cyanide by the reaction of sodium carbonate with carbon and nitrogen has been used to a limited extent; but no industrial processes have been developed for the production of nitrogen compounds through the formation of metal nitrides.

Hydrides of Nitrogen. *Ammonia*, NH_3, has already been discussed and it has been observed that its combination with protons leads to the formation of ammonium ions. The conversion of ammonia into nitric acid is discussed in a subsequent paragraph of this chapter.

Hydrazine, N_2H_4, is usually formed by the reaction of dilute solutions of ammonia with chlorine to form chloramine, which reacts with an excess of ammonia to form hydrazine.

$$2\,NH_3 + Cl_2 \longrightarrow NH_2Cl + NH_4Cl.$$
$$NH_2Cl + 2\,NH_3 \longrightarrow N_2H_4 + NH_4Cl.$$

Hydrazine reacts with water to form the weakly basic hydroxide, N_2H_5OH, which furnishes the positive ion, $N_2H_5^+$. Hydrazine is a good reducing agent.

Hydrazoic acid, HN_3, is formed by the reaction of nitrous acid with hydrazine.

$$N_2H_4 + HNO_2 \longrightarrow 2\,H_2O + HN_3.$$

The acid is stronger than acetic acid and yields a series of salts, the *azides*, which are similar to the chlorides in solubility. The free acid is an endothermic compound which explodes violently. The lead salt, lead azide, is used in making percussion caps.

Hydroxylamine, NH_2OH, may be prepared by the reduction of nitrous acid with sulfurous acid, and by the reduction of nitric acid and of nitrous acid in dilute solution by strong reducing agents. In acidic solutions hydroxylamine yields the positive ion, NH_3OH^+, by taking on a proton, and produces salts, such as NH_3OHCl.

Halides of Nitrogen. *Nitrogen trichloride* is formed by the reaction of an excess of chlorine with ammonium ions in strongly acidic solution.

$$NH_4^+ + 3\,Cl_2 \longrightarrow NCl_3 + 4\,H^+ + 3\,Cl^-.$$

This substance is a violently explosive oily liquid.

Nitrogen triiodide is formed by the reaction of iodine with a solution of ammonia.

$$4\,NH_3 + 3\,I_2 \longrightarrow NI_3 + 3\,NH_4^+ + 3\,I^-.$$

This substance separates as a brown precipitate of the composition, $NI_3(NH_3)$. It is fairly stable when moist but explodes at a slight touch when it is dry.

THE OXYACIDS OF NITROGEN

Nitrogen yields several oxyacids, the most important being nitric acid. The oxyacids of nitrogen are unstable in concentrated solutions, decomposing to yield products in which the oxidation number of nitrogen is decreased. Consequently, these acids are oxidizing agents. Even in dilute solutions their oxidizing properties are prominent.

Nitric Acid. This acid is a substance of great industrial importance. The production in the United States was approximately 200,000 tons in 1940. More than one half of the annual production is consumed in the formation of nitrocompounds and organic nitrates. Some of these compounds are used as high explosives and others are used in the manufacture of plastics, such as celluloid, and in the synthesis of dyes and drugs. The salts of nitric acid, the nitrates, have important applications, notably the use of sodium nitrate in mixed fertilizers.

Production of Nitric Acid from Ammonia. The preparation of nitric acid from ammonia is an important step in the production of nitrogen compounds from atmospheric nitrogen. Nearly 90% of the annual production of nitric acid in the United States is now from ammonia. The conversion is accomplished by the atmospheric oxidation of ammonia to nitric oxide, its subsequent union with oxygen to form nitrogen dioxide, and the reaction of nitrogen dioxide with water, yielding nitric acid. The reaction of ammonia with oxygen may produce either nitrogen and water or nitric oxide and water. In the presence of platinum gauze, which serves as a catalyst, the velocity of the reaction yielding nitric oxide is so greatly increased that an 85–95% conversion of ammonia into nitric acid may be obtained. Ammonia is introduced so as to form a mixture with about ten times its volume of air which has been preheated to 600°, just before the gases come in contact with the catalyst. The reaction is highly exothermic and the temperature rises to approximately 1000° as the reaction proceeds.

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O + 215{,}000\ \text{cal.}$$

The gases emerging from the contact chamber are cooled so that they serve to preheat the incoming air and no additional source of heat is required. Additional air is admitted to supply an excess

of oxygen for the conversion of nitric oxide into nitrogen dioxide, and the gases are passed into the absorption towers.

In the first tower, most of the nitric oxide combines with oxygen to form nitrogen dioxide. The rate of the reaction is low and the reaction is reversible at temperatures below 150°.

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2 + 27{,}800\ cal.$$

Low temperatures increase the yield of nitrogen dioxide in this mixture and the temperature is usually maintained at approximately 50°. In the absorption towers nitrogen dioxide reacts with water, forming nitric acid and nitrous acid.

$$2\ NO_2 + 2\ H_2O \rightleftharpoons H_3O^+ + NO_3^- + HNO_2.$$

Nitrous acid reacts with nitrogen dioxide, forming nitric acid and nitric oxide,

$$H_2O + HNO_2 + NO_2 \rightleftharpoons H_3O^+ + NO_3^- + NO.$$

By combining these two equations, the conversion of nitrogen dioxide into nitric acid may be represented by the equation:

$$3\ NO_2 + 3\ H_2O \rightleftharpoons 2\ H_3O^+ + 2\ NO_3^- + NO.$$

In warm concentrated solution this is the principal equilibrium and the conditions favor almost complete conversion of nitrogen dioxide into nitric acid and nitric oxide. The nitric oxide liberated in this reaction is again oxidized by the excess of oxygen present in the gases. Nearly complete absorption of the oxides of nitrogen may be secured by the regulation of the size of the absorption towers and the rate of the gas flow. The absorbing liquid in the final absorption tower is a solution of sodium carbonate; and practically complete absorption is obtained here with the formation of a mixture of the nitrate and nitrite.

$$CO_3^{--} + 2\ NO_2 \longrightarrow NO_3^- + NO_2^- + CO_2.$$

The acid produced in the towers is a moderately dilute acid which may be further concentrated, or may be converted directly into nitrates.

Production of Nitric Acid from Sodium Nitrate. Nitric acid may be prepared by the reaction of concentrated sulfuric acid with any nitrate, but sodium nitrate is commonly used in the process. This reaction was formerly the source of nearly all of the nitric acid prepared; but it now accounts for only a little more

than 10% of the annual production. In the laboratory method for the preparation of nitric acid, a mixture of sodium nitrate and concentrated sulfuric acid is heated in a glass retort, Fig. 110. Nitric acid is boiled out of this mixture and condensed.

$$NaNO_3 + H_2SO_4 \longrightarrow HNO_3 \uparrow + NaHSO_4.$$

In the industrial method, large cast iron retorts having a capacity of several tons of the nitrate mixture with concentrated sulfuric acid are used. Sodium hydrogen sulfate reacts with sodium nitrate at higher temperatures; but this second stage of the reaction is not feasible, because a large proportion of the nitric acid is decomposed at the higher temperature. If the reaction is carried out under reduced pressures, even lower temperatures are sufficient for the distillation of the nitric acid. The oxides of nitrogen which result from the decomposition of the acid may be recovered by passing the uncondensed gases into absorption towers similar to those used in the production of nitric acid from ammonia.

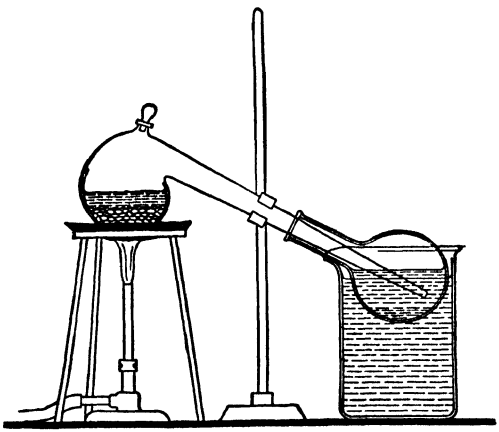

FIG. 110. — Laboratory Preparation of Nitric Acid.

Properties of Nitric Acid. The pure compound is a colorless liquid with a boiling point of 86°. It is soluble in water in all proportions. The solution containing 68% of nitric acid, specific gravity 1.41, boils at 120.5°, under a pressure of one atmosphere, without change in composition. Concentrated solutions of nitric acid are frequently yellow or brown in color. This is due to the dissolved nitrogen dioxide formed by the slow decomposition of nitric acid under the influence of light.

Chemical Reactions of Nitric Acid. The anhydrous substance is unstable and partially decomposes while being distilled under atmospheric pressure.

$$4\,HNO_3 \longrightarrow 2\,H_2O + 4\,NO_2 + O_2.$$

The acid may be dehydrated by the action of phosphorus pentoxide, yielding *nitrogen pentoxide*, N_2O_5.

$$2\,HNO_3 + P_2O_5 \longrightarrow N_2O_5 + 2\,HPO_3.$$

Nitric acid enters into a number of important reactions. These may be classified for further study into three important types: *viz.*, reactions as an acid; reactions as a nitrating agent; and reactions as an oxidizing agent.

Acid Reactions of Nitric Acid. The anhydrous substance is molecular in composition, and it reacts with water with the formation of hydronium and nitrate ions.

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-.$$

The solution is a strong acid, reacting with metal oxides and hydroxides, ammonia, and the salts of weak and insoluble or unstable acids. These reactions are represented by the following equations.

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O.$$
$$2\,H_3O^+ + CaO \longrightarrow 3\,H_2O + Ca^{++}.$$
$$H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O.$$
$$2\,H_3O^+ + CO_3^{--} \rightleftharpoons 3\,H_2O + CO_2.$$

Nitric acid reacts also with most of the common metals, but nitric oxide, instead of hydrogen, is the usual reduction product.

$$3\,Zn + 8\,H_3O^+ + 2\,NO_3^- \longrightarrow 3\,Zn^{++} + 2\,NO + 12\,H_2O.$$

This reaction is not strictly an acid reaction of nitric acid, since it involves both the hydronium and the nitrate ions. Many of the reactions of nitric acid differ from those of the hydroacids because of the oxidizing properties of the nitric acid.

Nitrating Action of Nitric Acid. Concentrated nitric acid reacts with some of the hydrocarbons and derivatives of these substances with the formation of products known as *nitro-compounds*. In this reaction, the nitro group, $-NO_2$, is substituted for an atom of hydrogen in the molecule of the organic compound. The hydrogen thus removed unites with the hydroxy group of atoms in molecular nitric acid to form water. This type of reaction is known as *nitration*. Thus, the reaction of nitric acid with benzene yields nitrobenzene.

$$C_6H_6 + HONO_2 \longrightarrow H_2O + C_6H_5NO_2.$$

The reaction of nitration takes place most readily in the presence of sulfuric acid which serves as a dehydrating agent. Under these conditions a maximum of three nitro groups may be introduced into the benzene molecule in the place of atoms of hydrogen. The product in this case is trinitrobenzene.

$$C_6H_6 + 3\ HONO_2 \longrightarrow 3\ H_2O + C_6H_3(NO_2)_3.$$

Benzene, toluene, and a number of other compounds derived from these substances undergo nitration. The most extensive uses of nitric acid are based on the reaction of nitration. Several of the nitro compounds are high explosives; *e.g.*, trinitrotoluene (T.N.T.) and trinitrophenol (picric acid). A number of other nitro compounds are valuable as intermediates in the production of synthetic dyes, drugs, lacquers, and plastics. Nitrobenzene may be reduced by iron and water to form aniline, $C_6H_5NH_2$.

$$C_6H_5NO_2 + 2\ Fe + 4\ H_2O \longrightarrow C_6H_5NH_2 + 2\ Fe(OH)_3.$$

Aniline itself is colorless, but it is used in the synthesis of a number of highly colored products known as aniline dyes.

Esterification with Nitric Acid. A number of organic compounds which contain hydroxide radicals react with nitric acid in the presence of sulfuric acid to yield compounds known as *nitrate esters.* The reaction is called esterification. Since this reaction takes place under conditions which are similar to those used for the nitration reaction, the products are commonly called nitro compounds. Glycerol, $C_3H_5(OH)_3$, reacts with the mixture of concentrated nitric and sulfuric acids to form the ester, glyceryl trinitrate, $C_3H_5(NO_3)_3$, also called "nitroglycerine."

$$C_3H_5(OH)_3 + 3\ HNO_3 \longrightarrow C_3H_5(NO_3)_3 + 3\ H_2O.$$

Cellulose in a similar reaction yields a nitrate ester known as guncotton. These substances are unstable and are valuable as high explosives. Esters of cellulose containing smaller proportions of the nitrate radical than guncotton, and called *pyroxylin,* are used in the production of celluloid, collodion, and other important products.

Oxidizing Action of Nitric Acid. In the preceding chapter, some of the reactions of nitric acid as an oxidizing agent have been illustrated. The oxidation number of nitrogen in nitric acid is 5 + and the compound is unstable in the presence of

reducing agents, readily decomposing to form products which contain nitrogen in lower oxidation numbers. The stages of oxidation of nitrogen in its common compounds are illustrated by the following formulas.

N^{5+}	N^{4+}	N^{3+}	N^{2+}	N^{1+}	N^{0}	N^{3-}
HNO_3	NO_2	HNO_2	NO	N_2O	N_2	NH_3

In these compounds, the valences of nitrogen are covalent bonds due to shared electrons; but the electron pairs are assumed to be held more strongly by the oxygen than nitrogen atoms. The positive nature of the oxidation numbers is interpreted in this way. In ammonia, the electron pairs are held more strongly by the nitrogen than hydrogen atoms.

It is evident that a number of reduction products of nitric acid are possible. The following ion-electron equations illustrate the half reactions involved in the reduction of nitric acid.

$$2\,H^+ + NO_3^- + 1\,\epsilon \rightleftharpoons NO_2 + H_2O.$$
$$3\,H^+ + NO_3^- + 2\,\epsilon \rightleftharpoons HNO_2 + H_2O.$$
$$4\,H^+ + NO_3^- + 3\,\epsilon \rightleftharpoons NO + 2\,H_2O.$$
$$10\,H^+ + 2\,NO_3^- + 8\,\epsilon \rightleftharpoons N_2O + 5\,H_2O.$$
$$10\,H^+ + NO_3^- + 8\,\epsilon \rightleftharpoons NH_4^+ + 3\,H_2O.$$

In the reduction of nitric acid, a mixture of products is often obtained; but the main product formed in any reaction depends on the concentration of the acid, the temperature, and the activity of the reducing agent. Nitrogen dioxide is the principal product formed by the reduction of concentrated nitric acid of specific gravity 1.4; but nitric oxide is the principal product in the reduction of the acid of specific gravity 1.2, which is approximately 6 N. From the equations for the half reactions it is seen that the oxidizing action of nitric acid is due to hydronium and nitrate ions.

The oxidation of representative substances of the various classes of reducing agents *by moderately concentrated nitric acid* is represented by the equations which follow. When silver is oxidized by nitric acid, a solution of silver nitrate is produced.

$$4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO.$$
$$[Ag \longrightarrow Ag^+ + 1\,\epsilon.] \times 3.$$
$$4\,H^+ + NO_3^- + 3\,Ag \longrightarrow 2\,H_2O + NO + 3\,Ag^+.$$

The ferrous ion is oxidized to the ferric ion.

$$4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO.$$
$$[Fe^{++} \longrightarrow Fe^{+++} + 1\,\epsilon.] \quad \times 3.$$
$$4\,H^+ + NO_3^- + 3\,Fe^{++} \longrightarrow 2\,H_2O + NO + 3\,Fe^{+++}.$$

Nitric acid reacts with the slightly soluble cupric sulfide to produce free sulfur and cupric ions.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO.] \quad \times 2.$$
$$[CuS \longrightarrow Cu^{++} + S + 2\,\epsilon.] \quad \times 3.$$
$$8\,H^+ + 2\,NO_3^- + 3\,CuS \longrightarrow 4\,H_2O + 2\,NO + 3\,Cu^{++} + 3\,S.$$

The non-metal, arsenic, is oxidized by nitric acid to arsenic acid.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO.] \quad \times 5.$$
$$[As + 4\,H_2O \longrightarrow H_3AsO_4 + 5\,H^+ + 5\,\epsilon.] \quad \times 3.$$
$$5\,H^+ + 5\,NO_3^- + 3\,As + 2\,H_2O \longrightarrow 5\,NO + 3\,H_3AsO_4.$$

The oxidation of substances *by concentrated nitric acid* usually yields nitrogen dioxide as the reduction product. The reaction of concentrated nitric acid with sulfur yields nitrogen dioxide and sulfuric acid.

$$[2\,H^+ + NO_3^- + 1\,\epsilon \longrightarrow NO_2 + H_2O.] \quad \times 6.$$
$$S + 4\,H_2O \longrightarrow SO_4^{--} + 8\,H^+ + 6\,\epsilon.$$
$$6\,H^+ + 6\,NO_3^- + S \longrightarrow 6\,NO_2 + 2\,H_2O + SO_4^{--} + 2\,H^+.$$

With active reducing agents, *dilute nitric acid* is reduced, in part at least, to the ammonia stage of oxidation and an ammonium salt is produced.

$$10\,H^+ + NO_3^- + 8\,\epsilon \longrightarrow NH_4^+ + 3\,H_2O.$$
$$[Zn \longrightarrow Zn^{++} + 2\,\epsilon.] \quad \times 4.$$
$$10\,H^+ + NO_3^- + 4\,Zn \longrightarrow NH_4^+ + 3\,H_2O + 4\,Zn^{++}.$$

Aqua Regia. A mixture of concentrated nitric and hydrochloric acids, in the approximate volume ratio of one of nitric to three of hydrochloric, is a more effective oxidizing agent than nitric acid alone. This mixture attacks gold and platinum with the formation of chlorauric and chloroplatinic acids, respectively. The acid mixture is called *aqua regia* because it dissolves the noble metals.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO.] \quad \times 4.$$
$$[Pt + 2\,H^+ + 6\,Cl^- \longrightarrow H_2PtCl_6 + 4\,\epsilon.] \quad \times 3.$$
$$22\,H^+ + 4\,NO_3^- + 3\,Pt + 18\,Cl^- \longrightarrow 8\,H_2O + 4\,NO + 3\,H_2PtCl_6.$$

This reaction is not due to an increased activity of the oxidizing agent, but to the fact that platinum is more easily oxidized in the presence of hydrogen and chloride ions than in the presence of the nitric acid alone. This is due to the combination of platinum with the hydrogen and chloride ions to form the complex product which removes the simple platinum ions practically completely from the solution.

Nitrous Acid. HNO_2. This acid may be prepared in solution by the addition of a stronger acid to a cold solution of a nitrite.

$$NO_2^- + H_3O^+ \rightleftharpoons HNO_2 + H_2O.$$

Solutions of nitrous acid are blue. The acid is weak and unstable, decomposing to form the trioxide which also decomposes at room temperature to give a mixture of nitric oxide and nitrogen dioxide.

$$2\,HNO_2 \rightleftharpoons H_2O + N_2O_3.$$
$$N_2O_3 \rightleftharpoons NO + NO_2.$$

Nitrous acid also decomposes, in a reaction similar to that of the hypochlorites, to form nitric acid and nitric oxide, both of these substances being more stable than nitrous acid.

$$3\,HNO_2 \longrightarrow H_3O^+ + NO_3^- + 2\,NO.$$

Nitrous acid contains nitrogen in an oxidation state of 3 +. It may, therefore, react as an oxidizing agent and also as a reducing agent. It oxidizes iodides to free iodine.

$$[HNO_2 + H^+ + 1\,\epsilon \longrightarrow H_2O + NO.] \times 2.$$
$$2\,I^- \longrightarrow I_2 + 2\,\epsilon.$$
$$2\,HNO_2 + 2\,H^+ + 2\,I^- \longrightarrow 2\,H_2O + 2\,NO + I_2.$$

Nitrous acid is oxidized to nitric acid by strong oxidizing agents such as acid permanganate. Nitrous acid, produced from nitrites at the time of the reaction, is extensively used in synthetic organic chemistry.

Hyponitrous Acid. $H_2N_2O_2$. This acid is formed by the oxidation of hydroxylamine by mercurous oxide or nitrous acid.

$$NH_2OH + HNO_2 \longrightarrow H_2N_2O_2 + H_2O.$$

The double formula of this acid is based on molecular weight determinations. The acid is unstable and decomposes irreversibly into water and nitrous oxide.

$$H_2N_2O_2 \longrightarrow H_2O + N_2O.$$

Explosives. In addition to gunpowder and ammonium nitrate, the substances which are most extensively used as explosives are organic compounds which contain nitrogen and oxygen. These compounds possess in common a certain instability due to the fact that they are endothermal compounds. In their decomposition they give rise to gaseous products, and a large amount of heat is evolved. The gaseous products are, consequently, heated to a high temperature and occupy a very great volume compared to that of the substance from which they are produced. A substance which exhibits too great instability is not a useful explosive, for its decomposition cannot be controlled so as to have the explosion occur at the desired place. The high explosives most extensively used are of two types: *esters of nitric acid* in which several nitrate radicals are present in one molecule of the compound; and *nitro compounds.*

Glyceryl nitrate, nitroglycerine, is an important high explosive. The pure substance decomposes with great violence from slight shock, yielding the oxides of carbon and hydrogen, and elementary nitrogen and oxygen.

$$4\ C_3H_5(NO_3)_3 \longrightarrow 12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2.$$

These gaseous substances are formed instantaneously so that great pressure is produced suddenly; and the explosion causes a terrific shattering effect. The instability of this substance is so great that a considerable amount of danger is involved in transporting and handling it. In 1867, Nobel discovered that nitroglycerine may be absorbed in finely divided porous earth, diatomaceous earth, to produce a powerful explosive which may be handled safely. This material, known as *dynamite,* is now commonly made by absorbing nitroglycerine in wood pulp or sawdust and adding ammonium nitrate. *Blasting gelatine* is prepared by dissolving guncotton in nitroglycerine, and adding sodium nitrate and sawdust or flour to regulate the rate of explosion.

Guncotton, cellulose trinitrate, also called trinitrocellulose, is a high explosive that decomposes with great violence when it is detonated by another explosive. Nobel discovered the fact that an ether-alcohol solution of guncotton is caused to set to a jelly by the addition of glyceryl trinitrate. The product can be rolled into cords and molded into various shapes and sizes. It leaves no

solid residue when it burns and is, consequently, a smokeless powder. *Cordite* contains about 65 parts of guncotton, 30 parts of nitroglycerine, and 5 parts of vaseline. This mixture of the two high explosives can be handled without great danger of explosion from shock, and can be used as a propellant in firearms. The two substances separately explode too rapidly to permit their use in firearms, because the shattering effect of the explosion would split the barrel of the gun before the inertia of the bullet is overcome. The propellant explosive is detonated by substances such as *fulminate of mercury*, $Hg(ONC)_2$, which may be exploded by shock. While it is wet, the fulminate may be molded and cut, and introduced into priming caps, without danger. When it is dry, the fulminate explodes when it is struck a sharp blow. The explosion of the priming cap detonates the charge in the cartridge.

Formerly, *black gunpowder*, a mixture consisting of 75% potassium nitrate, 15% charcoal, and 10% sulfur, was used as a propellant; but its use has been largely replaced by the nitrocellulose smokeless powders.

Nitro explosives are extensively used in shells for military purposes. *Trinitrotoluene*, T.N.T., $C_6H_2(CH_3)(NO_2)_3$, and *picric acid, trinitrophenol*, $C_6H_2(OH)(NO_2)_3$, are both used as high explosives in shells. These substances are sufficiently insensitive to shock so that they may be used to fill shells which are fired from guns. The more sensitive guncotton and glyceryl nitrate are not suitable for this use. The shells are exploded by a special charge which is ignited by a time fuse or by impact. Trinitrotoluene is often mixed with ammonium nitrate to give the high explosive, *amatol*, which is used in shells.

THE OXIDES OF NITROGEN

Nitrogen yields a series of oxides in which it exhibits oxidation states from 1 + to 5 +. The trioxide and pentoxide are produced by the dehydration of nitrous and nitric acids, respectively. These oxides are unstable and are not important. The other three oxides, *nitrous oxide*, N_2O, *nitric oxide*, NO, and *nitrogen dioxide*, NO_2, are important.

Nitrous Oxide. N_2O. This substance was first prepared by Priestley in 1772, by the reduction of nitric oxide by the action

of moist iron filings. Nitrous oxide is now prepared, both commercially and in the laboratory, by the gentle heating of ammonium nitrate, Fig. 111.

$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O + 9{,}000 \text{ cal.}$$

The decomposition of nitrous oxide into the elements is also exothermic; and, consequently, nitrous oxide is unstable, although the rate of its decomposition at ordinary temperatures is not appreciable.

$$2\,N_2O \longrightarrow 2\,N_2 + O_2 + 38{,}000 \text{ cal.}$$

If heated too strongly or detonated, ammonium nitrate decomposes as a high explosive into nitrogen, oxygen, and water.

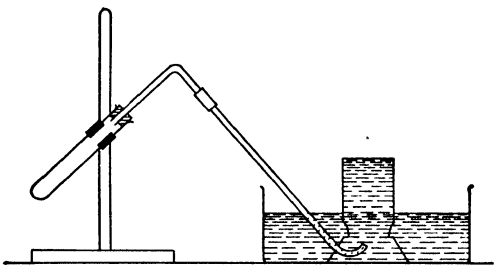

FIG. 111. — Laboratory Preparation of Nitrous Oxide.

Nitrous oxide is a colorless gas which has a critical temperature of 35°. It may be liquefied at 20° by a pressure of 50 atmospheres. Its solubility in water is only 1.3 volumes in 100 volumes of water at 20° and a pressure of 760 mm. Nitrous oxide supports combustion readily, yielding the oxides of the elements in the substance burned and free nitrogen. It does not cause the rusting of metals and does not support respiration. The introduction of a burning splinter into nitrous oxide heats a small amount of the gas so that it decomposes; and the reaction at the surface of the burning substance continues because the decomposition itself is exothermic. The gas is extensively used as an anaesthetic in dentistry and in some other surgical operations. The name "laughing gas" is due to the fact that the inhalation of a small amount of the gas produces a mild form of hysteria.

Nitric Oxide. NO. Since nitric oxide is the result of the reduction of nitric acid in moderate concentration, it is easily prepared in the laboratory by the action of the acid on metals such as copper. When prepared in this way, the gas product usually contains small proportions of nitrogen, nitrous oxide, and nitrogen dioxide. Nitric oxide is the most stable of the oxides of nitro-

gen toward heat and toward the action of reducing agents. It does not readily support combustion, although vigorously burning phosphorus continues to burn in the gas with the formation of nitrogen and the oxide of phosphorus. The formation of this oxide as an intermediate product in the conversion of ammonia into nitric acid was discussed in connection with the Ostwald process. The most important reaction of nitric oxide is its combination with oxygen to produce nitrogen dioxide.

Nitrogen Dioxide. NO_2. This brown gas is formed as the result of the combination of nitric oxide with oxygen. Hence, brown fumes are observed in the air over vessels in which nitric acid is being reduced, even though nitric oxide may be the direct product of the reduction. If highly concentrated nitric acid is employed as the oxidizing agent and if the activity of the reducing agent is low, nitrogen dioxide is the direct product of the reduction. The oxidation of elementary sulfur by concentrated nitric acid yields sulfuric acid, nitrogen dioxide, and water. Nitrogen dioxide results also from the thermal decomposition of the nitrates of the common metals, except sodium, potassium, and ammonium.

$$2\ Pb(NO_3)_2 \longrightarrow 2\ PbO + 4\ NO_2 + O_2.$$

At temperatures above 150°, nitrogen dioxide partially decomposes to form an equilibrium mixture with nitric oxide. At 620°, the decomposition is complete. At 22°, about 75% of the gas exists in the form of the tetroxide, N_2O_4, which has twice the molecular weight of nitrogen dioxide and is known as a *polymer* of the latter substance.

$$2\ NO_2 \overset{150°-620°}{\rightleftharpoons} 2\ NO + O_2.$$

$$2\ NO_2 \overset{0°-150°}{\rightleftharpoons} N_2O_4.$$

The most important reactions of nitrogen dioxide are those with water. A mixture of nitric and nitrous acids is formed with cold water, so long as the resulting solution is dilute.

$$2\ NO_2 + 2\ H_2O \longrightarrow HNO_2 + H_3O^+ + NO_3^-.$$

With warm water and with relatively larger amounts of nitrogen dioxide, the products are nitric acid and nitric oxide.

$$3\ NO_2 + 3\ H_2O \longrightarrow 2\ H_3O^+ + 2\ NO_3^- + NO.$$

These reactions are important in the production of nitric acid from ammonia.

EXERCISES

1. What is meant by the "fixation of nitrogen"? List reactions of elementary nitrogen which are available for this purpose.
2. Which two of these reactions are actually used for the fixation of nitrogen? Describe the process based on each.
3. How is nitric acid produced from ammonia? Give reasons for the conditions in each step of the process.
4. Write ionic equations representing the acid reactions of nitric acid.
5. Discuss the oxidizing activity of nitric acid and the conditions under which different products are obtained.
6. Using the ion-electron method, derive the equations for the reactions of nitric acid with each of the following substances:

(*a*) Iodine	(*f*) Bismuth
(*b*) Copper	(*g*) Sodium chloride
(*c*) Sodium bromide	(*h*) Phosphorus
(*d*) Sodium sulfite	(*i*) Arsenic trioxide
(*e*) Lead sulfide	(*j*) Ammonium chloride.

7. What is aqua regia? Write the equation to represent its reaction with gold to form chlorauric acid, $HAuCl_4$.
8. What is a nitration reaction? How do nitro compounds differ from nitrate esters?
9. Discuss the importance of the nitro compounds (*a*) as intermediates in organic syntheses and (*b*) as explosives.
10. List the oxides of nitrogen and show how they illustrate the law of multiple proportions.
11. What is the source of nitrous oxide? nitric oxide? nitrogen dioxide?
12. What is the most important reaction of each of these oxides?

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CHAPTER XIX

SULFUR. THE OXIDES AND OXYACIDS OF SULFUR. SELENIUM AND TELLURIUM

The elements of group VI of the Periodic System are oxygen, sulfur, selenium, and tellurium. The atoms of these elements contain six valence electrons and they react with electropositive elements to form compounds in which they have an oxidation number of 2 −. Oxygen differs notably from the other members of the group in that it does not tend to form compounds in a positive state of oxidation. This, however, is not particularly significant, because oxygen has been found to be a convenient reference element to which an oxidation number of 2 − is arbitrarily assigned in covalent compounds. The general importance of the element and its compounds and the widespread familiarity with its behavior have led to the separate discussion of oxygen in Chapter IV. Sulfur, selenium, and tellurium yield many compounds in positive oxidation states, the most important being in the 4 + and 6 + states. These elements exhibit the general group relationships already discussed in the consideration of the halogens. With increased atomic number, the non-metallic nature of the element decreases. Sulfur is distinctly non-metallic in nature and is more active than selenium and tellurium. Attention will be devoted primarily to sulfur and its compounds, with brief mention of some of the compounds of selenium and tellurium.

SULFUR

Elementary sulfur has been known from early times. Mention of brimstone, the stone that burns, occurs in early literature. Sulfur was considered by the alchemists to be an essential ingredient of all combustible substances, so that they regarded it as the very essence of fire.

Occurrence of Sulfur. *Elementary sulfur* occurs in regions of volcanic activity in various parts of the earth, for example,

Sicily, Iceland, Mexico, and Japan. The most important deposit in the United States is found in salt domes in Texas and in Louisiana. Sulfur in these deposits is not the product of volcanic action and its origin is not definitely known. *In the combined condition* sulfur occurs widely distributed in sulfides, *e.g.*, iron pyrites, and the sulfides of copper, zinc, lead, and other metals; and in the sulfates of calcium, barium, strontium, and magnesium. Sulfur is also a constituent of many complex substances of organic origin.

The Extraction of Sulfur. Prior to 1900, the Sicilian deposit was the main source of the world's supply of elementary sulfur; but the chief production is now from the deposits in Texas and Louisiana. *The sulfur of Sicily* occurs mixed with volcanic rock. The sulfur-bearing rock is mined and fed into kilns, where it is heated and the sulfur melted out. In order to purify the product

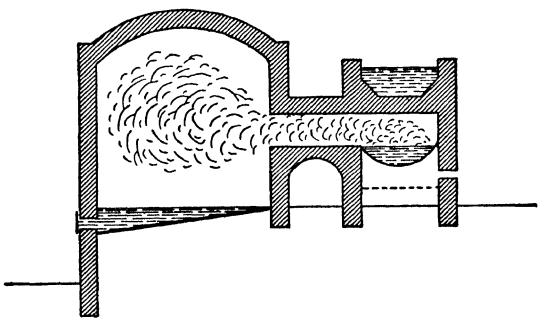

FIG. 112. — Purification of Sulfur.

obtained from the kiln, it is next distilled from iron retorts, the vapors being condensed in brick chambers, Fig. 112. So long as the chamber is cold, the vapor first condensed yields finely divided yellow particles known as *flowers of sulfur*. As the chamber becomes hotter the distillate takes the form of liquid sulfur. This is run off into molds in which it solidifies in the form called *roll sulfur*, or *brimstone*. The production of sulfur in Italy in 1938 was approximately 370,000 long tons.

In the Texas and Louisiana deposits, sulfur occurs in a limestone layer in the salt domes. These domes have a core of salt, above which is a layer of calcium sulfate, then the sulfur-bearing limestone. The limestone containing the sulfur lies at a distance of approximately 900 ft. below the surface of the earth and is covered

by sand, clay, and rock. About 1904, a process developed by Frasch made these deposits available as a source of sulfur. The process consists in melting sulfur from the rock by superheated water and forcing it to the surface by compressed air. For this purpose, borings are made through the overlying material, and four concentric pipes are driven down into the sulfur-bearing rock, Fig. 113. The largest of these is about eight inches in diameter. Through the two outer pipes, water heated under pressure to 180° is pumped down into the deposit. Sulfur melts at 114.5°. When a sufficient amount of molten sulfur has collected in the cavity around the ends of the pipes, hot compressed air is forced down the innermost pipe. By means of the pressure thus developed, the liquid sulfur is forced to rise through the remaining pipe. Reaching the surface, the sulfur flows into large wooden bins, where it solidifies in great masses, Figs. 114, 115, some containing as much as 100,000 tons. Some of these sulfur wells produce 500 tons per day and the purity of the product is approximately 99.5%. The production of sulfur in the United States in 1940 was estimated to be 2,725,000 tons.

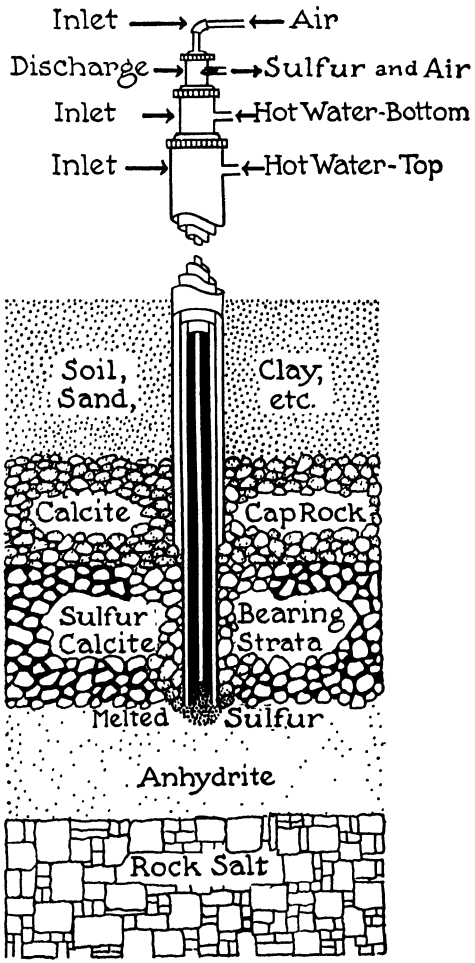

FIG. 113. — Sulfur Well. (Courtesy of Texas Gulf Sulphur Company, Inc.)

Production of Sulfur from Compounds. In a number of countries, particularly those having no extensive deposits of sulfur,

the element is obtained as a by-product of other processes. Large quantities of elementary sulfur are produced in Germany from coke plants and gasoline hydrogenation plants. The production of sulfur in Norway is from copper-iron pyrites. Exports from

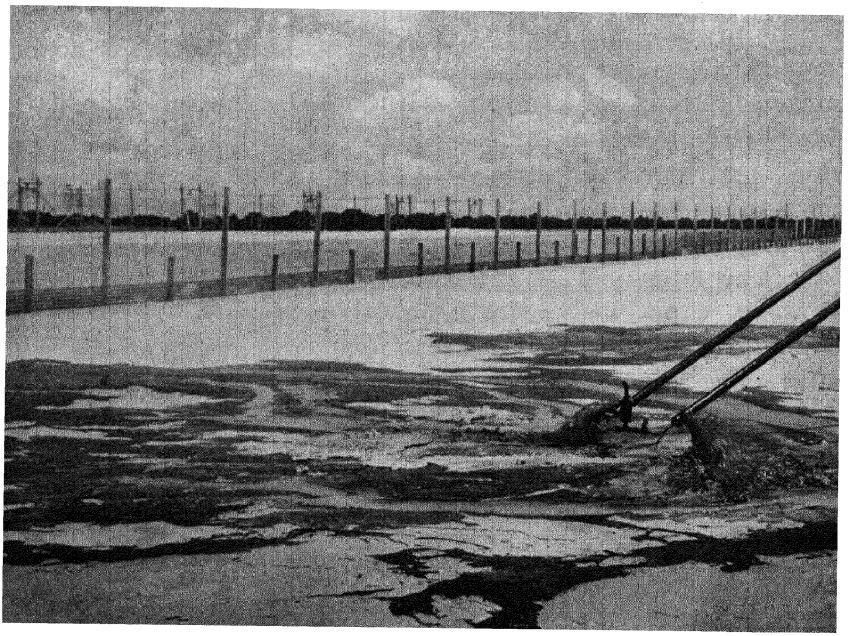

FIG. 114. — Sulfur Discharging into a Vat. (Courtesy of Texas Gulf Sulphur Company, Inc.)

Norway in 1938 were approximately 75,000 tons. Elementary sulfur is produced at metal sulfide smelters in Canada in British Columbia.

Properties of Sulfur. Solid sulfur exists in at least two allotropic forms. Both of these crystalline varieties are soluble in carbon disulfide but are insoluble in water. *Rhombic sulfur* is the stable variety at any temperature below 96°. Rhombic sulfur is a yellow solid with a specific gravity of 2.06 and a melting point of 112.8°. If kept at temperatures above 96° but below the melting point, it slowly changes into *monoclinic sulfur*. Monoclinic sulfur is easily obtained by melting sulfur and allowing the liquid to cool slowly. As the material solidifies, the monoclinic variety is formed, and long, transparent, needlelike crystals are

obtained. This material slowly changes into the rhombic form at ordinary temperatures. The specific gravity of monoclinic sulfur is 1.96 and the melting point 119°. When rhombic sulfur, which is being heated slowly, reaches the transition temperature, the monoclinic variety begins to form and the observed melting point of rhombic sulfur in the presence of this material is 114.5°.

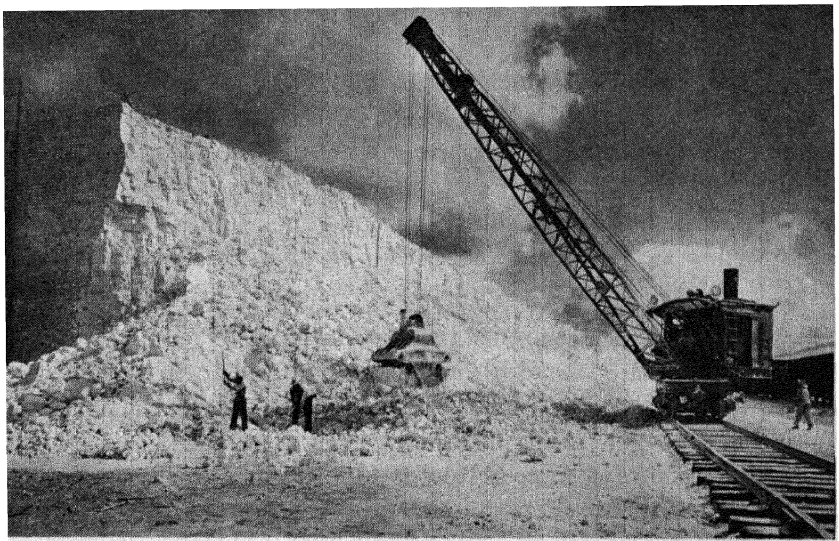

FIG. 115. — Sulfur Ready for Loading. (Courtesy of Texas Gulf Sulphur Company, Inc.)

Liquid Sulfur. A thin, straw-colored liquid is obtained when sulfur first melts. This liquid becomes darker in color and more viscous as the temperature is raised, and it is so viscous at about 200° that it flows very slowly from an inverted vessel. It becomes more fluid as the temperature is further raised and boils at 445°. There are two forms of sulfur in the liquid state. They are known as $S\lambda$ and $S\mu$. At 100°, the equilibrium mixture contains 3.6% $S\mu$ and at 445°, about 35%. An elastic mass may be obtained by cooling molten sulfur quickly from temperatures near the boiling point. This material is a supercooled solution of the two molecular modifications; and crystalline material separates in a day or two. The crystalline material may be dissolved in carbon disulfide, leaving a residue which is non-crystalline. This substance has the general appearance of a solid but it has no definite melting

point or crystalline structure and is known as *amorphous sulfur.* It is transformed into the stable rhombic variety only very slowly at ordinary temperatures.

Finely divided sulfur may be precipitated by the reaction of calcium polysulfide with an excess of an acid. This material is nearly white when it is first formed and is known as *milk of sulfur.*

Chemical Reactions of Sulfur. Molecular weight determinations show that sulfur in the gaseous state is composed of the molecules, S_8, S_6, and S_2, and that the relative amounts of these molecular varieties vary with the temperature. Since different molecular varieties of sulfur exist in the liquid, gaseous, and solid states, it is customary to represent elementary sulfur by the symbol, S.

The atomic number of sulfur is 16 and the atomic weights of its isotopes are 32, 33, 34, and 36, giving an average chemical atomic weight of 32.06. The element has six valence electrons and may be represented by the electronic formula $:\ddot{S}:$ indicating its tendency to gain two additional electrons and form the electrovalent sulfide ion, S^{--}. Sulfur unites with all of the common metals except gold and platinum. Metals which form ions in more than one oxidation state commonly yield the lower valent compound in their reactions with sulfur.

$$2\,Cu + S \longrightarrow Cu_2S.$$

Hydrogen burns in an atmosphere of gaseous sulfur to form hydrogen sulfide. Sulfur also unites with most of the other non-metallic elements, sharing electrons in covalent bonds and forming molecular products. Sulfur is usually considered to have an oxidation number of 2 — in these compounds if the other non-metals are less active than sulfur.

$$2\,P + 3\,S \longrightarrow P_2S_3.$$

With non-metallic elements, such as the halogens and oxygen, sulfur exhibits positive oxidation numbers.

Uses of Sulfur. Sulfur has a number of extensive and important uses. The consumption of sulfur in the United States in 1938 amounted to approximately 1,100,000 long tons. The distribution among some of the major industries is shown in Table 25.

TABLE 25

CONSUMPTION OF SULFUR IN THE UNITED STATES
(Long tons)

Industry	*1936*	*1937*	*1938*
Chemicals	620,000	777,000	484,000
Fertilizer and insecticides	266,000	415,000	220,000
Pulp and paper	260,000	302,000	174,000
Explosives	53,000	68,000	50,000
Dyes and coal tar products	46,000	49,000	40,000
Rubber	39,000	37,000	29,000
Paint and varnish	54,000	69,000	50,000
Food products	4,500	6,000	5,500
Miscellaneous	78,000	82,000	47,500

The distribution of the element is shown graphically in Fig. 116. The most extensive use of sulfur is in the production of sulfuric acid and other chemicals. The large consumption in the fertilizer

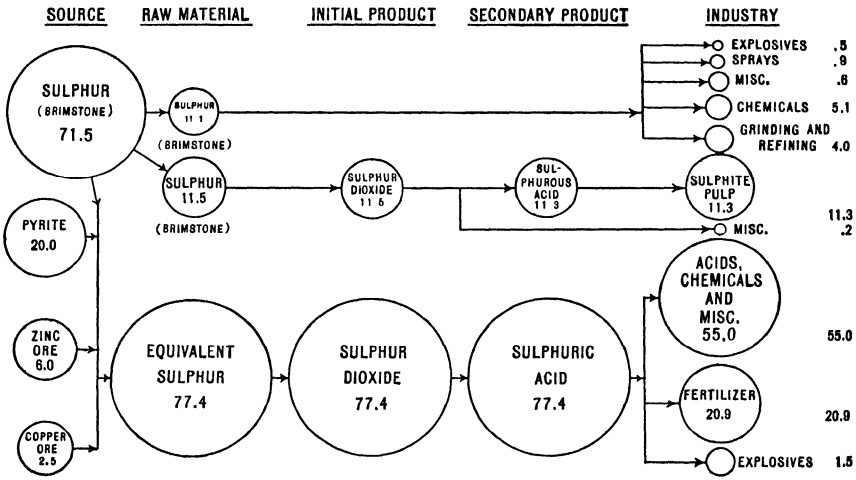

FIG. 116. — Major Sources of the Element Sulfur and Its Primary Industrial Applications in the United States. (Courtesy of Texas Gulf Sulphur Company, Inc.)

industry involves the use of sulfuric acid in the conversion of calcium phosphate into the superphosphate and in the preparation of ammonium sulfate. Finely divided sulfur destroys fungi on fruit trees and vines so that the element is used in the prepara-

tion of sprays, such as the lime-sulfur spray. Sulfur is used in the vulcanization of rubber, the manufacture of matches, and the preparation of dyes. Formerly, sulfur was essential for military purposes in the making of black gunpowder, a mixture of potassium nitrate, sulfur, and charcoal. Although black gunpowder no longer has important military uses, sulfur is nevertheless essential, for it is required in the manufacture of sulfuric acid which is necessary in the preparation of modern high explosives.

The discovery of the vulcanization of rubber was made by Goodyear in 1839, when he happened accidentally to drop a mixture of gum rubber and sulfur on a hot stove. He found that the product retained the desired elasticity and acquired strength and many other useful properties, while at the same time the stickiness which had prevented the extensive commercial application of rubber disappeared. The properties of the product depend in part on the amount of sulfur mixed with the gum and in part on the temperature and length of time of the heating process.

Hydrogen Sulfide. The hydride of sulfur is a weak acid which is important analytically because of the regulated concentration of the sulfide ion which may be secured through its use in solutions of different acidity and basicity. This substance is discussed with the other common binary acids in Chapter XV.

SULFUR DIOXIDE AND SULFUROUS ACID

Sulfur dioxide is the oxide of sulfur in its lower, common, positive oxidation number. It is found in volcanic gases and is the chief product of the combustion of sulfur. The oxide reacts with water to form sulfurous acid, which is unstable.

Preparation of Sulfur Dioxide. There are three varieties of reactions which may be employed conveniently in the preparation of sulfur dioxide: *viz.*, the combustion of sulfur and of metal sulfides; the reaction of sulfites with acids; and the reduction of sulfuric acid.

In commercial practice, sulfur dioxide is prepared by burning sulfur and naturally occurring sulfides, such as zinc sulfide, in air.

$$S + O_2 \longrightarrow SO_2\uparrow.$$

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2\uparrow.$$

Formerly, the combustion of iron pyrite, FeS_2, chiefly imported from Spain, was the leading source of sulfur dioxide.

$$4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2\uparrow.$$

With the development and expansion of the sulfur industry in Texas and Louisiana, the combustion of elementary sulfur has become the leading source of sulfur dioxide. In the production of metals from their sulfide ores the first step is the combustion of the sulfide, and the sulfur dioxide produced in this reaction is a by-product.

In the laboratory, sulfur dioxide is usually prepared by the reaction of hydrochloric acid with sodium sulfite. Sulfurous acid is a relatively weak acid and is unstable, so that it decomposes with the evolution of sulfur dioxide.

$$2\,H_3O^+ + SO_3^{--} \rightleftharpoons H_2SO_3 + 2\,H_2O.$$
$$H_2SO_3 \rightleftharpoons H_2O + SO_2\uparrow.$$

Sulfur dioxide may also be prepared in a laboratory method based on the reduction of concentrated sulfuric acid. When the concentrated acid is heated with reducing agents, such as copper, the chief reduction product of the acid is sulfur dioxide.

$$2\,H_2SO_4 + Cu \longrightarrow CuSO_4 + 2\,H_2O + SO_2\uparrow.$$

Properties of Sulfur Dioxide. Sulfur dioxide is a gas of disagreeable odor. When inhaled it produces a suffocating effect. It is more than twice as dense as air. The gas is easily liquefied by passing it through a tube immersed in a freezing mixture of salt and ice. Liquid sulfur dioxide boils at $-8°$ under a pressure of one atmosphere. It is stored in steel cylinders in which the pressure at room temperature is about three atmospheres. Under a pressure of one atmosphere, the gas dissolves in water to the extent of about 80 volumes to one at 0°, while at 20° the solubility is about 40 volumes to one of water.

Reactions of Sulfur Dioxide. Sulfur dioxide, dissolved in water, yields a solution of sulfurous acid. The combination of sulfur dioxide with water is a reversible process and a condition of equilibrium is reached. The rate of combination depends on the concentration of the dissolved sulfur dioxide, which depends on the pressure of the gas in contact with the liquid. The rate

of the decomposition depends on the concentration of sulfurous acid in the solution.

$$SO_2(gas) \rightleftharpoons SO_2(dissolved) + H_2O \rightleftharpoons H_2SO_3.$$

Hence, sulfurous acid decomposes and sulfur dioxide is evolved as a gas in the laboratory preparation, when the concentration of the acid becomes high due to the union of the hydrogen and sulfite ions.

Sulfur dioxide exhibits other reactions characteristic of acidic oxides; *viz.*, with basic hydroxides and basic oxides to form sulfites.

$$Ca(OH)_2 + SO_2 \longrightarrow H_2O + CaSO_3.$$

If the solution is saturated with sulfur dioxide, calcium hydrogen sulfite, $Ca(HSO_3)_2$ is formed.

$$CaSO_3 + H_2O + SO_2 \longrightarrow Ca^{++} + 2\,HSO_3^-.$$

The most important reaction of sulfur dioxide is its combination with oxygen under the proper conditions to form *sulfur trioxide.*

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3.$$

This reaction is discussed in detail as a step in the production of sulfuric acid. Sulfur dioxide also unites with chlorine, when activated by sunlight, to yield *sulfuryl chloride.*

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2.$$

Sulfurous Acid. H_2SO_3. Sulfurous acid is a weak and unstable acid which exists only in solution in equilibrium with the oxide and water. The acid yields two series of salts, normal sulfites and hydrogen sulfites. The hydrogen sulfites are acidic in nature because they contain the acid anion, HSO_3^-, which furnishes a low concentration of hydronium ions.

$$OH^- + H_2SO_3 \rightleftharpoons HSO_3^- + H_2O.$$
$$OH^- + HSO_3^- \rightleftharpoons SO_3^{--} + H_2O.$$

Sulfurous acid combines slowly with oxygen to form sulfuric acid, but it reacts rapidly with stronger oxidizing agents, such as nitric acid and hypochlorous acid.

$$HClO + H^+ + 2\,\epsilon \longrightarrow H_2O + Cl^-.$$
$$H_2SO_3 + H_2O \longrightarrow SO_4^{--} + 4\,H^+ + 2\,\epsilon.$$
$$HClO + H_2SO_3 \longrightarrow Cl^- + SO_4^{--} + 3\,H^+.$$

Or, $$HClO + H_2SO_3 + 3\,H_2O \longrightarrow Cl^- + SO_4^{--} + 3\,H_3O^+.$$

Uses of Sulfur Dioxide. The most extensive use of sulfur dioxide is in the manufacture of sulfuric acid. Sulfur dioxide is used directly in the bleaching of materials, such as wool, straw, and silk, which are damaged by the action of chlorine. This bleaching is due to the formation of addition products between the coloring material and the sulfurous acid formed by the combination of sulfur dioxide with water in contact with the goods. Since such compounds are not entirely stable, they slowly decompose with the evolution of sulfur dioxide; and some materials bleached by sulfur dioxide tend to resume their original color after a time. Sulfur dioxide is also employed as a disinfecting material in fumigation. It is used as the refrigerating substance in some household refrigerating machines.

The most extensive direct use of sulfur dioxide, aside from the manufacture of sulfuric acid, is in the paper industry. Calcium acid sulfite, which is prepared from calcium carbonate, sulfur dioxide, and water, is used to cause the disintegration of the wood. Lignin, the cementing material in the wood, is dissolved, the materials are bleached, and a relatively pure form of cellulose is obtained. From this, paper is manufactured.

SULFURIC ACID

This substance was known in the days of the alchemists; but its manufacture did not reach a commercial stage until 1765. It is the most important of the inorganic chemicals. Because it is used in so many processes in large amounts and its production and consumption respond quickly to changes in business activities, it is a good barometer of general business conditions. It has been said that the industrial development of any country can be estimated from its consumption of sulfuric acid.

The Production of Sulfuric Acid. The production of sulfuric acid involves three reactions: *viz.*, the combustion of sulfur or sulfides to form sulfur dioxide; the oxidation of sulfur dioxide to form the trioxide; and the combination of the trioxide with water to form sulfuric acid. The conversion of the dioxide into the trioxide is the only one of these reactions which presents any significant difficulties. Two important processes are in extensive use for effecting this change.

The Contact Process. The combination of sulfur dioxide with oxygen takes place very slowly at temperatures below 500°; and the reaction is exothermic and reversible.

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3 + 45{,}200 \text{ cal.}$$

Therefore, the application of heat to increase the velocity of the reaction decreases the yield of sulfur trioxide in the equilibrium mixture of the gases. At a temperature of 400°, the equilibrium mixture contains about 98% of sulfur trioxide; at 700°, about 60%; and at 1000° only an insignificant per cent. The velocity of the

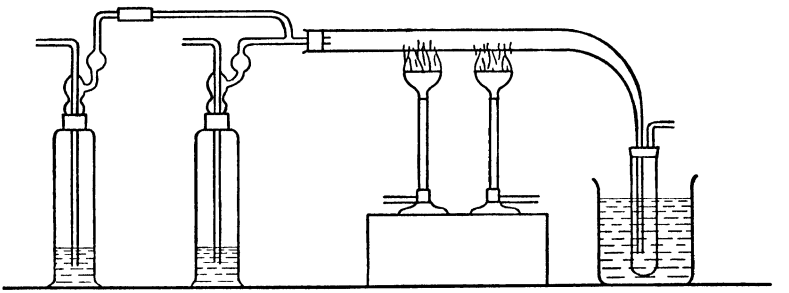

FIG. 117. — Laboratory Apparatus for the Preparation of Sulfur Trioxide.

reaction is too low at the lower temperatures and the yield of sulfur trioxide is too small at the higher temperatures. Finely divided platinum serves as a catalyst for this reaction so that equilibrium is attained in a short time at 400° in its presence. The yield of sulfur trioxide is determined by the temperature and pressure of the gases. The effect of the catalyst is a surface effect and the material is finely divided so as to give as great surface as possible for a small weight of the catalyst. In the laboratory preparation of sulfur trioxide, a mixture of sulfur dioxide and oxygen is passed over finely divided platinum supported on asbestos fiber, Fig. 117, heated to dull red heat. The product may be condensed in a tube surrounded by ice-cold water.

In industrial operation, a small amount of platinum is dispersed in a fine state of subdivision throughout a relatively large mass of inert supporting material. The "Grillo contact material" consists of magnesium sulfate containing a small amount of finely divided platinum. The contact material is placed on trays which fit into the converter shell, Fig. 118. Small amounts of impurities,

such as dust and arsenic trioxide, likely to be present in sulfur dioxide produced by the combustion of metal sulfides, "poison" the catalyst and decrease its efficiency. Therefore, the gas is purified before being brought in contact with the catalyst. An excess of oxygen is admitted with the sulfur dioxide, since this increases the extent of the conversion of sulfur dioxide into sulfur trioxide. The temperature tends to rise during the reaction; and, if allowed to continue, this would decrease the yield of sulfur trioxide. Therefore, the cold gases are led over the pipes which contain the catalyst, thus preventing too great a rise in temperature and at the same time preheating the entering gases to the temperature necessary for the reaction to start.

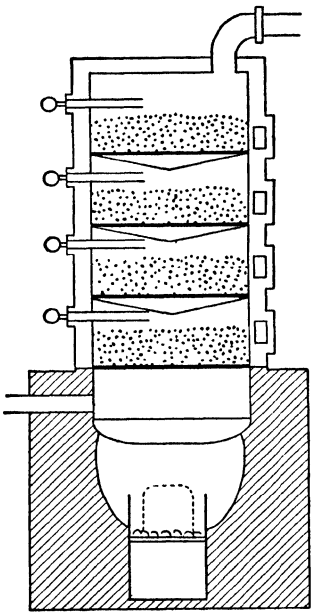

FIG. 118

The product of this reaction is sulfur trioxide mixed with an excess of air. The absorption of sulfur trioxide from this mixture is much more nearly complete in concentrated sulfuric acid than in water. A fog of minute droplets of sulfuric acid is formed when the gas mixture is passed into water, through the evaporation of water into the gas bubbles. These droplets move relatively slowly through the gas bubble and most of them are carried out of solution with the air. No fog is formed when the gas mixture is passed into concentrated sulfuric acid; and the gaseous molecules of sulfur trioxide pass from the gas bubble into the concentrated acid and are absorbed. During absorption sulfur trioxide reacts with water to form sulfuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

Additional water is introduced to maintain the acid at the desired concentration, usually 98%. If more concentrated acid is required, the addition of water is stopped and sulfur trioxide reacts with the remaining water in the solution to form sulfuric acid of 100% concentration. Fuming sulfuric acid, *oleum*, may be formed by

continuing the absorption of sulfur trioxide to form an equilibrium mixture of sulfuric acid, sulfur trioxide, and disulfuric acid.

$$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7.$$

Other catalysts for increasing the velocity of the reaction of sulfur dioxide with oxygen are known. Contact catalysts containing complex vanadium silicate products are said to be unaffected by some of the gaseous substances which poison the platinum catalyst. Consequently, this catalyst is suitable for use in contact process plants using the sulfur dioxide formed by burning metal sulfides in smelter operations. Sulfur dioxide from this source contains relatively large proportions of impurities. A large amount of sulfuric acid is now produced in plants using the vanadium catalyst.

The Lead Chamber Process. In this process, the oxidation of the sulfur dioxide is brought about by the action of nitric oxide and

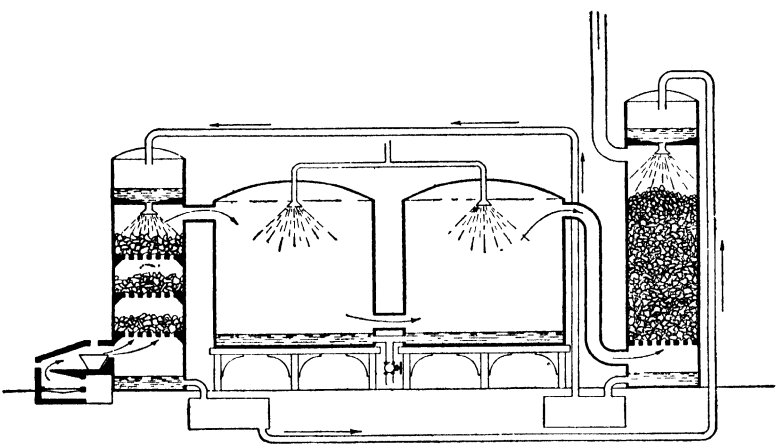

FIG. 119. — Diagram of Lead Chamber Plant. (From Holmes, *Introductory College Chemistry*.)

oxygen. The nitric oxide acts as a "carrier catalyst." The reactions take place at ordinary temperatures and the reacting substances are gaseous. Consequently, enough time must be allowed to permit the dissipation of the heat of reaction so that the oxidation of the sulfur dioxide may be as nearly complete as practicable. The gas mixture is allowed to drift slowly through large lead-lined chambers, Fig. 119, from which the process derives its name

There are usually three to six of these chambers which are 50 to 150 feet long, 15 to 25 feet high, and 20 to 30 feet wide.

Sulfur dioxide, formed by the combustion of sulfur or of metal sulfides, is passed from the burners through a dust flue, where solids settle out and the proper proportion of air is admitted. From the flue the gases enter the base of the Glover tower, where they become mixed with nitric oxide, and the oxidation to form sulfuric acid commences. The gas mixture is blown from this tower into the first of the chambers. Steam is also blown into the chambers and the reactions are completed. Various intermediate products are formed, but the essential reactions are represented by the equations:

$$2\,NO + O_2 \longrightarrow 2\,NO_2.$$

$$SO_2 + NO_2 + H_2O \longrightarrow H_2SO_4 + NO.$$

The acid collects on the floors of the chambers and flows into reservoirs.

Nitrogen dioxide is absorbed from the waste gases which pass from the last of the chambers into the Gay-Lussac tower, where they meet a counter current of concentrated sulfuric acid trickling down over tile. The product of the reaction which takes place is known as *nitrosyl sulfuric acid.*

$$H_2SO_4 + 2\,NO_2 \longrightarrow HNOSO_4 + HNO_3.$$

This acid is forced by compressed air to the top of the Glover tower. As it is admitted to this tower it is diluted with water or with some of the chamber acid. Passing down through this tower, the nitrosyl acid meets the hot gases from the sulfur burners. Nitric oxide is released and joins the gases passing on into the chambers.

$$2\,HNOSO_4 + 2\,H_2O + SO_2 \longrightarrow 3\,H_2SO_4 + 2\,NO.$$

The most concentrated product of the chamber process is the acid which collects in the reservoir at the base of the Glover tower.

Nitric oxide is not consumed in the process, but there is some mechanical loss because of incomplete absorption. Oxides of nitrogen must be admitted along with the gases entering the first tower to compensate this loss. The supply of nitric oxide is now secured in most of the lead chamber plants by the atmospheric oxidation of ammonia.

The concentration of the chamber acid is 60–65%. Its concentration may be increased to 77% by evaporation in lead pans. Lead is not extensively attacked by sulfuric acid at the lower concentrations because of the formation of a protective coating of lead sulfate. This coating is dissolved by concentrated solutions of sulfuric acid and the lead is attacked rapidly. The concentration of the acid may be further increased by evaporation in iron pans.

Comparison of the Two Processes. These two processes supplement each other in supplying the industrial demand for sulfuric acid. The product of the contact process is the more nearly pure and may be made of any desired concentration up to that of the fuming acid. The purification of the gases, necessary to prevent the poisoning of the catalyst, adds to the cost of production. The main product of the chamber process contains many impurities. The purification and concentration of the chamber product increase the cost of production. There are a number of direct uses for the more dilute acid, in which the presence of impurities is of no consequence. The lead chamber has been the cheaper process for the manufacture of this product; and the contact process is the better for securing pure, concentrated sulfuric acid. It is now claimed that the use of the vanadium catalyst, eliminating the necessity for the purification of the gases, makes it possible for the contact process to operate to produce the dilute acids in competition with the chamber plant.

Properties of Sulfuric Acid. Sulfuric acid is a colorless, oily liquid of specific gravity 1.83. When the pure compound is heated, it decomposes with the evolution of sulfur trioxide and the formation of a constant boiling solution, which contains 98.3% of sulfuric acid and boils at 338°. The acid dissolves in water in all proportions and heat is evolved during the process. Concentrated sulfuric acid exhibits a very low pressure of water vapor.

Chemical Reactions of Sulfuric Acid. Anhydrous sulfuric acid is a molecular material. It combines with water to form a number of hydrates, which may be represented by the formulas, $SO_3(H_2O)$, $(SO_3)_2(H_2O)$, $SO_3(H_2O)_2$, $SO_3(H_2O)_3$, $SO_3(H_2O)_5$. Since these hydrates are stable, sulfuric acid is a good *dehydrating agent.* It reacts with cellulose to leave a residue of carbon.

$$(C_6H_{10}O_5)_n \longrightarrow 5\,n\,H_2O + 6\,n\,C.$$

The important use of sulfuric acid in the production of nitro-compounds is due to its dehydrating action.

$$C_6H_6 + HONO_2 \longrightarrow C_6H_5NO_2 + H_2O.$$

Because of its high boiling point, sulfuric acid reacts with the salts of acids of lower boiling point. Either the normal or the hydrogen sulfate of the metal may be obtained from the solution.

$$2\,NaCl + H_2SO_4 \longrightarrow 2\,HCl\uparrow + Na_2SO_4.$$
$$NaNO_3 + H_2SO_4 \longrightarrow NHO_3\uparrow + NaHSO_4.$$

Sulfuric acid reacts with water to form hydronium ions in diluted solutions. The first ionization is complete in dilute solution; but the second ionization is not complete.

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-.$$
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{--}.$$

Consequently, sulfuric acid exhibits two series of ionic reactions, the reactions of hydronium ions and the reactions of sulfate ions.

Due to hydronium ions in solution, sulfuric acid exhibits the usual acid reactions. Either the normal or the hydrogen sulfate may be formed, depending on the relative proportions of the acidic and basic substances.

$$H_3O^+ + HSO_4^- + OH^- \longrightarrow 2\,H_2O + HSO_4^-.$$
$$HSO_4^- + OH^- \rightleftharpoons H_2O + SO_4^{--}.$$
$$2\,H_3O^+ + MgO \longrightarrow 3\,H_2O + Mg^{++}.$$
$$H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O.$$
$$2\,H_3O + Zn \longrightarrow H_2 + Zn^{++} + 2\,H_2O.$$

Due to the sulfate ions in solutions of sulfuric acid, it reacts with solutions of the metal ions which yield insoluble sulfates. The sulfates of barium, strontium, and lead have very low solubility and are readily precipitated. The sulfates of silver and calcium are only slightly soluble.

$$Ba^{++} + SO_4^{--} \rightleftharpoons BaSO_4\downarrow.$$
$$Sr^{++} + SO_4^{--} \rightleftharpoons SrSO_4\downarrow.$$
$$Pb^{++} + SO_4^{--} \rightleftharpoons PbSO_4\downarrow.$$

Oxidizing Action of Concentrated Sulfuric Acid. This acid is unstable in high concentration at elevated temperatures, decomposing into water and sulfur trioxide. Sulfur trioxide also

decomposes with the absorption of heat, producing sulfur dioxide and oxygen. During this decomposition, the oxidation number of sulfur decreases from 6 + to 4 +. This change is brought about still more readily in the presence of reducing agents, and hot concentrated sulfuric acid is an active oxidizing agent. Sulfur yields compounds in four common states of oxidation, and in others which are not so familiar.

S^{6+}	S^{4+}	S^{0}	S^{2-}
H_2SO_4	SO_2	S	H_2S

Consequently, there are three common reduction products of sulfuric acid. The product obtained in any specific reaction is determined primarily by the activity and the relative amount of the reducing agent. Under the conditions most frequently met, sulfur dioxide is the main reduction product.

The nature of the oxidation products formed in the reaction of hot concentrated sulfuric acid with the different classes of reducing agents is the same as that of the products when other acidic oxidizing agents are employed. Metallic bismuth yields bismuth sulfate in solution and sulfur dioxide is the reduction product.

$$\begin{array}{rl} [H_2SO_4 + 2\,H^+ + 2\,\epsilon \longrightarrow 2\,H_2O + SO_2.] & \times 3. \\ [Bi \longrightarrow Bi^{+++} + 3\,\epsilon.] & \times 2. \\ \hline 3\,H_2SO_4 + 6\,H^+ + 2\,Bi \longrightarrow 6\,H_2O + 3\,SO_2 + 2\,Bi^{+++}. & \end{array}$$

The reaction of hot concentrated sulfuric acid with elementary sulfur produces sulfur dioxide as both the oxidation product and the reduction product.

$$\begin{array}{rl} [H_2SO_4 + 2\,H^+ + 2\,\epsilon \longrightarrow 2\,H_2O + SO_2.] & \times 2. \\ S + 2\,H_2O \longrightarrow SO_2 + 4\,H^+ + 4\,\epsilon. & \\ \hline 2\,H_2SO_4 + S \longrightarrow 2\,H_2O + 3\,SO_2. & \end{array}$$

The activity of iodides is great enough to reduce hot concentrated sulfuric acid to hydrogen sulfide.

$$\begin{array}{rl} H_2SO_4 + 8\,H^+ + 8\,\epsilon \longrightarrow 4\,H_2O + H_2S. & \\ [2\,I^- \longrightarrow I_2 + 2\,\epsilon.] & \times 4. \\ \hline H_2SO_4 + 8\,H^+ + 8\,I^- \longrightarrow 4\,H_2O + H_2S + 4\,I_2. & \end{array}$$

Economic Importance of Sulfuric Acid. The economic importance of sulfuric acid and the prompt response in the demand for this substance to changes in business conditions are

shown by the figures for the consumption of sulfuric acid in the United States during the past ten years: 1930, 7,625,000 tons; 1932, 4,650,000 tons; 1934, 6,166,000 tons; 1936, 7,632,000 tons; 1938, 6,678,000 tons; 1940, 9,150,000 tons. The applications of this acid are involved either directly or indirectly in many fundamental industries. Its high boiling point is the basis of its use in the preparation of more volatile acids, such as hydrochloric and nitric. Due to its acid properties, it is employed in the conversion of natural phosphate rock into soluble acid phosphates suitable for fertilizers, in the manufacture of ammonium sulfate, in cleaning iron and steel to be galvanized or tinned, and in the preparation of sulfates. Sulfuric acid finds extensive application as a dehydrating agent in the manufacture of explosives, dyes, drugs, and many other commercial products. Large quantities of the acid are used in the petroleum industry, due in part to its oxidizing properties which render it suitable for the removal of organic sulfides. There are many additional applications of the substance, but those listed account for the largest part of the total consumption of the acid.

The distribution of the large amounts of sulfuric acid produced is shown in the following table arranged from figures given in *Chemical and Metallurgical Engineering*.[1]

TABLE 26

DISTRIBUTION OF SULFURIC ACID CONSUMED IN THE UNITED STATES IN THOUSANDS OF TONS

(Basis, 50 degree Be., 62.18% of H_2SO_4)

Industry	*1938*	*1939*	*1940*
Fertilizer	1,900	1,970	2,260
Petroleum refining	1,100	1,210	1,270
Chemicals	800	975	1,090
Coal products	585	740	900
Iron and steel	590	980	1,200
Other metallurgical	350	570	640
Paints and pigments	430	520	570
Explosives	140	160	175
Rayon and cellulose film	320	405	470
Textiles	90	116	125
Miscellaneous	355	387	450
Totals	6,660	8,230	9,150

[1] *Chem. Met. Eng.* **48**, number 2, 91 (1941).

Sulfates. The normal salts of sulfuric acid are the sulfates. The soluble sulfates are commonly prepared in solution by the reaction of the acid with the basic substances which furnish the appropriate metal ions. The slightly soluble sulfates, those of barium, strontium, and lead, are usually precipitated by mixing solutions which contain the essential ions. The sulfates are not readily decomposed by other acids, because they are themselves the salts of a strong acid of high boiling point. Specific sulfates are discussed in connection with the different metals.

The normal sulfates of the alkali and alkaline earth metals do not decompose readily when they are heated; but the sulfates of a number of the metals decompose to yield sulfur trioxide or sulfur dioxide and oxygen at high temperatures. Before the discovery of the contact process for the production of concentrated sulfuric acid, its preparation from ferrous sulfate, the vitriol of iron, was an important method. This is the basis for the name, "oil of vitriol." The heating of moist ferrous sulfate in air yields ferric hydroxysulfate.

$$4\,FeSO_4 + O_2 + 2\,H_2O \longrightarrow 4\,Fe(OH)SO_4.$$

When this substance is heated strongly it decomposes as represented by the equation,

$$2\,Fe(OH)SO_4 \longrightarrow Fe_2O_3 + H_2SO_4 + SO_3.$$

The condensed product, fuming sulfuric acid, was prepared extensively at Nordhausen and was called "Nordhausen sulfuric acid."

Sulfates may be decomposed by heating them with silica, with the formation of sulfur trioxide and the silicate of the metal.

$$CaSO_4 + SiO_2 \longrightarrow CaSiO_3 + SO_3.$$

They may also be reduced to sulfides by heating them with carbon.

$$CaSO_4 + 4\,C \longrightarrow CaS + 4\,CO.$$

These reactions suggest methods which might be used for the production of sulfuric acid from calcium sulfate, an abundant mineral.

Other Oxyacids of Sulfur. There are a number of additional oxyacids of sulfur, which are formed by the sharing of electrons between atoms of sulfur so as to form polyacids. Some of these are listed in Table 27.

TABLE 27

OXYACIDS OF SULFUR

Name	Formula	Name	Formula
Hyposulfurous acid	$H_2S_2O_4$	Dithionic acid	$H_2S_2O_6$
Sulfurous acid	H_2SO_3	Trithionic acid	$H_2S_3O_6$
Sulfuric acid	H_2SO_4	Tetrathionic acid	$H_2S_4O_6$
Thiosulfuric acid	$H_2S_2O_3$	Pentathionic acid	$H_2S_5O_6$
Pyrosulfuric acid	$H_2S_2O_7$	Peroxysulfuric acid	$H_2S_2O_8$

The sodium salt of *hyposulfurous acid* is prepared by the reaction of sodium sulfite with zinc hyposulfite, which is itself prepared by the reduction of sulfurous acid by zinc.

$$2\,H_2SO_3 + Zn \longrightarrow Zn^{++} + S_2O_4^{--} + 2\,H_2O.$$

$$Zn^{++} + S_2O_4^{--} + 2\,Na^+ + SO_3^{--} \longrightarrow ZnSO_3\downarrow + 2\,Na^+ + S_2O_4^{--}.$$

Sodium hyposulfite is used commercially to reduce indigo.

Pyrosulfuric acid may be prepared in the production of sulfuric acid by the contact process. It is an active dehydrating and oxidizing agent.

Peroxysulfuric acid may be prepared by the electrolysis of cold, concentrated sulfuric acid. The reaction at the anode is,

$$2\,HSO_4^- \longrightarrow H_2S_2O_8 + 2\,\epsilon.$$

The sodium salt is moderately soluble and crystallizes during the electrolysis of sodium bisulfate solutions. It is an active oxidizing agent. The acid hydrolyzes in two stages, the first product being peroxymonosulfuric acid, $H_2S_2O_5$, known as "Caro's Acid."

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5.$$

"Caro's acid" then hydrolyzes to form hydrogen peroxide.

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2.$$

SELENIUM AND TELLURIUM

These elements have the atomic numbers 34 and 52, respectively; and their atoms contain six valence electrons. They are much less abundant than sulfur. Selenium occurs in the free condition in sulfur deposits. It also occurs in selenides of copper, silver, and lead. Tellurium occurs chiefly in the tellurides of

copper, silver, and gold. There are a number of isotopes of each of these elements, six of selenium and eight of tellurium being known. Both selenium and tellurium yield an amorphous and several crystalline allotropes.

Selenium and tellurium could be recovered in considerable quantities from metallurgical operations; but they do not now have any extensive commercial applications. The largest use of selenium is in the production of ruby red glass. It is also used to some extent in the vulcanization of some types of rubber goods and in the preparation of copper alloys. Tellurium is used in small percentages in lead to increase the resistance to corrosion.

The Hydrides of Selenium and Tellurium. These compounds may be prepared by the direct union of the elements with hydrogen and by the reaction of acids with binary compounds. The elements are less active than sulfur and high temperatures are required to bring about the reaction with hydrogen. The reaction of hydrochloric acid with iron selenide and with magnesium telluride is a suitable source of the gases.

$$FeSe + 2\,H_3O^+ \longrightarrow Fe^{++} + H_2Se\uparrow + 2\,H_2O.$$
$$MgTe + 2\,H_3O^+ \longrightarrow Mg^{++} + H_2Te\uparrow + 2\,H_2O.$$

The stability of the hydrides decreases with atomic number. The reducing action of the negative ion, therefore, increases with atomic number. The gases have disagreeable odors and are very toxic.

The Dioxides of Selenium and Tellurium. These oxides are produced by the combustion of the elements. Selenium dioxide dissolves in water to form the weak selenious acid, H_2SeO_3. Tellurium dioxide does not unite readily with water but reacts with alkalies to form tellurites, from which the acid may be liberated.

$$TeO_2 + 2\,NaOH \longrightarrow H_2O + Na_2TeO_3.$$
$$Na_2TeO_3 + 2\,HCl \longrightarrow H_2TeO_3 + 2\,NaCl.$$

This behavior shows that tellurium is less actively non-metallic in nature than selenium.

Selenic and Telluric Acids. *Selenic acid, H_2SeO_4,* is formed by the action of strong oxidizing agents on selenious acid.

$$HClO + 2\,H^+ + 2\,\epsilon \longrightarrow H^+ + Cl^- + H_2O.$$
$$H_2SeO_3 + H_2O \longrightarrow SeO_4^{--} + 4\,H^+ + 2\,\epsilon.$$
$$HClO + H_2SeO_3 \longrightarrow 3\,H^+ + Cl^- + SeO_4^{--}.$$

Concentrated selenic acid is a strong oxidizing agent. The selenates are similar to the sulfates in solubility; but are less stable, and more active oxidizing agents than the sulfates. *Telluric acid*, H_6TeO_6, is slightly soluble in water and is weakly acidic. It loses water to form H_2TeO_4 when it is heated; and TeO_3 is the final product of the dehydration. The oxide, however, does not react with water. Telluric acid is also a good oxidizing agent.

EXERCISES

1. Describe the production of sulfur from the Texas and Louisiana deposits.
2. Describe the allotropic forms of sulfur and mention the conditions under which each is formed.
3. Write equations to represent the typical reactions of sulfur.
4. Discuss the equilibria of sulfur dioxide in aqueous solution. What is the effect on these equilibria of: (*a*) heating the solution; (*b*) increasing the pressure of sulfur dioxide gas; (*c*) the addition of a strong acid; (*d*) the addition of a base. Give reasons for each of these conclusions.
5. Write the expression for the equilibrium constant in the system involving sulfur dioxide, oxygen, and sulfur trioxide. Explain the effect on this system of: (*a*) the use of high temperatures; (*b*) high pressures; (*c*) an excess of oxygen; (*d*) the presence of a catalyst. Explain why the industrial process operates at a temperature of approximately 400° and atmospheric pressure.
6. Trace the flow of gases in the lead chamber process and write equations for the reactions which occur, indicating the part of the plant in which each occurs.
7. What are the relative advantages of the two processes for the production of sulfuric acid?
8. Represent by equations four ionic reactions of sulfuric acid which are due to the fact that it is an acidic substance.
9. Represent by equations derived by the ion-electron method the reaction of hot concentrated sulfuric acid with members of the common classes of reducing agents.

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CHAPTER XX

THE PHOSPHORUS FAMILY

The elements of the phosphorus family are *phosphorus*, *arsenic*, *antimony*, and *bismuth*. Together with nitrogen they constitute Group V of the Periodic System based on atomic numbers. The four elements make up a natural family which exhibits a transition from the non-metallic properties of the elements of the lower atomic numbers to the metallic properties of the elements of the higher atomic numbers. The atoms of the elements have five valence electrons and a maximum oxidation number of 5 +. The minimum oxidation number is 3 −; and they also yield compounds in intermediate stages of oxidation, the 3 + stage being common and important. The general group relationships are emphasized by a comparison of the behavior of the elements and of similar varieties of compounds.

The Occurrence of the Elements. The chief natural source of *phosphorus* and of its compounds is the mineral *phosphorite*, $Ca_3(PO_4)_2$. Large deposits of this mineral are found in many parts of the world, notably in Florida, Tennessee, and Montana and adjoining states. Calcium phosphate is the principal mineral constituent of bones and teeth, and complex organic compounds containing phosphorus are present in muscles, nerves, and brain tissue. Phosphorus compounds are contained in such foods as eggs, beans, peas, and wheat.

Arsenic, *antimony*, and *bismuth* do not occur as salts of oxy-acids, but are found as trioxides. The most extensive occurrence of the elements is in the sulfides: *arsenical pyrite*, $FeAsS$; *orpiment*, As_2S_3; *realgar*, AsS; *stibnite*, Sb_2S_3; and *bismuthinite*, Bi_2S_3. These elements occur also in the uncombined state.

Preparation of the Elements. The elements are liberated from their compounds by reduction. Phosphorus is prepared by heating a mixture of calcium phosphate, sand, and coke in an electric furnace, Fig. 120.

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \longrightarrow 3\,CaSiO_3 + 2\,P + 5\,CO.$$

Phosphorus and carbon monoxide emerge from the furnace in the gaseous state, and phosphorus is condensed beneath the surface of water. The charge is fed continuously into the furnace from a hopper at the top; and the calcium silicate is withdrawn as a slag.

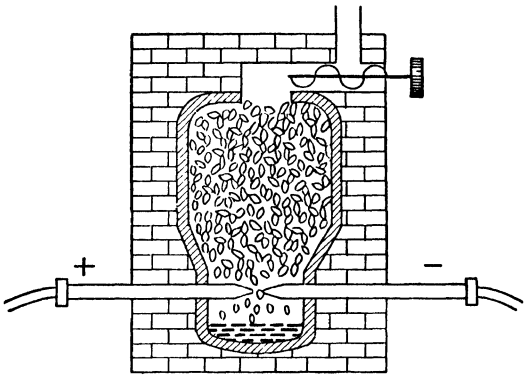


FIG. 120. — Production of Phosphorus.

Arsenic, *antimony*, and *bismuth* may be prepared by first roasting the sulfides to form the oxides and then reducing the oxides by heating with carbon.

$$2\,As_2S_3 + 9\,O_2 \longrightarrow 2\,As_2O_3 + 6\,SO_2.$$
$$As_2O_3 + 3\,C \longrightarrow 2\,As + 3\,CO.$$

Arsenic is also obtained by heating the arsenical pyrite.

$$FeAsS \longrightarrow FeS + As.$$

Antimony may be obtained by the direct reduction of the sulfide by heating it with iron.

$$Sb_2S_3 + 3\,Fe \longrightarrow 2\,Sb + 3\,FeS.$$

Bismuth is obtained from the naturally occurring oxide by reduction with carbon, and is separated from ores in which it occurs in the elementary state by melting the metal and allowing the liquid metal to flow away from the rock.

Arsenic is produced almost entirely as a by-product of the treatment of metal ores, such as those of copper, lead, and zinc. The principal production of antimony is in Bolivia, China, and Mexico. Less than 2% of the annual production of this metal is in the United States. Bismuth is obtained almost entirely as a by-product of the treatment of copper and lead ores.

Properties of the Elements. Phosphorus, arsenic, and antimony exist in more than one crystalline form. There are two familiar forms of phosphorus, white and red. *White phosphorus* is a soft, wax-like solid of specific gravity 1.82. The solid melts at 44.1° and vaporizes rapidly at ordinary temperatures. White phosphorus is very poisonous; and even small amounts lead to chronic poisoning if continually taken in, as when one works in an atmosphere containing some of the vapor. Among the harmful consequences is necrosis of the jaw. White phosphorus is soluble in carbon disulfide, but is practically insoluble in water. White phosphorus is the metastable form of the element, and it slowly changes into the red variety if it is heated or exposed to light. This change is catalyzed by the presence of iodine. A large amount of heat is evolved during this transition and white phosphorus is much more active than the red modification. White phosphorus ignites spontaneously if it is left exposed to air. Hence, it is usually stored and cut beneath the surface of water. *Red phosphorus* has no melting point, as it sublimes when it is heated. Its density varies and it is insoluble in both water and carbon disulfide. Red phosphorus is not poisonous. It does not ignite in air at temperatures below 240°. Red phosphorus is not a single modification of the element, but it appears to be a mixture of the white and a more stable variety known as *violet phosphorus*. There is no specific transition temperature between these allotropic forms. Red phosphorus is converted into the white variety by subliming it and condensing the vapor.

Arsenic may be obtained in an active, unstable modification known as *yellow arsenic*. This form results from the condensation of the vapor in cold carbon disulfide. Yellow arsenic changes rapidly into the stable form, *metallic arsenic*, a gray solid having high luster. It is very brittle and is readily broken down into a powder. It sublimes at 610° when it is heated under atmospheric pressure.

Antimony exists in modifications which are similar to those of arsenic. *The yellow variety* is unstable except at low temperatures. A form known as *explosive antimony* may be produced by the electrolysis of a concentrated solution of antimony trichloride. This form appears to be a solid solution of the trichloride in yellow antimony. When this material is struck or scratched, the

transition to the stable form takes place explosively. The stable modification of antimony is a *silvery white metal* which melts at 630.5° and is not as volatile as arsenic.

Bismuth is known in only one solid form. It is a lustrous, crystalline metal which is grayish-white in color. The melting point is low, 271°; and the metal is hard and brittle. Some of the specific properties of these elements are shown in Table 28.

TABLE 28

PROPERTIES OF THE ELEMENTS OF THE PHOSPHORUS FAMILY

	Phosphorus	*Arsenic*	*Antimony*	*Bismuth*
Atomic weight . . .	30.98	74.91	121.76	209.00
Atomic number . . .	15	33	51	83
Electron structure . .	2, 8, 5	2, 8, 18, 5	2, 8, 18, 18, 5	2, 8, 18, 32, 18, 5
Melting point . . .	44.1°	814° (36 atm.)	630.5°	271°
Boiling point	280°	610° (sublimes)	1440°	1450°
Specific gravity . . .	1.82	5.7	6.58	9.8

Chemical Reactions of the Elements. The elements of the phosphorus family combine directly with oxygen, sulfur, the halogens, and many of the metals. In all of these reactions, the less stable modification reacts more actively than the more stable variety because it contains the greater amount of energy. White phosphorus oxidizes slowly at ordinary temperatures and becomes ignited at 45°, while red phosphorus must be heated to 240° to cause it to burn. The slow oxidation of moist phosphorus to the trioxide is accompanied by the emission of a greenish yellow light. Some of the energy of the reaction is converted directly into light, a phenomenon known as *chemiluminescence*, or in this instance, *phosphorescence*. Phosphorus burns in an excess of air to produce the pentoxide, but the other members of the family yield trioxides under these conditions. The direct union of these elements with the halogens yields the trihalide as the first product. With an excess of the halogen the pentahalide is formed, except in the reactions of iodine; and the trihalides of bismuth are the most stable of these products. Direct union with sulfur produces a number of sulfides of these elements. The trisulfides of all of these elements may be formed; and the pentasulfides of phosphorus,

arsenic, and antimony result from the use of an excess of sulfur in the reaction. When these elements unite with metals, binary compounds which do not exhibit the properties of salts are formed.

$$3\ Ca + 2\ As \longrightarrow Ca_3As_2.$$

Phosphorus, arsenic, and antimony react with nitric acid to produce oxyacids in which these elements have the oxidation number 5 +, showing their non-metallic nature.

$$[4\ H^+ + NO_3^- + 3\ \epsilon \longrightarrow 2\ H_2O + NO.] \quad \times 5.$$
$$[P + 4\ H_2O \longrightarrow H_3PO_4 + 5\ H^+ + 5\ \epsilon.] \quad \times 3.$$
$$5\ H^+ + 5\ NO_3^- + 3\ P + 2\ H_2O \longrightarrow 3\ H_3PO_4 + 5\ NO.$$

Bismuth reacts with nitric acid to yield a solution of bismuth ions, indicating the metallic nature of the element.

$$4\ H^+ + NO_3^- + 3\ \epsilon \longrightarrow 2\ H_2O + NO.$$
$$Bi \longrightarrow Bi^{+++} + 3\ \epsilon.$$
$$4\ H^+ + NO_3^- + Bi \longrightarrow 2\ H_2O + NO + Bi^{+++}.$$

Uses of the Elements. The most extensive use of elementary *phosphorus* is in the manufacture of *matches*. The head of a match contains a mixture of an oxidizing agent and a substance of low kindling temperature. Formerly, white phosphorus was extensively used as the substance of low kindling temperature; but its use is now prohibited because of its poisonous nature and the sulfide, P_4S_3, is used in the common match. The ends of the match sticks are dipped into a paste containing an oxidizing agent, such as lead dioxide, potassium chlorate, or potassium nitrate, and the sulfide of phosphorus, together with powdered glass, dextrin, and glue. When the match head is dry, it is coated with varnish to exclude moisture and air. The mixture is easily ignited by friction. The "double dip" matches contain the phosphorus compound only in the tip, the larger portion of the match head being made up of a combustible substance, such as antimony sulfide, or organic material, and an oxidizing agent. Safety matches contain none of the phosphorus compound; but the striking surface on the box contains red phosphorus, dextrin, and a filler, such as powdered glass. The match head is composed of a good oxidizing agent and antimony trisulfide. This match head is brittle and cannot ordinarily be ignited by scratching it against a rough surface. When

it is rubbed against the specially prepared striking surface, a trace of red phosphorus on this surface is ignited, and this starts the combustion of the substances in the match head.

Phosphorus is used for military purposes in tracer bullets, incendiary bombs, and in the production of smoke screens. The element is used in the preparation of some of its compounds.

Elementary arsenic has no extensive commercial uses. A small amount of it is used in the manufacture of lead shot. The presence of about 0.5% of arsenic in lead increases the surface tension, and causes the lead to assume a spherical form when the molten metal is poured from a height in a shot tower. The use of arsenic increases the hardness of the shot. Arsenic is also added to some alloys which are to be used for products requiring soldering. Arsenical copper alloys do not lose strength when they are heated, because the annealing temperature is high.

The principal use of *antimony* is in the manufacture of its alloys. These alloys are hard and expand on solidification so that they completely fill the mold and produce sharp castings. Type metal contains 82% of lead, 15% of antimony, and 3% of tin; britannia metal, 90% of tin and 10% of antimony; babbitt metal, 90% of tin, 7% of antimony, and 3% of copper; and antifriction metal, 75% of tin, 12.5% of antimony, and 12.5% of copper. These per cents may be varied over an extensive range for special purposes. Approximately one half of the antimony used in the United States is in the production of a lead alloy for plates in storage batteries.

Bismuth is employed in the making of alloys of low melting point; *e.g.*, Wood's metal, 50% of bismuth, 25% of lead, and 12.5% each of tin and cadmium. This alloy melts at about 71°. Alloys of different melting points may be made by varying the proportions of the components. Such alloys are useful as plugs in automatic fire extinguisher systems, and as safety plugs in steam boilers.

The Hydrides. Although the elements of this family do not unite directly with hydrogen, hydrides are known: phosphine, PH_3; arsine, AsH_3; stibine, SbH_3; and bismuthine, BiH_3. These compounds are unstable, gaseous substances which are highly combustible. They may be formed by the reaction of the binary metal compounds with water.

$$Ca_3P_2 + 6\,H_2O \longrightarrow 3\,Ca(OH)_2 + 2\,PH_3\uparrow.$$
$$Zn_3As_2 + 6\,H_2O \longrightarrow 3\,Zn(OH)_2 + 2\,AsH_3\uparrow.$$
$$Mg_3Sb_2 + 6\,H_2O \longrightarrow 3\,Mg(OH)_2 + 2\,SbH_3\uparrow.$$
$$Mg_3Bi_2 + 6\,H_2O \longrightarrow 3\,Mg(OH)_2 + 2\,BiH_3\uparrow.$$

Phosphine may be prepared also by the reaction of white phosphorus with a boiling hot solution of a strong base, such as potassium hydroxide, the products being phosphine and the hypophosphite ion, $H_2PO_2^-$. This reaction is analogous to that of the halogens with cold potassium hydroxide solution. Since the hydride of phosphorus is not an acid, it does not form a binary salt as in the reaction of the halogens. This reaction is one of oxidation-reduction, part of the phosphorus going to a positive valence condition in potassium hypophosphite and part to a negative valence in phosphine.

$$4\,P + 3\,K^+ + 3\,OH^- + 3\,H_2O \longrightarrow 3\,K^+ + 3\,H_2PO_2^- + PH_3\uparrow.$$

When prepared in this way, phosphine is spontaneously combustible due to the presence of a small amount of the vapor of the liquid hydride, P_2H_4, Fig. 121. In order to prevent an explosion

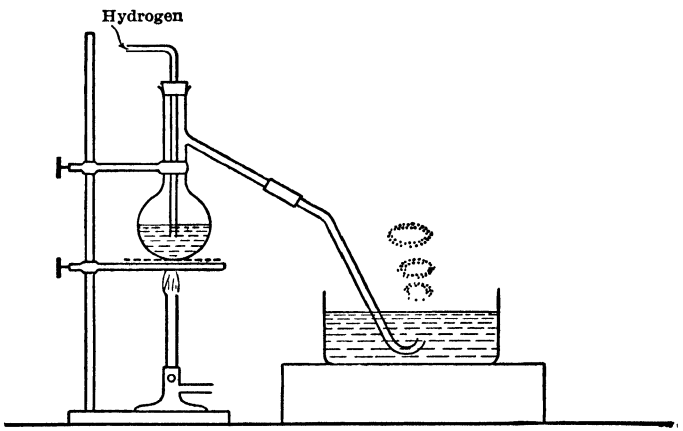


FIG. 121. — Preparation of Phosphine.

air is displaced from the flask in which the reaction is carried out. This may be done by passing a current of hydrogen or illuminating gas through the flask.

Phosphine is a colorless, highly poisonous gas, which is insoluble in water. It exhibits some similarity to ammonia in that phos-

phonium compounds (*e.g.*, phosphonium iodide, PH_4I) can be obtained. These compounds, however, do not show the properties of salts.

Arsine and *stibine* may also be formed by the reduction of arsenic and antimony compounds, respectively, by zinc in acidic solution.

$$H_3AsO_4 + 8\,H^+ + 8\,\epsilon \longrightarrow AsH_3 + 4\,H_2O.$$
$$[Zn \longrightarrow Zn^{++} + 2\,\epsilon.] \qquad \times 4.$$
$$H_3AsO_4 + 8\,H^+ + 4\,Zn \longrightarrow AsH_3 + 4\,H_2O + 4\,Zn^{++}.$$

Arsine and stibine decompose when they are heated, and a deposit of arsenic or of antimony is obtained when a tube through which the gases are passing is heated, Fig. 122. Arsine burns with a lavender flame, forming water and arsenic trioxide. If this flame is allowed to strike against a piece of cold, white porcelain, a brown stain of elementary arsenic may be observed. This spot is removed by a solution of sodium hypochlorite, while the corresponding spot produced by antimony is not dissolved by sodium hypochlorite. The formation of arsine is the basis of a very delicate test, the Marsh test, for the presence of arsenic.

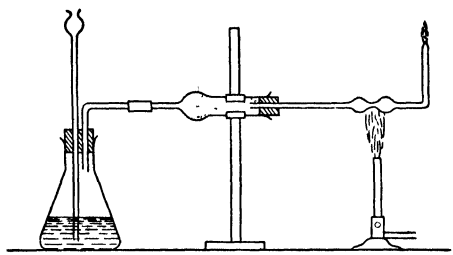


FIG. 122. — Preparation of Arsine.

The Halides. The combination of these elements with the halogens has been mentioned. The chlorides are the most common and important of these halides. *Phosphorus trichloride* is a colorless liquid which combines with chlorine to form *phosphorus pentachloride*, a white solid. The pentachloride sublimes when heated and at 250° it is decomposed to the extent of 80% at equilibrium,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

The trichlorides of antimony and bismuth may be formed by the reaction of hydrochloric acid with the oxides of the elements.

$$Bi_2O_3 + 6\,H_3O^+ + 6\,Cl^- \rightleftharpoons 2\,Bi^{+++} + 6\,Cl^- + 9\,H_2O.$$

The halides of the elements of the phosphorus family are hydrolyzed. On this account the halides of phosphorus fume in moist

air. The hydrolysis of phosphorus trichloride is complete and irreversible. $PCl_3 + 6\ H_2O \longrightarrow H_3PO_3 + 3\ H_3O^+ + 3\ Cl^-$.

Arsenic trichloride is practically completely decomposed by water, but the reaction is reversible in concentrated hydrochloric acid solutions.

$$AsCl_3 + 6\ H_2O \rightleftharpoons H_3AsO_3 + 3\ H_3O^+ + 3\ Cl^-.$$

With both antimony and bismuth trichlorides, the reaction yields the oxychloride and is readily reversible.

$$SbCl_3 + 3\ H_2O \rightleftharpoons SbOCl\downarrow + 2\ H_3O^+ + 2\ Cl^-.$$

The Sulfides. The sulfides of *phosphorus* are formed by the direct union of the elements, when they are heated together in equivalent amounts. The compounds P_2S_5 and P_4S_3 are stable. The pentasulfide is used in certain organic reactions and the trisulfide, P_4S_3, is used in the manufacture of some types of matches.

Both *realgar*, AsS, and *orpiment*, As_2S_3, occur as natural minerals. The trisulfide and the pentasulfide may be prepared by precipitation through the reaction of hydrogen sulfide with acidic solutions of arsenious and arsenic compounds, respectively.

$$2\ HAsO_2 + 3\ H_2S \longrightarrow As_2S_3\downarrow + 4\ H_2O.$$
$$2\ H_3AsO_4 + 5\ H_2S \longrightarrow As_2S_5\downarrow + 8\ H_2O.$$

These sulfides do not dissolve in concentrated hydrochloric acid; but they react with basic solutions containing a high concentration of the sulfide ion, forming the complex thioarsenite and thioarsenate, respectively.

$$As_2S_3 + 3\ S^{--} \longrightarrow 2\ AsS_3^{---}.$$
$$As_2S_5 + 3\ S^{--} \longrightarrow 2\ AsS_4^{---}.$$

Arsenic trisulfide reacts with a solution of ammonium disulfide or polysulfide to form the thioarsenate.

$$As_2S_3 + 2\ S_2^{--} + S^{--} \longrightarrow 2\ AsS_4^{---}.$$

When solutions of the thiosalts are made acidic, the sulfides are reprecipitated.

$$2\ AsS_3^{---} + 6\ H_3O^+ \longrightarrow As_2S_3\downarrow + 3\ H_2S + 6\ H_2O.$$
$$2\ AsS_4^{---} + 6\ H_3O^+ \longrightarrow As_2S_5\downarrow + 3\ H_2S + 6\ H_2O.$$

The mineral *stibnite*, Sb_2S_3, is black but precipitated antimony trisulfide is orange-red. Antimony trisulfide is soluble in hydro-

chloric acid of high concentration, but does not dissolve in acid more dilute than about 2.5 N. Like arsenic trisulfide, it reacts with sulfide and polysulfide ions to form the thio-complex ions.

$$Sb_2S_3 + 3\ S^{--} \longrightarrow 2\ SbS_3^{---}.$$
$$Sb_2S_3 + 2\ S_2^{--} + S^{-} \longrightarrow 2\ SbS_4^{---}.$$

Antimony trisulfide is reprecipitated when the solution of the antimonite is acidified; but the tetrasulfide is obtained from the solution of the thioantimonate.

$$2\ SbS_3^{---} + 6\ H_3O^{+} \longrightarrow Sb_2S_3\downarrow + 3\ H_2S + 6\ H_2O.$$
$$2\ SbS_4^{---} + 6\ H_3O^{+} \longrightarrow Sb_2S_4\downarrow + 3\ H_2S + S\downarrow + 6\ H_2O.$$

Bismuth sulfide occurs in nature and is readily precipitated by the passage of hydrogen sulfide into solutions of bismuth salts.

$$2\ Bi^{+++} + 3\ H_2S + 6\ H_2O \longrightarrow Bi_2S_3\downarrow + 6\ H_3O^{+}.$$

The precipitate may be dissolved by moderately concentrated hydrochloric acid and by nitric acid. It does not react with either ammonium sulfide or polysulfide.

THE OXIDES AND HYDROXIDES

There are a number of oxides and hydroxides of the elements of this family. The more important of these compounds are listed in Table 29. The hydroxides of phosphorus give up hydrogen ions

TABLE 29

OXIDES AND HYDROXIDES OF THE PHOSPHORUS FAMILY

Oxides	P	As	Sb	Bi
Monoxide	—	—	—	BiO
Trioxide	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
Tetroxide	P_2O_4	As_2O_4	Sb_2O_4	Bi_2O_4
Pentoxide	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5
Acids				
Hypo -ous	H_3PO_2	—	—	—
Ortho -ous	H_3PO_3	H_3AsO_3	H_3SbO_3	$Bi(OH)_3$
Pyro -ous	$H_4P_2O_5$	—	—	—
Meta -ous	—	$HAsO_2$	$HSbO_2$	—
Hypo -ic	$H_4P_2O_6$	—	—	—
Ortho -ic	H_3PO_4	H_3AsO_4	—	—
Pyro -ic	$H_4P_2O_7$	$H_4As_2O_7$	$HSb(OH)_6$	—
Meta -ic	HPO_3	$HAsO_3$	$HSbO_3$	$HBiO_3$

and are acidic in nature. The hydroxides of arsenic are more weakly acidic; those of antimony, amphoteric; and the hydroxide of bismuth shows no acidic properties.

The Oxides of Phosphorus. The trioxide and pentoxide, corresponding to the common oxidation states, are the important oxides of phosphorus.

Phosphorus pentoxide, P_2O_5, is formed as a dense white smoke when phosphorus and its combustible compounds burn in a free supply of air or oxygen. The oxide reacts vigorously with water to form a mixture of the ortho- and meta-acids, and with bases to form phosphates.

$$P_2O_5 + H_2O \longrightarrow 2\ HPO_3.$$
$$P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4.$$
$$P_2O_5 + 6\ OH^- \longrightarrow 3\ H_2O + 2\ PO_4^{---}.$$

The pressure of water vapor in contact with phosphorus pentoxide is so low that the oxide is an excellent drying agent.

Phosphorus trioxide, P_2O_3, is formed when phosphorus is burned in a limited supply of air. Some phosphorus pentoxide is formed at the same time, but the trioxide is more volatile than the pentoxide and the two may be separated by passing the combustion products through a plug of glass wool to filter out the solid phosphorus pentoxide. Phosphorus trioxide condenses to a white solid which melts at 22.5°. It reacts slowly with cold water to form phosphorous acid and with strong bases to yield phosphites.

$$P_2O_3 + 3\ H_2O \longrightarrow 2\ H_3PO_3.$$
$$P_2O_3 + 4\ OH^- \longrightarrow 2\ HPO_3^{--} + H_2O.$$

When heated in a sealed tube, phosphorus trioxide yields the tetroxide and elementary phosphorus.

$$4\ P_2O_3 \longrightarrow 3\ P_2O_4 + 2\ P.$$

The Phosphoric Acids. There are three acids containing phosphorus in the oxidation state of 5 +. The common acid, H_3PO_4, is named *orthophosphoric acid.* The acid which differs from the ortho-acid by one mole of water per mole of the acid is *metaphosphoric acid,* HPO_3. The acid which is of intermediate hydration is *pyrophosphoric acid,* $H_4P_2O_7$.

Orthophosphoric acid, H_3PO_4, may be prepared in the pure state by the oxidation of phosphorus by moderately concentrated nitric acid and by the union of the anhydride with water,

$$3\,P + 5\,H^+ + 5\,NO_3^- + 2\,H_2O \longrightarrow 3\,H_3PO_4 + 5\,NO.$$
$$P_2O_5 + 3\,H_2O \longrightarrow 2\,H_3PO_4.$$

A commercial grade of phosphoric acid is prepared by mixing sulfuric acid of specific gravity 1.5 with pulverized phosphate rock and heating the mixture with steam.

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 \longrightarrow 3\,CaSO_4 + 2\,H_3PO_4.$$

Most of the calcium sulfate precipitates and is removed by filtration. The solution is then concentrated by evaporation. Phosphoric acid is also manufactured by an electric furnace method. A mixture of calcium phosphate, coke, and sand is heated in an electric furnace and elementary phosphorus is vaporized.

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \longrightarrow 3\,CaSiO_3 + 5\,CO + 2\,P.$$

Air is admitted to the gas flue and the phosphorus burns, producing the pentoxide, which is then absorbed in water to form phosphoric acid. Phosphoric acid may be crystallized from solution by evaporation under reduced pressure. The solid melts at 42.3°. It yields a hydrate, $(H_3PO_4)_2H_2O$, which melts at 29.4°. The acid is stable and, unlike the similar compounds of the other members of the group in this oxidation state, it is a very weak oxidizing agent.

Phosphoric acid is a moderately weak acid yielding chiefly its primary ionization products in 0.1 N. solution.

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-.$$

The dihydrogen phosphate ion is dissociated to only a limited extent, so that the concentration of the phosphate ion in an acid solution is slight.

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{--}.$$
$$HPO_4^{--} + H_2O \rightleftharpoons H_3O^+ + PO_4^{---}.$$

Pyrophosphoric acid, $H_4P_2O_7$, is formed by the dehydration of orthophosphoric acid at 215°.

$$2\,H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O\uparrow.$$

The rate of conversion of pyrophosphoric acid into the ortho-acid is slow in cold water, but rapid in hot water. This substance is a solid which melts at 61°. It may be distinguished from the other phosphoric acids by its reaction with zinc acetate to form a precipitate.

Metaphosphoric acid, HPO_3, is formed by heating the ortho- or pyro- acid to temperatures above 400°.

$$H_3PO_4 \longrightarrow HPO_3 + H_2O\uparrow.$$
$$H_4P_2O_7 \longrightarrow 2\,HPO_3 + H_2O\uparrow.$$

Metaphosphoric acid is a transparent, glass-like solid which sublimes without decomposition when it is strongly heated. The hydration of this acid to form orthophosphoric acid takes place only slowly in cold water. Most of the metaphosphates are insoluble and the acid yields a precipitate with the calcium ion.

Phosphates. The salts of the phosphoric acids are the phosphates. Since orthophosphoric acid ionizes in three stages, it yields the dihydrogen, the monohydrogen, and the normal phosphate, depending on the relative proportions of the acid and base.

$$H_3PO_4 + OH^- \rightleftharpoons H_2O + H_2PO_4^-.$$
$$H_2PO_4^- + OH^- \rightleftharpoons H_2O + HPO_4^{--}.$$
$$HPO_4^{--} + OH^- \rightleftharpoons H_2O + PO_4^{---}.$$

These reactions are reversible and the normal phosphates react with acids, such as sulfuric and phosphoric acids, to form hydrogen phosphates.

$$Ca_3(PO_4)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,CaHPO_4.$$
$$2\,CaHPO_4 + H_2SO_4 \longrightarrow CaSO_4 + Ca(H_2PO_4)_2.$$

The conversion of calcium phosphate into the dihydrogen phosphate is an important reaction in the preparation of the soluble superphosphate for use in fertilizers. These salts will be discussed further in Chapter XXIX, dealing with the phosphates.

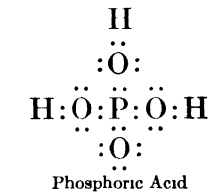
Phosphorous acid. H_2HPO_3. This substance is a weak acid which is formed by the union of the trioxide with cold water and by the hydrolysis of phosphorus trichloride.

$$P_2O_3 + 3\,H_2O \longrightarrow 2\,H_2HPO_3.$$
$$PCl_3 + 6\,H_2O \longrightarrow H_2HPO_3 + 3\,H_3O^+ + 3\,Cl^-.$$

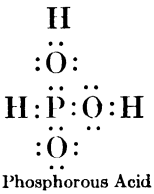
With an excess of phosphorus trichloride, *pyrophosphorous acid* is formed.

$$2\ PCl_3 + 11\ H_2O \longrightarrow H_4P_2O_5 + 6\ H_3O^+ + 6\ Cl^-.$$

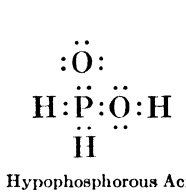
The phosphorous acid molecule contains only two replaceable hydrogen atoms. Consequently, it is assumed that one of the hydrogen atoms is attached directly to the phosphorus atom. The relation of phosphoric, phosphorous, and hypophosphorous acids to each other is shown by the electronic formulas.



Phosphoric Acid



Phosphorous Acid



Hypophosphorous Acid

Phosphorous acid is a reducing agent, but is not highly active.

$$H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2\ H^+ + 2\ \epsilon.$$

When phosphorous acid is heated, it decomposes to form phosphoric acid and phosphine.

$$4\ H_3PO_3 \longrightarrow 3\ H_3PO_4 + PH_3.$$

Hypophosphorous acid, HH_2PO_2, may be prepared by the reaction of sulfuric acid with barium salt.

$$Ba(H_2PO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\ HH_2PO_2.$$

The salts of this acid are prepared by the reaction of phosphorus with a soluble metal hydroxide.

$$3\ OH^- + 4\ P + 3\ H_2O \longrightarrow 3\ H_2PO_2^- + PH_3.$$

The acid is a strong reducing agent. It also decomposes to yield phosphine and phosphoric acid when it is heated.

$$2\ H_3PO_2 \longrightarrow PH_3 + H_3PO_4.$$

The Oxides and Oxyacids of Arsenic. *Arsenic trioxide*, As_2O_3, is formed when arsenic and combustible arsenic compounds burn in air or oxygen. Commercially, the oxide, known as *white arsenic*, is obtained from the flue dust of smelters in which sulfide ores containing arsenic (*e.g.*, many of the copper sulfide ores) are roasted. The oxide is resublimed and condensed to a white solid. The trioxide is slightly soluble in water, reacting to form arsenious

acid. Approximately 25,000 tons of white arsenic were consumed in the United States in 1940. More than one half of this quantity was used in the production of insecticides; approximately 14% in the preparation of weed-killing compounds, such as sodium arsenite; and 5% in the glass industry. Arsenious oxide is a deadly poison, 0.06–0.2 g. being ordinarily a fatal dose, although the system may develop a tolerance which permits larger amounts.

Arsenious acid, $HAsO_2$, is produced in solution by the reaction of the oxide with water.

$$As_2O_3 + H_2O \longrightarrow 2\ HAsO_2.$$

The trioxide is somewhat amphoteric, but its acidic properties predominate. The oxide reacts with sodium hydroxide solution to form the arsenites, both the orthoarsenite, Na_3AsO_3, and the metarsenite, $NaAsO_2$, being produced. The acid is so weak that the soluble salts are highly hydrolyzed. The trioxide also reacts with concentrated hydrochloric acid to form the trichloride.

$$As_2O_3 + 6\ H_3O^+ + 6\ Cl^- \rightleftharpoons 2\ AsCl_3 + 9\ H_2O.$$

This compound is practically completely hydrolyzed in dilute solution.

Arsenic acid, H_3AsO_4, may be prepared by the oxidation of the trioxide by strong oxidizing agents, such as hypochlorous acid.

$$[HClO + H^+ + 2\ \epsilon \longrightarrow H_2O + Cl^-.] \times 2.$$
$$As_2O_3 + 5\ H_2O \longrightarrow 2\ H_3AsO_4 + 4\ H^+ + 4\ \epsilon.$$
$$2\ HClO + As_2O_3 + 3\ H_2O \longrightarrow 2\ Cl^- + 2\ H^+ + 2\ H_3AsO_4.$$

This acid is unstable and decomposes when it is heated to yield, successively, pyroarsenic acid, metarsenic acid, arsenic pentoxide, and arsenic trioxide. Calcium and lead arsenates have extensive uses as insecticides.

Oxides and Oxyacids of Antimony. *The trioxide*, formed by the direct union of the elements, is both basic and acidic.

$$Sb_2O_3 + 6\ H_3O^+ \longrightarrow 2\ Sb^{+++} + 9\ H_2O.$$
$$Sb_2O_3 + 2\ OH^- + 3\ H_2O \longrightarrow 2\ Sb(OH)_4^-.$$

The trihydroxide also is amphoteric and may be formed by the reaction of a limited excess of a basic hydroxide with an antimony salt, and by the reaction of an acid with an antimonite.

$$Sb^{+++} + 3\ OH^- \rightleftharpoons Sb(OH)_3\downarrow.$$
$$Sb(OH)_4^- + H_3O^+ \rightleftharpoons Sb(OH)_3\downarrow + 2\ H_2O.$$

Antimony pentoxide is formed by the oxidation of the metal with nitric acid. It is only slightly soluble and separates as a precipitate having the composition, $HSb(OH)_6$ or $HSbO_3(H_2O)_3$. The potassium salt is soluble in water but the sodium salt is only slightly soluble.

The Oxides and Hydroxides of Bismuth. In its lower oxidation state, bismuth exhibits the chemical properties of a metallic element. Its oxide and hydroxide are basic, so that they react with hydronium ions.

$$Bi_2O_3 + 6\,H_3O^+ \longrightarrow 2\,Bi^{+++} + 9\,H_2O.$$
$$Bi(OH)_3\downarrow + 3\,H_3O^+ \longrightarrow Bi^{+++} + 6\,H_2O.$$

The trihydroxide is easily precipitated from salt solutions.

$$Bi^{+++} + 3\,OH^- \rightleftharpoons Bi(OH)_3\downarrow.$$

The hydroxide does not react with an excess of a strong base. The bismuth ion hydrolyzes to form the bismuthyl ion, BiO^+, unless an excess of hydrogen ions is present in solution.

$$Bi^{+++} + 2\,OH^- \rightleftharpoons BiO^+ + H_2O.$$

Bismuthyl nitrate and the carbonate have medicinal uses, particularly for the treatment of infections in the alimentary canal. The bismuthyl ion is readily reduced to the elementary metal.

$$[BiO(OH) + H_2O + 3\,\epsilon \longrightarrow Bi + 3\,OH^-.] \times 2.$$
$$[2\,OH^- + Sn(OH)_4^{--} \longrightarrow SnO_3^{--} + 3\,H_2O + 2\,\epsilon.] \times 3.$$
$$2\,BiO(OH) + 3\,Sn(OH)_4^{--} \longrightarrow 2\,Bi + 3\,SnO_3^{--} + 7\,H_2O.$$

Bismuthyl oxalate, $(BiO)_2C_2O_4$, decomposes when heated to form bismuth monoxide.

$$(BiO)_2C_2O_4 \longrightarrow 2\,BiO + 2\,CO_2.$$

Bismuth pentoxide may be formed by the action of strong oxidizing agents on the trioxide. In a concentrated sodium hydroxide solution, *sodium bismuthate*, $NaBiO_3$, the salt of the meta acid, may be formed.

$$ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-.$$
$$BiO(OH) + 3\,OH^- \longrightarrow BiO_3^- + 2\,H_2O + 2\,\epsilon.$$
$$ClO^- + BiO(OH) + OH^- \longrightarrow Cl^- + BiO_3^- + H_2O.$$

This substance is a powerful oxidizing agent, vigorous enough to oxidize manganous ion to the permanganate in acidic solution.

$$[HBiO_3 + 5\,H^+ + 2\,\epsilon \longrightarrow Bi^{+++} + 3\,H_2O.] \times 5.$$
$$[Mn^{++} + 4\,H_2O \longrightarrow MnO_4^- + 8\,H^+ + 5\,\epsilon.] \times 2.$$
$$5\,HBiO_3 + 2\,Mn^{++} + 9\,H^+ \longrightarrow 5\,Bi^{+++} + 2\,MnO_4^- + 7\,H_2O.$$

Orthobismuthates are not known, although the tetroxide, Bi_2O_4, is probably a bismuth bismuthate, $BiBiO_4$.

Test for the Ions of Arsenic, Antimony, and Bismuth. Analytically, arsenic and antimony are members of the tin group and bismuth of the copper group of cations. The group precipitation of the sulfides and the separation of the tin and copper groups have already been discussed. The separation of the sulfides of arsenic and antimony may be accomplished by dissolving antimony sulfide in concentrated hydrochloric acid, arsenic sulfide remaining as a residue. When the acidic solution of the antimony salt is diluted and saturated with hydrogen sulfide, the formation of a precipitate of the characteristically orange-red antimony trisulfide may serve as a test for this element. The presence of arsenic may be determined by the oxidation of the sulfide to arsenic acid and the precipitation of magnesium ammonium arsenate from ammoniacal solution.

$$[2\,H^+ + NO_3^- + 1\,\epsilon \longrightarrow H_2O + NO_2.] \times 10.$$
$$As_2S_5 + 8\,H_2O \longrightarrow 2\,H_3AsO_4 + 5\,S + 10\,H^+ + 10\,\epsilon.$$
$$10\,H^+ + 10\,NO_3^- + As_2S_5 \longrightarrow 10\,NO_2 + 2\,H_3AsO_4 + 2\,H_2O + 5\,S.$$
$$H_3AsO_4 + Mg^{++} + NH_4^+ + 3\,OH^- \longrightarrow MgNH_4AsO_4 + 3\,H_2O.$$

Bismuth sulfide is dissolved by nitric acid and bismuthyl hydroxide is then precipitated. This hydroxide is reduced to metallic bismuth by the action of sodium stannite, giving a jet black deposit.

EXERCISES

1. Discuss the relation of the oxidation numbers of the elements of the phosphorus family to the structures of their atoms.
2. How is each of the elements of this family prepared?
3. Discuss allotropy as illustrated by the elements of the phosphorus family.
4. Write equations to represent the reactions of the elements of the phosphorus family with oxygen, sulfur, chlorine, metals, and with nitric acid.
5. Discuss the group relationships in chemical properties exhibited by the elements of the phosphorus family, taking into account the following three

groups of reactions: (*a*) the elements with nitric acid; (*b*) the trihydroxides with sodium hydroxide and with hydrochloric acid; (*c*) the reaction of the trihalides with water.

6. What two methods are used industrially for the preparation of phosphoric acid?
7. What two methods may be used for the preparation of the hydrogen phosphate salts?
8. Explain the fact that the sodium salts of the acids of the elements of the phosphorus family exhibit basic reactions in solution.
9. Explain the necessity for the use of a basic solution for the precipitation of magnesium ammonium phosphate. Why is ammonia used to make the solution basic and why is ammonium chloride added?
10. What is a thio-salt? How are these salts formed? How may they be decomposed to reprecipitate the simple sulfides?

SUPPLEMENTARY READINGS

Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Volumes VIII (1928) and IX (1929).

Weeks, *The Discovery of the Elements.*

Waggaman, "Volatilization Process for Phosphoric Acid," *Ind. Eng. Chem.* **24,** 983 (1932).

CHAPTER XXI

THE ELEMENTS OF GROUP IV

The elements, *carbon*, *silicon*, *germanium*, *tin*, and *lead*, constitute Group IV of the Periodic System based on atomic numbers. The atoms of these elements contain four valence electrons. The kernels of the atoms of carbon and silicon have the structure of the inert gases; but the atoms of the other three elements in the group have a shell of eighteen electrons within the valence shell. In this family, as in the phosphorus family, there is a transition from the non-metallic properties of the elements of the lower atomic numbers to the metallic properties of those of the higher atomic numbers. The common oxidation states of the metals in this family are 2 + and 4 +; but other states are also common for the elements of the lower atomic numbers. Carbon may exhibit oxidation numbers from 4 − to 4 + in a series of complex compounds. The related group, Group IV–B, contains the elements *titanium*, *zirconium*, *hafnium*, and *thorium*. These elements are each the second member of a transition series in which the outer shell of electrons in the kernel of the atom contains ten electrons, two more than in the corresponding inert gas. The electron distribution in the titanium atom, for example, is 2, 8, 10, 2; and the other elements occupy corresponding positions in the succeeding long periods. However, two of the electrons in this shell, in addition to those in the valence shell, are easily removed and the usual oxidation number of the elements is 4 +.

CARBON AND SILICON

These two elements are distinctly non-metallic and exhibit a number of similar reactions. Carbon atoms show to a pronounced degree the property of sharing electrons with other carbon atoms to build up complex structures. This makes possible the existence of hundreds of thousands of carbon compounds containing only a few other elements. These compounds are called *organic com-*

pounds because many of them are the products of animal and vegetable organisms, and formerly they were obtained only from such sources as these. The name is retained as a convenient classification, although such compounds may now be synthesized from simpler materials. Some of the classes of organic compounds are discussed in Chapters XXXIV and XXXV. Although silicon may form a limited series of compounds similar to the hydrocarbons, these substances are not important. The complex compounds of silicon contain oxygen and a number of metallic elements. The position of silicon in the mineral substances in the outer part of the earth is as important as that of carbon in the animal and vegetable matter. Some of the properties of the two elements are listed in Table 30.

TABLE 30

SOME PROPERTIES OF CARBON AND SILICON

	Carbon	*Silicon*
Atomic weight	12.01	28.06
Atomic number	6	14
Isotopes	12, 13	28, 29, 30
Electron structure	2, 4	2, 8, 4
Melting point	Graphite 3500°	1427°
Boiling point	4827°	2287°
Density (20°) g. per ml.	Diamond, 3.51 Graphite 2.25	2.4

Occurrence of Carbon. In addition to its occurrence in animal and vegetable matter, carbon occurs in coal, natural gas, and petroleum which have resulted from changes affecting organic matter which accumulated in the remote past. Carbon occurs in the elementary condition in coal and in diamonds and graphite. Carbon dioxide is present in air; and carbonates are found widely distributed, the most common being limestone, marble, and dolomite.

Allotropic Forms of Carbon. Carbon exists in two distinct crystalline forms, the diamond and graphite. *Diamonds* are octahedral in shape and are colorless when pure, though many of the stones are colored by the presence of small proportions of impurities. This form of carbon has a specific gravity of 3.5 and

is the hardest substance known. Diamonds possess a high index of refraction of light, and the stones are cut so as to form facets which give the maximum brilliance. Diamonds which are worthless as gems because of imperfections are used on account of their hardness for cutting glass and for the tips of drills. Diamonds are obtained chiefly from South Africa and Brazil. The largest diamond, the famous Cullinan, weighed 3032 carats, 606.4 grams. Small diamonds were made by Moissan in 1894, by suddenly cooling a solution of carbon in melted iron. Under the conditions of temperature and pressure existing within the mass, carbon separates from the iron in the form of minute diamonds; but diamonds prepared in this way are too small to have any practical value.

Graphite is made up of leaf-like crystals between which there is but slight friction. It is soft and has a specific gravity of only 2.25. Graphite is used in the preparation of various lubricants. Mixtures of graphite and clay are used in making pencils, the hardness of the pencil depending on the proportions of the substances in the mixture. Graphite does not combine readily with oxygen and is used in stove polishes; and graphite crucibles are employed in certain high temperature reactions. Graphite is a fairly good conductor of electricity and is used in the form of electrodes for arc lights and electric furnaces.

Graphite occurs in deposits in Ceylon, Siberia, and Madagascar. Graphite is the product formed by the condensation of carbon vapor. Acheson's process for the manufacture of graphite consists in passing an electric current through anthracite coal or coke containing a small proportion of sand. The resistance to the passage of the current generates a large amount of heat, and carbon is converted to graphite at the high temperature.

The chars, such as charcoal and coke, are the products of the *destructive distillation* of wood and coal, respectively. When wood is destructively distilled, the solid residue is charcoal, and among the volatile products are water, wood alcohol, acetic acid, and acetone. The destructive distillation of coal yields by-products such as illuminating gas, ammonia, and a tarry material called coal tar; and the non-volatile residue is coke. When bones are destructively distilled, the residue consists largely of calcium phosphate and amorphous carbon. Most of the calcium phosphate is removed by treating the residue with hydrochloric acid, and a

form of carbon, called *boneblack*, is obtained. A very pure form of carbon may be secured by the decomposition of sugar. The carbon in the chars is commonly called amorphous carbon; but examination by X-ray methods shows that it has a crystalline structure similar to that of graphite. The chars are very porous and they give a large surface area relative to the mass of the material. Some of the chars have the property of adsorbing other substances to a large extent. Boneblack is used on this account in the purification of cane sugar solutions; and some forms of charcoal, such as coconut charcoal, are used in the canisters of gas masks. Charcoal is activated by heating it in steam for a long time so as to remove adsorbed substances as completely as possible.

Carbon black is formed as a sooty deposit when a smoky gas flame is cooled. A similar deposit may be formed from the flame of burning oil. Large volumes of natural gas are burned annually so as to produce carbon black, by causing the flame to impinge on a cold metal surface. The production of carbon black in the United States in 1939 was 268,000 tons. Approximately 89% of the consumption of this material is in the rubber industry, 6% in the production of ink, and 2% in paint. The use of carbon black in rubber increases the toughness and improves the product for making automobile tires.

Coal. The decomposition of vegetable matter in the absence of air, as beneath the surface of water in a swamp, leads to the formation of peat. Further decomposition of the peat with the loss of some of the volatile matter produces lignite, or brown coal. If a mass of this material is subjected to high temperature and great pressure, as has happened in past geologic ages in extensive land upheavals, the transformation proceeds further, the organic compounds are partially decomposed with the evolution of volatile materials, and first bituminous and then anthracite coal are formed. The composition of coal varies greatly from one deposit to another, but it is made up largely of amorphous carbon, and contains also complex compounds of carbon and hydrogen.

Chemical Reactions of Carbon. The element does not exhibit either positive or negative electrovalent states; but its reactions involve electron sharing with the formation of covalent bonds. Carbon is not active at ordinary temperatures, but ex-

hibits a number of important reactions at high temperatures. The reaction of carbon with oxygen is highly exothermic; and the combination of oxygen with carbon and carbon compounds furnishes the greater portion of the energy used in industrial operations. Graphite oxidizes only slowly at high temperatures and diamonds must be heated to 800° to cause them to burn in oxygen. Depending on the relative amount of oxygen in contact with the burning material, the product is either carbon monoxide or carbon dioxide.

$$2\,C + O_2 \longrightarrow 2\,CO + 52{,}860 \text{ cal.}$$
$$C + O_2 \longrightarrow CO_2 + 94{,}390 \text{ cal.}$$

Hot carbon is an excellent reducing agent and coke is the most extensively used of the reducing substances for the liberation of metals from their oxide ores.

$$ZnO + C \longrightarrow Zn + CO.$$

Carbon combines with many of the metals and with a few of the non-metals, *e.g.*, sulfur and silicon.

$$Ca + 2\,C \longrightarrow CaC_2.$$
$$C + 2\,S \longrightarrow CS_2.$$
$$C + Si \longrightarrow SiC.$$

Carbon Dioxide. This gas is present in air in proportions varying from 3.5 parts in 10,000 of air in the country to 1% or more in crowded rooms. It is formed in natural processes by the respiration of animals and by the decay of animal and vegetable matter. In the presence of chlorophyll in the green leaves of plants, under the influence of light, carbon dioxide reacts with water to form carbohydrates and release a portion of its oxygen to the air. These two changes tend to keep the total proportions of carbon dioxide and oxygen approximately constant. Carbon dioxide is present in effervescent spring waters.

Preparation of Carbon Dioxide. There are a number of reactions which yield carbon dioxide. The most convenient laboratory method for the preparation of the gas is based on the reaction of an acid with a carbonate.

$$CaCO_3 + 2\,H_3O^+ \longrightarrow Ca^{++} + 3\,H_2O + CO_2\uparrow.$$

The industrial preparation of carbon dioxide employs the combustion of coke, the decomposition of limestone, and the fermentation of sugar.

$$C + O_2 \longrightarrow CO_2.$$
$$CaCO_3 \longrightarrow CaO + CO_2.$$
$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2.$$

Carbon dioxide may be concentrated and separated from other gaseous material by absorbing it in a solution of potassium carbonate under pressure, with the formation of the bicarbonate.

$$CO_3^{--} + H_2O + CO_2 \rightleftharpoons 2\,HCO_3^-.$$

When the conversion to the bicarbonate is complete, the pressure is reduced and the bicarbonate solution is heated. Carbon dioxide is evolved and is then dried, liquefied, and stored in steel cylinders.

Properties of Carbon Dioxide. Carbon dioxide is a colorless and odorless gas which has a density about one and one-half times that of air. At 15° and a pressure of one atmosphere, it is soluble to the extent of one volume of the gas in one volume of water. Carbonated water is a solution of the gas under a pressure of three or four atmospheres. The critical temperature of carbon dioxide is 31.1°, and the critical pressure is 73 atmospheres. The vapor pressure of the liquid is 59 atmospheres at 20°. If the liquid is allowed to flow out from a cylinder, it evaporates very rapidly; and the heat of vaporization is high enough to cause the remainder of the liquid to freeze to a snow-like solid. This solid has a vapor pressure of one atmosphere at − 78.5°, and the solid sublimes.

Reactions of Carbon Dioxide. Carbon dioxide is a very stable compound. Under a pressure of 760 mm., it is decomposed to the extent of only 2% at 2000°.

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

Active metals such as magnesium burn in an atmosphere of carbon dioxide to form free carbon and the oxide of the metal. Carbon reduces the dioxide almost completely to the monoxide at 1000°.

$$2\,Mg + CO_2 \longrightarrow C + 2\,MgO.$$
$$C + CO_2 \longrightarrow 2\,CO.$$

Carbon dioxide forms a weakly acidic solution in water, and reacts with metal oxides and hydroxides to form carbonates.

$$CO_2 + 2\,H_2O \rightleftharpoons H_3O^+ + HCO_3^-.$$
$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{--}.$$
$$CO_2 + CaO \longrightarrow CaCO_3.$$
$$CO_2 + 2\,OH^- \rightleftharpoons H_2O + CO_3^{--}.$$

With an excess of carbon dioxide the bicarbonate is formed in the presence of water.

Uses of Carbon Dioxide. Carbon dioxide is extensively used in carbonating water in the preparation of soft drinks, and in the production of sodium bicarbonate, sodium carbonate, and basic lead carbonate. The substance does not burn or support combustion. One type of fire extinguisher contains sodium hydrogen carbonate and a bottle of sulfuric acid, Fig. 123. When the tank is inverted, the acid is poured into the carbonate solution and the reaction causes the water to become saturated with carbon dioxide. The excess of the gas rises to the top of the tank and creates a pressure which forces the solution out through the nozzle. The carbon dioxide carried by the solution mixes with the air surrounding the fire and reduces the concentration of oxygen below that necessary to support combustion.

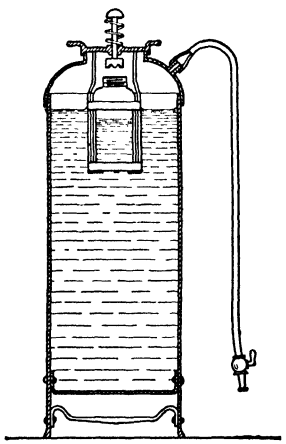


FIG. 123. — Fire Extinguisher.

Solid carbon dioxide is used as a refrigerant. Carbon dioxide snow, formed when the liquid evaporates rapidly, is compressed into large blocks, known as "dry ice." Much lower temperatures may be maintained with this refrigerant than with water ice. The solid evaporates directly so that no liquid is formed; and the gas prevents the development of aerobic bacteria (bacteria which grow only in the presence of oxygen). This causes dry ice to be especially suited for use in the shipping of fruit and vegetables. Processes have been developed for the quick freezing of meats, fruit, and vegetables, so as to provide a preserved product which retains as nearly as possible the flavor of fresh food.

Carbonates. Carbonic acid is a weak, unstable acid which exists only in solution. It yields two series of salts, the carbonates and the bicarbonates. The normal salts, with the exception of those of sodium, potassium, and ammonium, are slightly soluble and are usually prepared by precipitation. The bicarbonates are more soluble than the carbonates. They are easily prepared by the reaction of weakly acidic solutions with the carbonates. These salts are discussed in Chapter XXX, dealing with salts.

Acetic Acid. $HC_2H_3O_2$. This substance, with wood alcohol and acetone, is produced by the destructive distillation of wood. The condensed acid liquor is neutralized with slaked lime and solid calcium acetate is obtained by evaporation of the solution. Acetic acid is distilled from a mixture of the acetate and sulfuric acid.

$$Ca(C_2H_3O_2)_2 + H_2SO_4 \longrightarrow 2\,HC_2H_3O_2 \uparrow + CaSO_4.$$

Acetic acid is also prepared by a synthetic process based on the reaction of acetylene with water, under the proper experimental conditions, to form acetaldehyde which is then oxidized to acetic acid. Pure glacial acetic acid is a liquid which freezes at 16.7°. In aqueous solution it is a weak acid which finds extensive use in the laboratory. It is also used in the preparation of its salts and in the synthesis of a number of organic products, *e.g.*, cellulose acetate, which has among its uses the manufacture of noninflammable film for photographic use, and the manufacture of shatterproof glass.

Vinegar, which is crude, dilute acetic acid, flavored by the presence of natural products present in the fruit juices, is prepared by the oxidation of the alcohol in hard cider with atmospheric oxygen in the presence of a microörganism, *bacterium aceti.*

$$C_2H_5OH + O_2 \longrightarrow HC_2H_3O_2 + H_2O.$$

The cider is allowed to trickle over beech shavings which have been inoculated with the microörganism. A plentiful supply of air is admitted and the oxidation proceeds rapidly because of the large amount of surface contact obtained in this manner.

Carbon Monoxide. This oxide is the product of the incomplete combustion of carbon and carbon compounds. It is formed by the reaction of steam with hot carbon, Fig. 124.

$$H_2O + C \longrightarrow H_2 + CO.$$

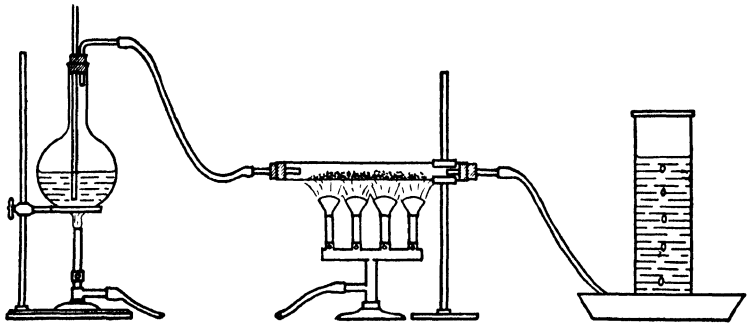


FIG. 124. — Formation of Carbon Monoxide.

The pure gas may be formed by the dehydration of oxalic and formic acids through the action of concentrated sulfuric acid, Fig. 125.

$$H_2C_2O_4 \longrightarrow H_2O + CO_2 + CO.$$
$$HCHO_2 \longrightarrow H_2O + CO.$$

In the former case, the carbon dioxide is absorbed by a base, carbon monoxide escaping absorption. Since the formation of carbon monoxide from carbon results in the evolution of only about one third of the amount of energy given out in the combustion of

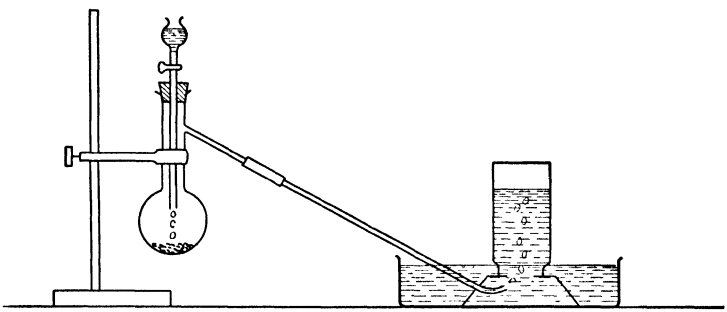


FIG. 125. — Carbon Monoxide from Formic Acid.

carbon to carbon dioxide, the presence of carbon monoxide in the waste gases from any burner or internal combustion engine represents an economic loss. Because carbon monoxide burns with the evolution of a large amount of heat per mole, it is an important fuel and is a component of most of the manufactured fuel gases. Its industrial use is chiefly as a fuel and reducing agent. Carbon monoxide reacts with chlorine in the sunlight and in the

presence of charcoal as a catalyst to form *carbonyl chloride, phosgene*, $COCl_2$.

Carbon monoxide resembles nitrogen in some of its physical properties, such as the melting point, boiling point, density, critical temperature, and critical pressure. The gas is only slightly soluble in water. Carbon monoxide is highly poisonous; and it is not readily adsorbed in gas masks because it has a low critical temperature. The oxidation of carbon monoxide is catalyzed in the presence of a mixture of the oxides of manganese and copper, known as "hopcalite"; and the gas masks for use in an atmosphere containing carbon monoxide employ this catalyst. The breathing of air containing more than 6–7 parts of carbon monoxide in 10,000 of air is dangerous. Carbon monoxide combines with the haemoglobin of the blood corpuscles to form a product which is stable enough to prevent the combination of the haemoglobin with oxygen. Leaky gas fittings may cause the presence of this gas in houses; and its presence in the exhaust gases from internal combustion engines is the cause of danger in a closed garage where an automobile engine is running.

Calcium Carbide. CaC_2. This substance is an electric furnace product made by heating lime and coke to a temperature of 3000°.

$$CaO + 3\,C \longrightarrow CaC_2 + CO.$$

Calcium carbide reacts with water, forming acetylene which is important as a fuel in the oxy-acetylene torch.

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2\uparrow + Ca(OH)_2.$$

Calcium carbide also combines with nitrogen forming calcium cyanamide, an important step in the fixation of atmospheric nitrogen by the cyanamide process.

Silicon Carbide. SiC. This substance, Fig. 126, was discovered in 1891 by Acheson, who was attempting to prepare a substance which could be used instead of emery as an abrasive. He placed a mixture of coke and clay in an iron bowl which served as one pole for the passage of an electric current. An arc light carbon inserted into the mixture was the other pole. The resistance to the passage of the current caused a high temperature and the contents of the bowl melted. After the experiment, he noticed a few bright specks on the end of the carbon. These he found to be

hard enough to cut glass and to grind off the polished surface of a diamond.

This experiment was the beginning of the great industry of manufacturing abrasives. Grinding wheels are fashioned by

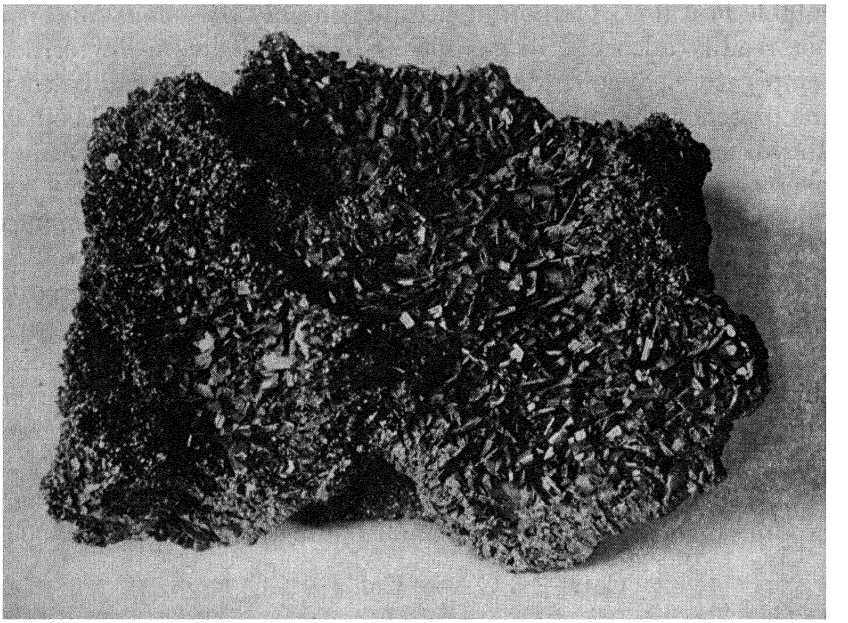


FIG. 126. — Silicon Carbide Crystals. (Courtesy of The Carborundum Company.)

crushing the abrasive and cementing it together by means of a mixture of clay and feldspar. The applications of silicon carbide run through the whole range of the industries.

"Carborundum Brand Silicon Carbide" is now manufactured in large quantities at Niagara Falls by the Acheson process, Fig. 127. An electric current is passed through a mixture of sand and coke containing varying amounts of sawdust and common salt. The resistance to the passage of the current generates heat and produces the high temperature necessary for the reaction. The result of the reaction may be expressed by the following equation.

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO\uparrow.$$

The sawdust is used to make the mixture porous so that the carbon monoxide may pass through the charge and escape, and the

salt forms chlorides with certain impurities in the charge and aids in their elimination. When silicon carbide is heated to a temperature somewhat higher than that required for its formation, it decomposes, silicon escaping as a gas, and carbon is left in the form of graphite.

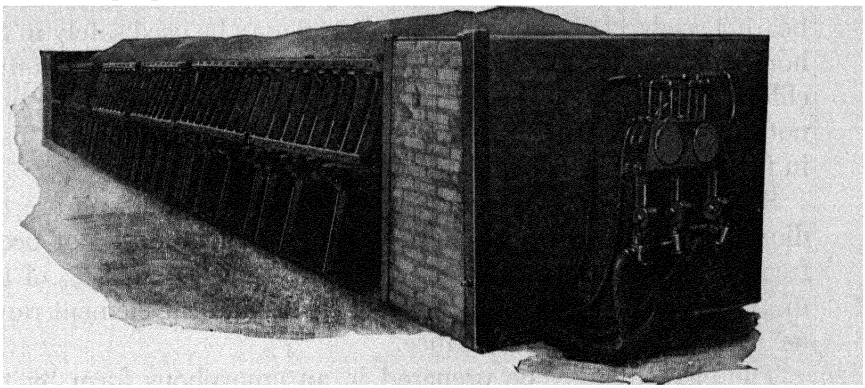


FIG. 127. — Carborundum Brand Silicon Carbide Furnace. (Courtesy of The Carborundum Company.)

Carbon Disulfide. CS_2. This compound is prepared by heating charcoal and sulfur in the absence of air in an electric furnace.

$$C + 2\,S \longrightarrow CS_2 - 19{,}600 \text{ cal.}$$

Carbon disulfide is very volatile and has a boiling point of 46°. Hence, the product must be condensed, for it emerges from the furnace in the form of a gas. Carbon disulfide burns in air with the formation of carbon dioxide and sulfur dioxide.

$$CS_2 + 3\,O_2 \longrightarrow CO_2 + 2\,SO_2.$$

This reaction is highly exothermic, because the heat of formation of carbon disulfide is liberated in addition to the heats of combustion of carbon and sulfur. Carbon disulfide is used as a solvent for fats, sulfur, phosphorus, and iodine. It is extensively used in the preparation of carbon tetrachloride. The vapor of carbon disulfide is poisonous, and the substance may be used for killing rats, mice, prairie dogs, ants, etc.

Carbon Tetrachloride. CCl_4. When chlorine is passed into carbon disulfide containing iodine as a catalyst, the reaction represented by the following equation occurs.

$$CS_2 + 3\,Cl_2 \longrightarrow CCl_4 + S_2Cl_2.$$

Both products are liquids, but carbon tetrachloride has the lower boiling point, 77°, and is separated from the sulfur monochloride, boiling point 136°, by distillation. Carbon tetrachloride is a colorless liquid which is insoluble in water. It dissolves fats and tars readily and is used in extracting grease from wool and oil-bearing seeds. It is noninflammable and may be used safely in the household for cleaning grease spots from clothing. Carbon tetrachloride is easily volatilized and forms a heavy vapor which does not support combustion. Under the name "Pyrene" it is used in fire extinguishers.

Silicon. The important natural compounds of silicon are the dioxide and the complex silicates. The element does not occur free in nature. Compounds of silicon make up about 87% of the matter in the outer part of the solid earth; and the element ranks next after oxygen in abundance.

The element may be prepared in an amorphous form by the reduction of silica with magnesium and of silicon tetrachloride with sodium, at high temperatures.

$$SiO_2 + 2\ Mg \longrightarrow Si + 2\ MgO.$$
$$SiCl_4 + 4\ Na \longrightarrow Si + 4\ NaCl.$$

Silicon is prepared commercially by heating a mixture of sand and coke in an electric furnace, using a smaller proportion of coke than in the production of carborundum. The chief importance of the element is in the steel industry; and *ferrosilicon*, a compound of silicon and iron, is produced for this use by reducing a mixture of silica and iron oxide with carbon in an electric furnace. This substance is used in the production of silicon steels such as *duriron* which contains 16% of silicon and is acid resistant. The addition of ferrosilicon in small quantities serves also to remove bubbles of entrapped gases which would cause flaws in the steel.

The atoms of elementary silicon contain four valence electrons; and the element combines with other substances by electron sharing. Silicon yields binary compounds with many of the metals, a few of the non-metals, and with oxygen and hydrogen. Although silicon dioxide is a very stable compound, the elements do not unite readily, since a surface layer of the oxide is formed. Silicon combines vigorously with fluorine, chlorine, and bromine,

and less actively with iodine. It reacts with water in basic solution to produce hydrogen and a silicate.

$$Si + H_2O + 2\,OH^- \longrightarrow 2\,H_2 + SiO_3^{--}.$$

Silicides of the Metals. The combination of silicon with metals at high temperatures yields binary compounds known as silicides. When a mixture of powdered sand and an excess of magnesium powder is heated, a portion of the silicon formed by the reduction of the oxide combines with the excess of the magnesium to form the binary product, *magnesium silicide.*

$$SiO_2 + 2\,Mg \longrightarrow Si + 2\,MgO.$$
$$Si + 2\,Mg \longrightarrow Mg_2Si.$$

This compound does not exhibit the structure or properties of a salt. It reacts with hydrochloric acid to form a mixture of hydrides of silicon, of which the simplest is silico-methane, SiH_4, which is analogous to methane, CH_4.

$$Mg_2Si + 4\,HCl \longrightarrow 2\,MgCl_2 + SiH_4\uparrow.$$

The hydrides of silicon are spontaneously combustible in air and burn with the formation of silicon dioxide and water.

$$SiH_4 + 2\,O_2 \longrightarrow SiO_2 + 2\,H_2O.$$

Halides of Silicon. The halogens unite directly with silicon to form the tetrahalides. Silicon ignites spontaneously in an atmosphere of fluorine, but must be heated to start the reaction with the other halogens. These compounds are hydrolyzed with the formation of the hydroacid of the halogen. *Silicon tetrafluoride* is the most stable of these compounds. Silica and the silicates are attacked by hydrofluoric acid with the formation of the tetrafluoride. The hydrolysis of this substance is incomplete, producing *fluosilicic acid,* H_2SiF_6, a moderately strong acid.

$$3\,SiF_4 + 2\,H_2O + x\,H_2O \longrightarrow 2\,H_2SiF_6 + SiO_2(H_2O)_x.$$

The potassium salt of this acid is only slightly soluble; and the lead salt, $PbSiF_6$, is a soluble salt which is used in the electrorefining of lead.

Silicon tetrachloride is prepared by the reaction of chlorine with a hot mixture of silica and carbon.

$$SiO_2 + 2\,C + 2\,Cl_2 \longrightarrow SiCl_4 + 2\,CO.$$

Silicon tetrachloride fumes strongly in moist air on account of its hydrolysis to form hydrogen chloride and hydrated silica.

$$SiCl_4 + 2\,H_2O + x\,H_2O \longrightarrow 4\,HCl + SiO_2(H_2O)_x.$$

On account of this property it is used to some extent in the production of smoke screens.

Silicon Dioxide. Silica. SiO_2. This substance occurs extensively in the form of quartz and sand. It is sometimes colored by the presense of impurities, as in smoky quartz, rose quartz, and the amethyst. Onyx, agate, and jasper consist of silica containing ferric oxide as an impurity, and opal and flint are hydrated forms of silica. Infusorial earth, used as a polishing powder, is finely divided silica, which was deposited as the skeletal remains of minute organisms.

Silicon dioxide is a very stable oxide, as is indicated by the high heat of its formation.

$$Si + O_2 \longrightarrow SiO_2 + 201{,}400 \text{ cal.}$$

This oxide corresponds to the silicic acids, but does not unite directly with water to form these acids. When silica is fused with sodium hydroxide, sodium silicate is formed.

$$2\,NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O.$$

Most of the other non-metal oxides are more volatile than silica, and are evolved when a mixture of their salts with silica is heated.

$$CaCO_3 + SiO_2 \longrightarrow CO_2 + CaSiO_3.$$

Silicon dioxide reacts with hydrofluoric acid, forming the volatile substance silicon tetrafluoride.

$$SiO_2 + 2\,H_2F_2 \longrightarrow SiF_4\uparrow + 2\,H_2O.$$

Silica melts at about 1700° to form a viscous liquid. Silica is used in making many forms of laboratory apparatus, such as combustion tubes, beakers, crucibles, and flasks. Quartz glass does not soften below 1500°, while ordinary glass does soften at lower temperatures. Its coefficient of expansion is so small that hot silica may be cooled suddenly without breaking. Quartz glass transmits ultraviolet light much more readily than glass. Hence, it is used in the manufacture of ultraviolet lamps, certain optical instruments, and cells in which photochemical effects are investigated.

Silicic Acids. The addition of a strong acid to a solution of a soluble silicate results in the formation of a gelatinous precipitate of hydrated silica. When this product is strongly heated, water is driven out and dehydrated silicon dioxide is left as a residue. The dehydrated product, *silica gel*, adsorbs a number of substances to a high degree, and has many industrial uses based on this property. Pure silicic acids cannot be obtained, but salts corresponding to orthosilicic acid, H_4SiO_4, and metasilicic acid, H_2SiO_3, exist. There are also salts of a large number of hypothetical polysilicic acids: *e.g.*, $H_2Si_2O_5$, $H_8Si_3O_{10}$, $H_4Si_3O_8$. The salts of these acids are discussed in Chapter XXX.

GERMANIUM, TIN, AND LEAD

These elements are the metals of Group IV; but the nonmetallic character predominates in the compounds in which they have an oxidation state of 4 +, and they show similarities to silicon. The stability of the compounds in the oxidation state of 2 + is increasingly great with rise in the atomic number in this family. The hydroxides of the three elements are amphoteric. The most important compounds of tin and lead are those in which the metals have an electrovalence of 2 +. Some of the properties of these elements are shown in Table 31. The variation in properties for the entire group may be observed by comparing the data in this table with those in Table 30, page 407.

TABLE 31

PROPERTIES OF GERMANIUM, TIN, AND LEAD

	Germanium	*Tin*	*Lead*
Atomic weight	72.6	118.7	207.2
Atomic number	32	50	82
Isotopes	70, 72, 73, 74, 76	112, 114, 115, 116, 117, 118, 119, 120, 122, 124	204, 206, 207, 208
Electron structure	2, 8, 18, 4	2, 8, 18, 18, 4	2, 8, 18, 32, 18, 4
Oxidation states	2+, 4+	2+, 4+	2+, 4+
Typical ions	Ge^{++}, GeO_3^{--}	Sn^{++}, $Sn(OH)_4^{--}$ $SnO_3(H_2O)_x^{--}$	Pb^{++}, $Pb(OH)_4^{--}$
Melting point	958°	231.8°	327.5°
Boiling point	2700°	2260°	1620°
Density (20°) g. per ml.	5.36	7.31	11.34

Germanium. Some of the sulfide ores of silver, lead, and zinc contain germanium. The metal may be prepared by the reduction of germanium dioxide with carbon at moderately high temperature. Germanium is a grayish-white metal, as predicted by Mendeléef before its discovery, and it is hard and brittle. The metal is not important industrially.

The most stable *compounds of germanium* are those in the oxidation state of 4 +. The dioxide, GeO_2, is formed by burning the sulfide. The oxide reacts with hydrochloric acid to form the tetrachloride, $GeCl_4$, and with sodium hydroxide to form sodium germanate, Na_2GeO_3. The oxide in the lower oxidation state, GeO, reacts with acids to form germanous salts and with bases to form germanites. The germanous ion is readily oxidized.

Tin. The metal was known and used by people of ancient times. As early as 1000 B.C., the Phoenicians secured tin ore from Cornwall, England. The most important ore of tin is the dioxide, *cassiterite*, SnO_2. The Malay States, Bolivia, and the Dutch East Indies furnish the major portion of the world's supply of tin. No important deposits of tin have been discovered in the United States. The world production of tin in 1939 was approximately 181,000 tons. Only 34 tons were produced in the United States, and nearly all of this was from an Alaskan deposit.

The Production of Tin. The ore is crushed and washed to remove impurities as completely as is feasible. It is then heated in air to remove sulfur and arsenic if they are present. The oxide is next reduced by heating it with carbon in a furnace.

$$SnO_2 + C \longrightarrow Sn + CO_2.$$

The melting point of tin is much lower than that of other metals likely to be present; and the crude product may be purified by melting out the tin on a sloping hearth. The process is known as "liquation."

Properties and Reactions of Tin. The metal exists in three solid forms with definite transition temperatures. At ordinary temperatures, the stable form, β-tin, is a white crystalline metal which is very malleable and has little tensile strength. At 161°, there is a transition into another form, γ-tin. At temperatures below 18°, a gray modification, α-tin, is the stable form, but the rate of transition is slow and the change does not occur to any

considerable extent unless the metal is kept at a low temperature for a long time. Gray tin is very brittle and easily crumbles to a powder. The transition of the white into the gray tin is called "tin pest," because of the appearance of the surface of the metal during the early stages of the change. White tin has a specific gravity of 7.31 and melts at 232°.

Tin is not tarnished by air, but slowly displaces hydrogen from acids, such as hydrochloric acid, with the formation of stannous compounds.

$$Sn + 2\,H_3O^+ \longrightarrow H_2 + Sn^{++} + 2\,H_2O.$$

Tin reacts with nitric acid to form stannic acid, or hydrated stannic oxide, which contains indefinite and variable proportions of water, and with sodium hydroxide in solution forming sodium stannite.

$$3\,Sn + 4\,HNO_3 + 10\,H_2O \longrightarrow 3\,H_2SnO_3(H_2O)_3\downarrow + 4\,NO.$$
$$Sn + 2\,H_2O + 2\,OH^- \longrightarrow Sn(OH)_4^{--} + H_2.$$

These reactions indicate the non-metallic properties of tin in the oxidation state of 4 +, and the amphoteric nature in the 2 + state.

Uses of Tin. Approximately 73,000 tons of tin were consumed in the United States in 1938, nearly 40,000 tons in the manufacture of tinplate. Thin sheets of iron are cleaned by the action of dilute sulfuric acid to remove any surface oxide. The cleaned metal is then dipped into melted tin and a thin coating of tin adheres to the iron. Tinplate is employed in the manufacture of tin cans for storing foods and other materials. The iron is protected from the corrosive action of moisture and organic acids by the adherent layer of tin. Block tin is not appreciably attacked by water, so that it is suitable for use in pipes and stills for distilled water. Tinfoil has many familiar uses, although foil composed of lead, tin-lead alloys, and aluminum, and thin sheets of cellophane are now used to a large extent instead of tin. More than 20,000 tons of tin were used in 1938 in the production of alloys. The approximate composition of some of the alloys of tin is shown in Table 32.

Compounds of Tin. Tin forms compounds in two oxidation states, 2 + and 4 +. The most important of these compounds are the oxides and hydroxides, the halides, and the sulfides.

TABLE 32

ALLOYS OF TIN

Name	*Composition (Per Cent)*
Britannia	Sn, 90–95; Sb, 5–10; Cu, 1–3
Babbitt	Sn, 70–90; Sb, 7–24; Cu, 2–22
Bell metal	Sn, 20–25; Cu, 75–80
Solder (medium)	Sn, 50; Pb, 50
Pewter (old)	Sn, 80; Pb, 20
Pewter (modern)	Sn, 85–90; Sb, 10–15
Aluminum solder	Sn, 86; Zn, 9; Al, 5
Type metal	Sn, 5–35; Sb, 8–20; Pb, 60–85
Wood's metal	Sn, 12.5; Pb, 25; Bi, 50; Cd, 12.5

The Oxides and Hydroxides. *Stannous hydroxide,* $Sn(OH)_2$, is precipitated by the reaction of an equivalent amount of sodium hydroxide with a solution of stannous chloride. The precipitate contains varying proportions of water, but is commonly represented by the simple formula, $Sn(OH)_2$.

$$Sn^{++} + 2\ OH^- \rightleftharpoons Sn(OH)_2\downarrow .$$

The hydroxide is amphoteric and yields the hydroxide complex ion with an excess of sodium hydroxide.

$$Sn(OH)_2 + 2\ OH^- \rightleftharpoons Sn(OH)_4^{--}.$$

The stannite is an active reducing agent in basic solution.

Stannous oxide, SnO, is formed by heating the hydroxide and by oxidizing the metal in a limited supply of air. This oxide burns in an excess of air to form the dioxide.

Tin dioxide, SnO_2, is formed by the combustion of the metal in an excess of air and by the dehydration of the hydrated oxide. The dioxide reacts with melted sodium hydroxide to form sodium stannate, Na_2SnO_3.

$$SnO_2 + 2\ NaOH \longrightarrow Na_2SnO_3 + H_2O.$$

This salt is soluble in water and is decomposed by the action of acids, with the precipitation of "α-stannic acid," which is in reality an hydrous oxide, since the proportions of water are not definite.

$$SnO_3^{--} + 2\ H_3O^+ + H_2O \longrightarrow H_2SnO_3(H_2O)_3\downarrow .$$

This oxide is amphoteric and reacts readily with both basic and acidic solutions. Another form of the hydrous oxide, known as "β-stannic acid," formed by the reaction of nitric acid with tin, is not soluble in an excess of acid. The difference in the two forms is a physical rather than a chemical difference.

Chlorides of Tin. The metal yields two chlorides, *stannous chloride*, $SnCl_2$, and *stannic chloride*, $SnCl_4$. *Stannous chloride* is the product of the reaction of the metal with hydrochloric acid,

$$Sn + 2\,H_3O^{++} + 2\,Cl^- \longrightarrow H_2 + Sn^{++} + 2\,Cl^- + 2\,H_2O.$$

A precipitate of the basic chloride is formed when stannous chloride is dissolved in water. The reaction is reversible and is prevented by the presence of an excess of hydrochloric acid. Stannous chloride is a good reducing agent and becomes oxidized to the stannic salt by oxygen of the air in the presence of hydrochloric acid. For this reason, an excess of tin is kept in bottles containing solutions of stannous chloride so that any stannic compounds formed in this way may again be reduced to the stannous condition.

Stannic chloride may be prepared by the oxidation of stannous chloride, but it is prepared commercially by heating tin with an excess of chlorine. Tin scrap may be de-tinned in this way.

$$Sn + 2\,Cl_2 \longrightarrow SnCl_4.$$

Stannic chloride is a colorless liquid which fumes strongly in moist air because of the reaction with water to form hydrochloric acid and hydrated stannic oxide. In solutions of stannic chloride which are acidic with hydrochloric acid, a complex chlorostannate ion, $SnCl_6^{--}$, is formed. Stannic chloride is used as a mordant and as a fireproofing material for cotton goods. It reacts with sodium hydroxide to produce sodium stannate.

$$SnCl_4 + 6\,NaOH \longrightarrow 6\,Na^+ + SnO_3^{--} + 4\,Cl^- + 3\,H_2O.$$

The fabric is soaked in a solution of the stannate, dried, and then treated with a solution of ammonium sulfate. In this manner, stannic acid is formed in close contact with the fiber, to which it adheres firmly; and the stannic acid adsorbs the dye.

Sulfides of Tin. Tin yields two sulfides, brown *stannous sulfide*, SnS, and yellow *stannic sulfide*, SnS_2. These sulfides may be formed by the direct union of the elements and by the passage of

hydrogen sulfide into dilute acidic solutions of stannous and stannic salts, respectively. The sulfides are dissolved by concentrated hydrochloric acid. Stannic sulfide reacts with ammonium sulfide, and stannous sulfide with the polysulfide, to produce the thiostannate complex ion.

$$SnS_2 + S^{--} \longrightarrow SnS_3^{--}.$$
$$SnS + S_2^{--} \longrightarrow SnS_3^{--}.$$

Stannic sulfide is used as a gilding pigment under the name of "mosaic gold." For this purpose, it is prepared by heating a mixture of tin and sulfur with ammonium chloride and mercury. The mercury and ammonium chloride are volatilized from this mixture, leaving stannic sulfide in a yellow, crystalline form. The part which ammonium chloride and mercury play in this process is not definitely known.

Tests for the Ions of Tin. The sulfides of tin are precipitated, along with the sulfides of the other ions in the tin and copper groups, by the passage of hydrogen sulfide into a 0.3 N. hydrochloric acid solution of these ions. After the separation of the tin and copper groups through the use of ammonium polysulfide, the stannic ion is separated from the arsenic and antimony because of the greater solubility of its sulfide. Stannic tin is then reduced to the stannous condition by reaction with metallic iron.

$$SnCl_6^{--} + Fe \longrightarrow Sn^{++} + Fe^{++} + 6\ Cl^-.$$

The presence of the stannous ion is shown by the formation of a white precipitate of mercurous chloride, or a black precipitate of metallic mercury, by reaction with mercuric chloride solution.

$$Sn^{++} + 2\ Hg^{++} + 8\ Cl^- \longrightarrow SnCl_6^{--} + Hg_2Cl_2\downarrow.$$

Lead. The most important lead ore is *galena*, *PbS*, which occurs in large quantities in the United States, Australia, Mexico, and other countries. *Cerussite*, $PbCO_3$, is also an important ore which is found in Utah, Colorado, and Arizona. Lead is produced from its ores in a number of states, Missouri, Idaho, and Utah being the leading producers. The world's production of lead in 1939 was approximately 1,800,000 tons; and the United States' production was about 420,000 tons.

The Production of Lead. There are several processes for the production of lead from its ores. These are discussed in

Chapter XXIV dealing with the production of the metals. A process of reduction is required to liberate the metal. One of the methods involves the conversion of the naturally occurring sulfide and carbonate into the oxide by heating them in air.

$$2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2.$$
$$PbCO_3 \longrightarrow PbO + CO_2.$$

The oxide is then reduced by heating it with carbon.

$$PbO + C \longrightarrow Pb + CO.$$

The procedure may be modified in many details, as will be discussed in the later chapter.

Properties and Reactions of Lead. Lead is a dense metal having a specific gravity of 11.3 and a melting point of 327°. It is malleable but has little tensile strength. The metal is so soft that it can be extruded under pressure through a die to form lead pipe. Lead may be hardened by alloying it with a small proportion of antimony. The metal becomes superficially oxidized when it is exposed to air, so that it presents a dull gray appearance although a clean surface shows high luster.

Lead is the element of highest atomic number in this group. Although it is just above hydrogen in activity, it reacts only slowly with acidic solutions. Lead reacts slowly with pure water and the hydroxide formed does not adhere to the surface of the metal. If carbonates, phosphates, or sulfates are in the water, a protective coating is formed and further corrosion of the metal is prevented. Soluble lead compounds are poisonous, so that it is not safe to drink water which has stood in contact with lead, as in lead pipes, unless the water contains impurities which cause the formation of the protective coating.

Lead unites with oxygen to form lead monoxide, PbO, at temperatures above 545°, and red lead, Pb_3O_4, at lower temperatures. It also unites with the halogens and with sulfur. Lead reacts with nitric acid to form lead nitrate, and with acetic acid in contact with air to form lead acetate. It reacts with sodium hydroxide solution to form the complex plumbite ion.

$$3\,Pb + 8\,H_3O^+ + 2\,NO_3^- \longrightarrow 3\,Pb^{++} + 12\,H_2O + 2\,NO.$$
$$2\,Pb + 4\,HC_2H_3O_2 + O_2 \longrightarrow 2\,Pb(C_2H_3O_2)_2 + 2\,H_2O.$$
$$Pb + 2\,H_2O + 2\,OH^- \longrightarrow Pb(OH)_4^{--} + H_2.$$

Uses of Lead. There are a number of extensive industrial uses of lead and the consumption of this metal in the United States in 1938 was approximately 545,000 tons. Secondary lead, recovered from scrap and from discarded and obsolete articles, accounted for about 225,000 tons. The most extensive use of the metal is in the manufacture of storage batteries, an alloy containing 6% of antimony being used for this purpose. The metal is also used extensively in cable coverings, lead shot, lead pipes, lead foil, and in acid plants, such as lead chamber plants for sulfuric acid. Lead forms several important alloys. Most of these contain tin also and have been listed in Table 32, page 424. The second most important use of lead is in the production of white lead, used as a pigment in paint.

Compounds of Lead. Lead yields compounds in the oxidation states 2 + and 4 +. In the lower state, there are two series of compounds, the simple lead salts and the plumbites. In the higher state, lead dioxide is the common compound.

The Oxides and Hydroxides of Lead. *Lead monoxide*, litharge, PbO, is prepared by heating lead in air at temperatures above 545°. It is also produced by heating lead with sodium nitrate.

$$Pb + NaNO_3 \longrightarrow PbO + NaNO_2.$$

The oxide reacts with acids to form electrovalent ions, Pb^{++}, and with alkalies to form the plumbite ion, $Pb(OH)_4^{--}$. When an equivalent amount of sodium hydroxide is added to a solution of a lead salt, the hydroxide is precipitated. The proportions of water in this gelatinous precipitate are indefinite; and the precipitate is the hydrous oxide, $PbO(H_2O)_x$, usually written $Pb(OH)_2$.

$$Pb(H_2O)_6^{++} + 2\,OH^- \rightleftharpoons Pb(OH)_2(H_2O)_4\downarrow + 2\,H_2O$$

or

$$Pb^{++} + 2\,OH^- \rightleftharpoons Pb(OH)_2\downarrow.$$

This substance reacts with an excess of the alkali to form the plumbite.

$$Pb(OH)_2(H_2O)_4 + 2\,OH^- \rightleftharpoons Pb(OH)_4(H_2O)_2^{--} + 2\,H_2O$$

or

$$Pb(OH)_2 + 2\,OH^- \rightleftharpoons Pb(OH)_4^{--}.$$

The oxide is used in glazing pottery and in manufacturing glass and enamels. Mixed with glycerol, it forms a good cement for glass and stoneware.

Red lead or minium, Pb_3O_4, is made by heating lead monoxide in air at temperatures below 500°. The composition of the product varies, depending on the temperature at which it is heated. At 430° the composition is represented by the formula, Pb_3O_4, or Pb_2PbO_4. This compound is decomposed by nitric acid with the precipitation of lead dioxide.

$$4\,H_3O^+ + Pb_3O_4 \longrightarrow 2\,Pb^{++} + PbO_2\downarrow + 6\,H_2O.$$

This oxide is used in making flint glass and as a pigment in red paint, such as that used for the first coat on structural iron.

Lead dioxide, PbO_2, may be prepared by the oxidation of lead monoxide or the plumbite in alkaline solution by hypochlorites.

$$Pb(OH)_4^{--} + ClO^- \longrightarrow PbO_2\downarrow + H_2O + 2\,OH^- + Cl^-.$$

It is slightly soluble in water and does not react with acids, but reacts with concentrated solutions of the alkalies to form plumbates. Lead dioxide is a strong oxidizing agent, especially in acidic solutions. The importance of lead dioxide in the storage battery is discussed in Chapter XXXII.

Lead Salts. The divalent lead ion yields salts with most of the common anions. The nitrate and acetate are the common soluble lead salts, and the chloride is only moderately soluble in cold water. Some of the specific salts are discussed in later chapters dealing with salts.

The test for lead ions is usually based on the precipitation of yellow lead chromate. Separation from interfering ions must precede the final test. If the concentration of lead ions is high, they yield a precipitate of lead chloride along with silver chloride and mercurous chloride. Lead chloride may be extracted from this precipitate with hot water. Lead sulfide precipitates with the other sulfides of the copper group of cations. The sulfide dissolves in nitric acid solution, and forms a white precipitate of lead sulfate with sulfuric acid, thus permitting a separation from bismuth, cupric, and cadmium ions. This precipitate is dissolved in hot ammonium acetate solution; and the final confirmatory test for the presence of lead is made by the addition of a solution of potassium chromate.

$$Pb^{++} + CrO_4^{--} \rightleftharpoons PbCrO_4\downarrow.$$

TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

Since the atoms of these elements may lose four electrons, their ions have the configuration of the inert gases and an oxidation number of 4 +. Titanium also forms compounds in which its oxidation states are 2 + and 3 +. The oxides and hydrated oxides of the elements, except thorium, are amphoteric. The basic character becomes more pronounced with increasing atomic number. Some of the properties of the elements are listed in Table 33.

TABLE 33

PROPERTIES OF TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

	Titanium	*Zirconium*	*Hafnium*	*Thorium*
Atomic weight	47.9	91.22	178.6	232.12
Atomic number	22	40	72	90
Isotopes	46, 47, 48, 49, 50	90, 91, 92, 94, 96	176, 177, 178, 179, 180	232
Electron structure	2, 8, 10, 2	2, 8, 18, 10, 2	2, 8, 18, 32, 10, 2	2, 8, 18, 32, 18, 10, 2
Oxidation states	2+, 3+, 4+	4+	4+	4+
Melting point	1800°	1700°	1700°	1845°
Density (20°) g. per ml.	4.5	6.4	12.1	11.2

Occurrence. The elements occur in the combined state in many rocks. It is estimated that 0.58% of the outer part of the earth is titanium and this is seventh among the metals in the order of abundance. The per cents of the other elements of the group are smaller. The most important *titanium ores* are *ilmenite*, $FeTiO_3$; *rutile*, TiO_2; *and arizonite*, $Fe_2O_3(TiO_2)_3$. Ilmenite is produced in the United States in Virginia, Arkansas, and California; but the main supply is from British India. Rutile is mined in this country and is imported from Australia and Brazil. *Zirconium* occurs in *baddeleyite*, ZrO_2, and *zircon*, $ZrSiO_4$. *Hafnium* is present in the zirconium minerals to the extent of 1–2%. *Thorium* occurs in *thorite*, $ThSiO_4$, and as *thorianite*, ThO_2. It is also obtained from monazite sand.

Production of the Metals. The preparation of the pure metals is difficult since they combine with carbon and form alloys

with metals used for the reduction. The reduction of the oxides with aluminum produces an aluminum alloy. Zirconium may be distilled from the aluminum alloy. The pure metals have few uses. Ferro-titanium is used in the steel industry. Zirconium is used in copper alloys and, in the form of wire, in radio tubes. Ferro-zirconium and zirconium-silicon alloys are used in the steel industry because they remove oxygen, nitrogen, and sulfur.

Compounds. Titanium forms unstable compounds in the 2 + oxidation state, and more stable products in the 3 + state. Its most stable compounds are in the 4 + state, like the other members of the group.

The Oxides and Hydroxides. *Titanous oxide*, TiO, and *titanous hydroxide*, $Ti(OH)_2$, are basic substances which are active reducing agents. *The dioxide* reacts with both acids and bases to form titanium salts and titanates, respectively. The dioxide which is produced from ilmenite is an important white pigment in paint. The hydrous oxide is produced by the reaction of an alkali with the chloride. This substance is important as a mordant. *Zirconium dioxide* reacts with fused metal hydroxides and carbonates to form zirconates. The oxide is now used commercially as a constituent of enamels. Zirconium yields the hydrous oxide when a moderate excess of sodium hydroxide is added to a zirconium salt. *The oxide of hafnium* closely resembles that of zirconium, except that it is slightly more basic. *Thorium dioxide* has no acidic properties, but dissolves slowly in acids. The hydrated oxide, or hydroxide, $ThO_2(H_2O)_2$, may be obtained by precipitation. Mixtures of thorium oxide containing about 1% of cerium oxide give out a brilliant white light when they are heated to incandescence. Gas mantles, such as the Welsbach mantle, for use with gas flames contain a mixture such as this.

The Salts. The halides of these elements may be formed by direct union, and by the reaction of the oxides and hydrous oxides with the hydrohalic acid. These salts hydrolyze to give acidic solutions. Titanium tetrachloride yields the oxide and the other halides yield the oxysalt when they are evaporated unless an excess of the acid is present. The nitrates and sulfates may be prepared in solution by the reaction of the acid with the appropriate hydroxide or oxide. The phosphates and sulfides may be precipitated.

EXERCISES

1. Discuss the allotropic forms of carbon and their industrial importance.
2. Illustrate the chemical reactions of carbon by means of equations.
3. Describe the preparation of carbon dioxide both in the laboratory process and in the industrial processes.
4. What equilibria exist in a solution of carbon dioxide? Discuss the effect on these equilibria of: (*a*) heating the solution; (*b*) cooling the solution; (*c*) increasing the pressure of carbon dioxide gas; (*d*) the addition of a base; (*e*) the addition of an acid.
5. How is carbon monoxide produced industrially? Discuss its importance.
6. How are the binary compounds of carbon with calcium, silicon, sulfur, and chlorine prepared? Of what importance are these compounds?
7. Compare the properties and reactions of silicon with those of carbon.
8. Compare the properties of germanium, tin, and lead with those of carbon and silicon. How may you account for the differences in behavior?
9. Discuss the production and uses of tin.
10. Write equations to represent the reactions of tin and lead.
11. Compare the elements of Group IV–B with those of Group IV in structure of the atoms and in properties.

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CHAPTER XXII

GROUP III. BORON AND ALUMINUM

Boron and *aluminum* are the first two elements in Group III. There are a number of other elements in the group. *Gallium*, *indium*, and *thallium* differ structurally from boron and aluminum in that their atoms have a shell of eighteen electrons beneath the valence shell of three electrons. Since they have stable electron shells inside of the valence shell, they are classified as members of Group III. *Scandium*, *yttrium*, *lanthanum*, and *actinium* are first members of transition series of elements. The atoms of each of these elements contain an additional electron above the number in the next lower inert gas, in the shell just beneath the valence shell. In scandium, for example, the electron distribution is 2, 8, 9, 2. Progressive increases in the number of electrons in this shell, with increasing atomic number, lead to a final complete shell of eighteen electrons in copper. Yttrium, lanthanum, and actinium occupy similar positions in the fourth, fifth, and sixth long periods, respectively. The other rare earth elements occupy the same position as lanthanum in the fifth period in Group III–B of the periodic system according to atomic numbers. As might be expected from the general relationships of the periodic system, the transition from non-metallic to metallic nature occurs high in the group, and boron is the only distinctly non-metallic element in the group.

Boron. This element occurs in boric acid and in the borates. In the western part of the United States, deposits of *cole*, *manite*, $Ca_2B_6O_{11}(H_2O)_5$, *borax*, $Na_2B_4O_7(H_2O)_{10}$ and *kernite*-$Na_2B_4O_7(H_2O)_4$, are found. These deposits have resulted from the long-continued evaporation of inland bodies of water. The element may be prepared in an amorphous form as a brown powder by the reduction of the oxide with magnesium.

$$B_2O_3 + 3\ Mg \longrightarrow 2\ B + 3\ MgO.$$

If the product is heated in an electric furnace, in an atmosphere of hydrogen, crystalline boron may be obtained.

The Properties and Reactions of Boron. Some of the properties of boron are shown along with the properties of aluminum in Table 34, page 436. The crystalline substance is brittle and is very hard. Boron burns to form the oxide when it is heated in air, and also unites directly with the halogens.

$$4\,B + 3\,O_2 \longrightarrow 2\,B_2O_3.$$
$$2\,B + 3\,Cl_2 \longrightarrow 2\,BCl_3.$$

Boron reacts with melted alkalies to form borates and with acidic oxidizing agents to form boric acid.

$$2\,B + 2\,KOH + 2\,H_2O \longrightarrow 2\,KBO_2 + 3\,H_2.$$
$$B + HNO_3 + H_2O \longrightarrow H_3BO_3 + NO.$$

The Oxide and Hydroxide of Boron. *Boric oxide, B_2O_3,* is formed by strongly heating boric acid. The product is a hard, brittle, glass-like solid at room temperature. It reacts with the metal oxides to form metaborates.

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2.$$

The oxide also combines with water to form boric acid.

Boric acid, H_3BO_3, is a weak acid which is only slightly soluble in cold water. The solubility increases with rise in temperature, 4.8 g. in 100 g. of water at 20° and 28.7 g. at 100°. Boric acid is usually prepared as a precipitate by the reaction of sulfuric acid with borax.

$$B_4O_7^{--} + 2\,H_3O^+ + 3\,H_2O \longrightarrow 4\,H_3BO_3.$$

Boric acid is a mild antiseptic which is used as an eye wash and for wet dressings for infected sores.

The acid decomposes when it is heated, forming metaboric acid, tetraboric acid, and finally boric oxide.

$$H_3BO_3 \longrightarrow HBO_2 + H_2O.$$
$$4\,HBO_2 \longrightarrow H_2B_4O_7 + H_2O.$$
$$H_2B_4O_7 \longrightarrow 2\,B_2O_3 + H_2O.$$

The reaction of sodium hydroxide with boric acid yields the tetraborate. This salt crystallizes from solution as the decahydrate, $Na_2B_4O_7(H_2O)_{10}$, at temperatures below 60°.

$$4\,H_3BO_3 + 2\,OH^- \rightleftharpoons B_4O_7^{--} + 7\,H_2O.$$

The salts of boric acid will be discussed in a later chapter. Boric acid reacts with methanol in the presence of sulfuric acid to form methyl borate, $(CH_3)_3BO_3$. This compound is volatile and burns with a green flame. A test for borates may be based on this property.

Binary Compounds of Boron. *The borides* of magnesium, aluminum, and several other metals may be formed by the direct union of the elements.

$$2\ B + 3\ Mg \longrightarrow Mg_3B_2.$$

A compound called boron carbide, B_4C, is formed when boric oxide is reduced by coke in an electric furnace. This compound is a very hard substance which is used in dies for drawing wire and in jeweled bearings, where great resistance to abrasion is required.

The halides of boron may be prepared by the direct union of the elements, or by heating boric oxide with carbon in an atmosphere of the halogen.

$$B_2O_3 + 3\ C + 3\ Cl_2 \longrightarrow 2\ BCl_3 + 3\ CO.$$

The fluoride and chloride are gaseous at room temperature, and the bromide and iodide are volatile liquids. Boron fluoride hydrolyzes to produce boric and fluoboric acids.

$$4\ BF_3 + 3\ H_2O \longrightarrow H_3BO_3 + 3\ HBF_4.$$

The other halides of boron are completely hydrolyzed to form the hydrohalic acid and boric acid.

$$BCl_3 + 6\ H_2O \longrightarrow H_3BO_3 + 3\ H_3O^+ + 3\ Cl^-.$$

Boron yields several hydrogen compounds which, by analogy to the hydrocarbons, are called *hydroborons*, such as B_2H_6, B_4H_{10}, B_6H_{12}. The reactions and compounds of boron indicate a behavior similar to that of silicon in Group IV.

Aluminum. This element is the only industrially important metal in Group III. Aluminum is the most abundant metal found in the outer crust of the earth. Complex silicates containing aluminum are the most abundant of the minerals: *e.g.*, *orthoclase*, $KAlSi_3O_8$; *muscovite*, $KAl_3H_2(SiO_4)_3$; and *kaolin*, $Al_2H_4Si_2O_9$. *Bauxite*, containing the hydrated oxide of aluminum, $Al_2O_3(H_2O)$ and $Al_2O_3(H_2O)_3$, is the commercial source of aluminum; and *cryolite*, Na_3AlF_6, is used in the production of the metal from bauxite. In the United States, 96% of the bauxite produced in

1939 was from Arkansas, the remainder coming from Alabama and Georgia. The countries producing the largest amounts of bauxite are France, Hungary, Surinam, British Guiana, Yugoslavia, Italy, and the United States.

Aluminum was first prepared by Oersted in 1825, by the reduction of the chloride with potassium amalgam, and by Wöhler in 1827 by reduction with potassium. A method for the commercial preparation of the metal by the reduction of the chloride with sodium was developed by the French chemist Deville, about 1850. The price, however, remained too high to permit the development of extensive uses of the metal. The problem of producing aluminum at low cost was solved independently by Hall in the United States and by Heroult in France in 1886. Both investigators hit upon the same method, the electrolysis of aluminum oxide dissolved in cryolite. An account of the production of this important metal from its ore will be found in Chapter XXIV together with other metallurgical procedures. The world production of aluminum in 1939 was estimated to be about 647,000 tons. The production in the United States was approximately one fourth of the total, and a larger quantity of the metal was produced in Germany than in any of the other countries.

Properties of Aluminum. Some of the physical properties of boron and aluminum are listed in Table 34.

TABLE 34

PROPERTIES OF BORON AND ALUMINUM

	Boron	*Aluminum*
Atomic weight	10.82	26.97
Atomic number	5	13
Isotopes	11, 10	27
Electron structure	2, 3	2, 8, 3
Oxidation state	3+	3+
Typical ions	BO_3^{---}, $B_4O_7^{--}$	Al^{+++} $Al(OH)_4^-$
Melting point	2300°	658°
Boiling point	2550°	1800°
Density (20°) g. per ml.	2.4	2.7

In addition to its low density and melting point, aluminum is malleable and ductile and may be given a relatively high tensile strength by cold working, such as rolling. Aluminum is a good

conductor of heat and electricity. With wires of equal size, copper is the better conductor of electricity; but with wires of equal weight for unit length, aluminum is about twice as good a conductor as copper.

Chemical Reactions of Aluminum. Atoms of aluminum contain three valence electrons and readily form trivalent positive ions. Aluminum is an active metal but its surface becomes coated with a thin, transparent film of the inactive oxide which protects it. Therefore, aluminum does not appear to rust in air or to react with water. The oxide coating does not adhere to an amalgamated surface; and the amalgamated metal rusts rapidly and displaces hydrogen from water.

$$4\,Al + 3\,O_2 \longrightarrow 2\,Al_2O_3.$$
$$2\,Al + 6\,HOH \longrightarrow 3\,H_2\uparrow + 2\,Al(OH)_3.$$

The oxide film is dissolved by basic solutions and aluminum reacts with water containing dissolved sodium hydroxide.

$$2\,Al + 6\,H_2O + 2\,OH^- \longrightarrow 2\,Al(OH)_4^- + 3\,H_2.$$

Aluminum combines directly with the halogens, with sulfur, and with carbon. It reacts readily with dilute sulfuric acid and with hydrochloric acid, but the metal becomes "passive" in contact with nitric acid. The passivity of a metal is usually attributed to the formation of a surface film of the oxide. At high temperatures, aluminum reacts with the oxides of a number of the metals to liberate the metal and form aluminum oxide.

Uses of Aluminum. As would be expected from a consideration of its properties, aluminum serves many purposes. Large amounts of the metal are used in the manufacture of cooking utensils and household appliances. It is extensively used in the form of foil instead of tin foil. Powdery flakes of aluminum mixed with a varnish make a silvery paint for protecting wood and metals. Aluminum cables find extensive application for the long-distance transmission of electricity. Due to its lightness and strength and the fact that it is resistant to corrosion, aluminum is an important metal in the manufacture of all types of transportation vehicles.

Aluminum forms many alloys which possess the desirable properties of lightness and strength. The principal alloying elements used with aluminum are copper, silicon, manganese, magnesium, and zinc. *Duralumin*, the strongest of the aluminum alloys, con-

tains about 94% of aluminum, 4% of copper, 0.5% of manganese, 0.5% of magnesium, with smaller per cents of silicon and iron. This alloy is extensively used in the construction of airplanes, motor trucks, and busses, and in other fields of transportation. To protect it from corrosion, duralumin may be coated with a thin layer of pure aluminum, forming a product marketed as "Alclad sheet."

There are also uses of aluminum which are dependent on its activity. It is used in the steel industry to combine with, and thus remove, oxygen which would cause flaws in the steel. Mixtures of aluminum and ammonium nitrate have been used in bombs for aerial bombing raids. The production of some of the metals from their oxide ores employs the reducing action of aluminum, a process called *aluminothermy*. An important example of this is in thermit welding. "Thermit," a mixture of aluminum and an oxide of iron, is placed in a clay crucible and ignited by means of an ignition powder consisting of barium peroxide and magnesium powder. A violent reaction follows and the iron oxide is reduced, liberating the metal, which sinks to the bottom of the crucible.

$$3\ Fe_3O_4 + 8\ Al \longrightarrow 4\ Al_2O_3 + 9\ Fe.$$

The melted iron is allowed to flow from the crucible into a sand mold about the cleaned and preheated ends of the metal to be welded. Repairs to heavy machinery may be made in this way without the necessity of dismantling the machine. The thermit mixture is also used as a military weapon.

The Oxide and Hydroxide of Aluminum. Aluminum oxide occurs naturally in several forms. *Corundum* and *emery*, which contains also some magnetite, are hard substances used as abrasives. *Alundum*, an artificial corundum, is prepared by melting the oxide in an electric furnace. It is also used as an abrasive and as a refractory material. The *ruby* is a crystalline form of the oxide colored by a trace of chromium; and the *sapphire* is colored by the presence of iron and titanium. Synthetic gems, which are chemically identical with those found in nature, are produced by fusing the oxide and allowing it to crystallize under the proper conditions. The use of bauxite as the ore of aluminum metal has been discussed. Bauxite has other extensive uses. Approximately 24% of the total bauxite consumption in the United States

in 1939 was in the manufacture of abrasives, 23% in the production of aluminum compounds, 2.5% in oil refining, and 1% in the refractory industry, the remainder going into the production of the metal.

A gelatinous precipitate, commonly called *aluminum hydroxide*, is formed in the presence of a limited excess of hydroxide ions. The ratio of water to the oxide is indefinite and the compound is an hydrous oxide. The substance is usually represented by the formula $Al(OH)_3$, although the formula, $Al(OH)_3(H_2O)_3$, more nearly describes its composition. Solutions of salts of weak acids, such as the carbonates and sulfides, contain a high enough concentration of hydroxide ions to cause the precipitation of aluminum hydroxide.

$$Al^{+++} + 3\ OH^- \longrightarrow Al(OH)_3\downarrow .$$

This hydroxide is amphoteric, yielding low concentrations of both hydroxide and hydronium ions.

$$Al(OH)_3\downarrow \rightleftharpoons Al^{+++} + 3\ OH^-.$$
$$Al(OH)_3\downarrow + 2\ H_2O \rightleftharpoons H_3O^+ + Al(OH)_4^-.$$

Therefore, aluminates are formed in the presence of an excess of a strong base. When the hydrous oxide is heated to drive out water, a porous form of alumina is obtained. This material absorbs water so readily that it is a good dehydrating agent.

Salts of Aluminum. The element yields two series of salts: the aluminum salts containing the simple Al^{+++} ion, and the aluminates containing the $Al(OH)_4^-$ ion. Both of these ions are hydrated and may be represented more accurately by the formulas $Al(H_2O)_6^{+++}$ and $Al(OH)_4(H_2O)_2^-$, $Al(OH)_5H_2O^{--}$, and $Al(OH)_6^{---}$, respectively. The most important of these salts are the chloride and sulfate which are discussed in Chapters XXVIII and XXIX, respectively.

Analytical Properties of the Aluminum Ion. The aluminum ion is analytically a member of the iron group, which contains also chromic and ferric ions. The hydroxides are precipitated in ammoniacal solution containing a soluble ammonium salt, such as ammonium chloride. The hydroxides of aluminum and chromium may be separated from ferric hydroxide by reaction with sodium hydroxide in the presence of an oxidizing agent such as sodium peroxide, forming sodium aluminate and sodium chro-

mate. The soluble aluminate and chromate may be separated from the ferric hydroxide by filtration. Aluminum hydroxide may be precipitated from this solution as a white gelatinous precipitate by boiling it with ammonium chloride until the concentration of the hydroxide ion is small.

$$Al(OH)_4^- + NH_4^+ \rightleftharpoons Al(OH)_3\downarrow + NH_3 + H_2O.$$

Gallium, Indium, and Thallium. These metals occur widely distributed in very small percentages, associated with the compounds of other metals, particularly in certain zinc sulfide ores. Some iron pyrites contains thallium; and the metal could be produced in fairly large quantities from the flue dust in sulfuric acid works using this material, if there were a demand for it.

The metals may be prepared by reduction with zinc and by electrolysis. Gallium has a melting point of 30°, and the liquid is easily supercooled so that it may remain a liquid at room temperature. The melting points of indium and thallium are 155° and 303°, respectively. The metals oxidize slowly at room temperature, and burn when they are heated in air. They combine readily with the halogens and displace hydrogen from acids.

The compounds of the metals in the trivalent state are similar to those of aluminum. The hydroxides are precipitated by the reaction of soluble bases with solutions furnishing the metal ions. The trihydroxides of gallium and indium are amphoteric; but thallium hydroxide is only weakly basic. They yield halides, sulfates, and other salts similar to those of aluminum. Thallium also forms a series of compounds containing the thallous ion, Tl^+. The hydroxide, TlOH, is a soluble, strong base. These compounds are not at present very important.

Scandium, Yttrium, and the Rare Earths. There are fifteen elements of atomic numbers 57–71, which closely resemble scandium and yttrium. Although the valence shells of these atoms contain two electrons, the common oxidation number is 3 +. One of the nine electrons in the next shell may also be lost by the atom during chemical reactions. Cerium yields compounds in the 4 + state also. The fourteen elements which follow lanthanum differ from lanthanum and from each other only in the number of electrons in the fourth shell. All of these atoms contain two electrons in the outermost shell, the sixth shell, and nine

in the fifth shell; but the number in the fourth shell increases progressively with increased atomic number, from eighteen in the atom of lanthanum to thirty-two in the atom of lutecium. The similarities of the elements and their compounds are so great that their separation is difficult. There are small differences in the solubilities of some of their compounds so that separation may be effected by repeated fractional crystallization.

The elements of atomic numbers 57–62 are the *cerium group: viz.*, lanthanum, cerium, praseodymium, neodymium, illinium, and samarium. These elements occur as phosphates in the mineral *monazite* and in complex silicates in *cerite.* Yttrium and the elements of atomic numbers 63–71 are the *yttrium group: viz.*, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium. They occur in *gadolinite*, a complex silicate, and in other rare minerals. The metals may be prepared, like aluminum, by the electrolysis of the oxide dissolved in the fluoride. The metals are active, combining readily with oxygen and with the halogens, and displacing hydrogen from water. An alloy known as "misch metal" is obtained from the rare earth residues in monazite sand. It contains about 70% of cerium and some iron. The alloy is known as a pyrophoric alloy, since it gives sparks when it is scratched. It is used in gas lighters and in cigarette lighters. The Welsbach mantle, formerly extensively used in illumination by gas, is composed of 99% of thorium dioxide and 1% of cerium dioxide. It catalyzes the combustion reaction so that the temperature becomes high enough to heat the mantle to incandescence, producing a brilliant white light. The use of gas as an illuminant has been largely replaced by electricity, so that the production of these mantles is no longer an important industry.

EXERCISES

1. Discuss the structural relationships shown by the atoms of the elements of Group III.
2. Represent by equations the preparation of boric acid from borax and the reaction of the acid with sodium hydroxide.
3. Discuss the uses of aluminum and the properties upon which each use depends.
4. How do you account for the fact that aluminum, an active metal, does not rust in air and may be used to protect other metals which do corrode, such as iron?

5. How do hydrous oxides differ from the hydroxides?
6. Explain the dissolving of aluminum hydroxide by a solution of sodium hydroxide.
7. Explain the precipitation of aluminum hydroxide by boiling a basic solution containing the aluminate ion with ammonium chloride.
8. How do the elements of Group III–B differ from those of Group III? What are the rare earth metals?

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CHAPTER XXIII

GROUP II. THE ALKALINE EARTH METALS

The elements of Group II of the classification of the elements according to their atomic numbers are *beryllium*, *magnesium*, *calcium*, *strontium*, *barium*, and *radium*. The atoms of each of these elements contain two electrons more than the atoms of the next lower inert gas, and they exhibit the oxidation number 2 +. All of the elements in the group are metallic in nature, although the hydroxide of beryllium has amphoteric properties. Calcium, strontium, and barium have long been known as the alkaline earth metals, and the name is now commonly applied to the entire group.

Occurrence of the Metals. The alkaline earth metals do not occur naturally in the uncombined state. The most important of the *beryllium* compounds found in nature is the mineral, *beryl*, $Be_3Al_2(SiO_3)_6$. When colored green due to the presence of chromium compounds, it is the gem, *emerald*. *Magnesium* occurs as the chloride and sulfate in salt beds and in some salt wells. It occurs also in *magnesite*, $MgCO_3$, *dolomite*, $MgCO_3CaCO_3$, and in complex silicates such as *talc*, $H_2Mg_3(SiO_3)_4$, and *asbestos*, $CaMg_3(SiO_3)_4$. Important natural compounds of *calcium*, in addition to *dolomite*, are *limestone*, $CaCO_3$, *gypsum*, $CaSO_4(H_2O)_2$, *phosphorite*, $Ca_3(PO_4)_2$, and *fluorspar*, CaF_2; of *strontium*, *celestite*, $SrSO_4$, and *strontianite*, $SrCO_3$; of *barium*, *barite*, $BaSO_4$, and *witherite*, $BaCO_3$. *Radium* is obtained from uranium ores in which it is present in very small proportions.

Production of the Metals. These metals, like the alkali metals, may be prepared by the electrolysis of fused salts, usually the chlorides. Beryllium and magnesium may also be prepared by the reduction of the oxides with carbon; but calcium and the metals of higher activity cannot be prepared satisfactorily by carbon reduction. Metals of high activity combine with the excess of carbon to produce the metal carbide. The active metals

are not produced by the electrolysis of aqueous solutions of their salts, because hydrogen instead of the metal is liberated at the cathode of the cell under these conditions. The electrolysis of the fused chloride, however, produces the metal at the cathode and chlorine at the anode. The procedure is the same in principle for all of these metals but there are differences in details because of differences in the properties of the metals and of the chlorides. Magnesium is the most important of the alkaline earth metals. The world production in 1938 was estimated to be 22,000 metric tons, though exact figures were not made public. The production in Germany was approximately 12,000 tons; in Great Britain, 2200 tons; in the United States, 2100 tons; and in Japan, 2000 tons. Smaller quantities of beryllium and calcium are prepared, but strontium and barium have no important industrial uses. The preparation of beryllium and magnesium is discussed in Chapter XXIV.

The Properties of the Metals. These elements are characterized by the properties usually ascribed to metals. The freshly cleaned surfaces of the metals are lustrous, but soon tarnish. The metals may be hammered and rolled. Beryllium is a hard metal but barium is rather soft. Beryllium has low ductility. The metals are good conductors of electricity. Several of the physical properties of the elements are shown in Table 35.

TABLE 35

PROPERTIES OF THE ALKALINE EARTH METALS

	Be	Mg	Ca	Sr	Ba
Atomic weight	9.02	24.32	40.08	87.63	137.36
Atomic number	4	12	20	38	56
Isotopes	9	24, 25, 26	40, 44, 42, 43, 46, 48	84, 87, 90	138, 136, 134, 137, 135, 132
Electron structure	2, 2	2, 8, 2	2, 8, 8, 2	2, 8, 18, 8, 2	2, 8, 18, 18, 8, 2
Melting point	1300°	650°	851°	757°	850°
Boiling point	1500°	1107°	1487°	1384°	1640°
Density (20°) g. per ml.	1.73	1.75	1.55	2.6	3.75

Reactions of the Metals. All of the metals of this group burn in air with the formation of oxides. Barium yields the peroxide.

They also combine to some extent with nitrogen when they burn in air, with the formation of nitrides, particularly in the combustion of magnesium and calcium. These metals lose electrons actively and stand high in the electromotive series of the metals. The rate at which they react with water is much slower than the position in the electromotive series would lead one to expect. This may be due to the formation of a film of the oxide or hydroxide which either persists or dissolves only slowly. Beryllium and magnesium do not react noticeably with water unless the protective coating is removed. Magnesium displaces hydrogen rapidly from hot water containing ammonium chloride, because magnesium hydroxide dissolves under these conditions and a clean surface of the metal is continually exposed. Similarly, beryllium reacts with water containing dissolved sodium hydroxide, because the oxide of beryllium is amphoteric and is dissolved by the basic solution. The metals also displace hydrogen from acids and exhibit the usual reactions of metals with non-metals, forming stable salts by direct union with the halogens and sulfur. In all of these reactions the metals form simple divalent positive ions. They also react with less active non-metals, such as phosphorus and carbon, to form binary compounds which are not ionic in structure. The atoms of beryllium are the smallest and of radium the largest in the group. Consequently, the valence electrons of beryllium are held most firmly and of radium least firmly, and the others are intermediate. Therefore, beryllium is the least active member of the group; and there is a regular increase in activity from metal to metal in the order of increased atomic number, and radium is chemically the most active member of the group.

Uses of the Metals. Magnesium is the only one of these metals which has extensive commercial uses. The principal use of the metal is now in structural products. It yields a number of important alloys, such as those with aluminum, zinc, and manganese. A new die-casting alloy, called "Dowmetal R," having increased toughness, is of the following composition: 85–95% of aluminum; 0.13% of manganese; 0.4–0.8% of zinc; and the remainder magnesium. These alloys are light and have high tensile strength. An alloy has been produced experimentally which has a strength exceeding 60,000 pounds per square inch. These

alloys may be cast, rolled, drawn, and forged. They are employed principally in aircraft construction; and the demand for magnesium for this purpose has increased greatly during 1940. An important development during 1938 was the process for the treatment of magnesium alloys with sodium hydroxide under pressure to form a dense, adherent film which resists corrosion and protects the metal. Protective coatings are also produced by electrolytic treatment in a solution of chromic acid and various salts.

Magnesium ribbon is used for the removal of residual gases from radio tubes. The hot metal combines with both oxygen and nitrogen. The metal is used as a deoxidizing and desulfurizing agent in the refining of other metals. Large amounts of magnesium powder are used in signal flares and in flash-light powders.

The chief use of *beryllium* is in the production of its alloys with copper. These alloys are hard and strong and may be tempered. They are particularly important in springs, because they possess high elasticity and great endurance. The properties of the copper-beryllium system are affected to a great extent by the presence of other metals. Beryllium-nickel-copper alloys, containing 2.25% of beryllium, have tensile strengths above 200,000 pounds per square inch. The present high price of the metal prevents more extensive applications. Beryllium alloys have come into use in the manufacture of parts of airplane engines.

Calcium has limited industrial uses. Its cost is too great to permit its general use in steel making, but it is used as a deoxidizing agent for stainless steel and other special alloy steels. The metal is also used as a reducing agent for the production of rare metals, such as titanium, vanadium, and uranium.

Compounds of the Metals. *The oxides and hydroxides* of these metals are basic, and beryllium hydroxide also exhibits acidic properties. Consequently, beryllium yields two varieties of ions in solution, Be^{++} and $Be(OH)_4^{--}$. The hydroxides of beryllium and magnesium have low solubility, while the hydroxides of calcium, strontium, and barium are at least moderately soluble, and exist in the ionic state in solution. The ions of beryllium and magnesium hydrolyze to give acidic solutions.

$$Mg(H_2O)_6^{++} + H_2O \rightleftharpoons Mg(OH)(H_2O)_5^{+} + H_3O^{+}.$$
$$Be(H_2O)_4^{++} + H_2O \rightleftharpoons Be(OH)(H_2O)_3^{+} + H_3O^{+}.$$

These reactions are shown more simply,

$$Mg^{++} + 2\,H_2O \rightleftharpoons MgOH^+ + H_3O^+.$$
$$Be^{++} + 2\,H_2O \rightleftharpoons BeOH^+ + H_3O^+.$$

The ions of the other metals in this family are stable in solution. These ions form stable salts with most of the negative ions, those which are insoluble being precipitated from solution, and those which are soluble being crystallized from concentrated solutions. Following the general scheme of classification already indicated, these salts are discussed subsequently in Chapters XXVII–XXX.

Analytical Properties of the Ions. The ions of the alkaline earth metals do not form complex ions with the exception of a few complex ions containing beryllium. The ions are colorless and yield white precipitates unless the negative ion is colored. Most of the compounds containing these ions are soluble; and, with the exception of beryllium, they are present in the filtrate from the nickel group in the general scheme of analysis. Beryllium hydroxide is slightly soluble and is amphoteric. Therefore, this ion accompanies aluminum in the analytical procedure. Beryllium hydroxide, however, is dissolved by bicarbonate solutions while aluminum hydroxide is not. Barium, strontium, and calcium ions yield a white carbonate precipitate with ammonium carbonate in the presence of ammonium hydroxide and ammonium chloride. Magnesium carbonate is soluble in solutions containing the ammonium ion.

$$MgCO_3\downarrow + NH_4^+ \longrightarrow Mg^{++} + NH_3 + HCO_3^-.$$

Under the conditions used for the precipitation of the carbonates of the calcium group ions,

$$CO_3^{--} + NH_4^+ \rightleftharpoons NH_3 + HCO_3^-,$$

thus reducing the concentration of the carbonate ion so greatly that

$$[Mg^{++}] \times [CO_3^{--}] < S_{MgCO_3}.$$

The concentration of the hydroxide ion is so low that

$$[Mg^{++}] \times [OH^-]^2 < S_{Mg(OH)_2}.$$

Nevertheless, the concentration of the carbonate ion is great enough to cause the precipitation of the carbonates of barium, calcium, and strontium.

$$[Ba^{++}] \times [CO_3^{--}] > S_{BaCO_3}.$$

Magnesium ions, consequently, remain in the filtrate from which the carbonates of barium, calcium, and strontium have been filtered.

The separation of barium, strontium, and calcium ions from each other is based on differences in the solubilities of the chromates and sulfates. Barium chromate may be precipitated from weakly acidic solutions without precipitating the chromates of strontium and calcium. Strontium sulfate may be separated from calcium ions in solution by the addition of a low concentration of ammonium sulfate.

$$Sr^{++} + SO_4^{--} \rightleftharpoons SrSO_4\downarrow.$$

The presence of calcium ions may then be shown by the addition of oxalate ions, with the precipitation of calcium oxalate.

$$Ca^{++} + C_2O_4^{--} \rightleftharpoons CaC_2O_4\downarrow.$$

The test for the presence of magnesium ions in the filtrate from the calcium group precipitation is made by the addition of a soluble phosphate to the ammoniacal solution, producing a white precipitate of magnesium ammonium phosphate.

$$Mg^{++} + NH_4^+ + HPO_4^{--} + OH^- \rightleftharpoons MgNH_4PO_4\downarrow + H_2O.$$

Flame Colors. Volatile compounds of some of the metal ions impart characteristic colors when they are strongly heated in the colorless flame of the Bunsen burner. Calcium compounds give a brick-red color; strontium compounds, a crimson color; and barium compounds a green color. It will be recalled that volatile sodium compounds give a yellow color; potassium compounds, a violet color; and lithium compounds, a crimson color. The compounds of beryllium and magnesium are not volatile enough to produce flame colors in this manner.

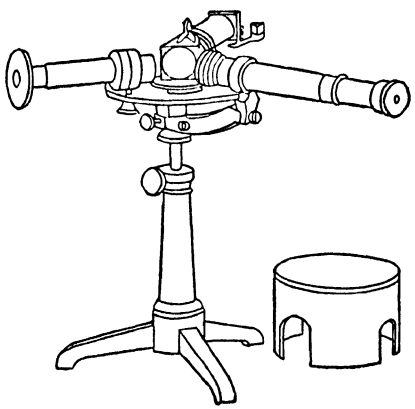

FIG. 128. — Spectroscope.

The characteristic flame colors are due to light waves of definite wave length which are emitted when the ions of the metals are present in the flame. By means of the spectroscope, Fig. 128, a

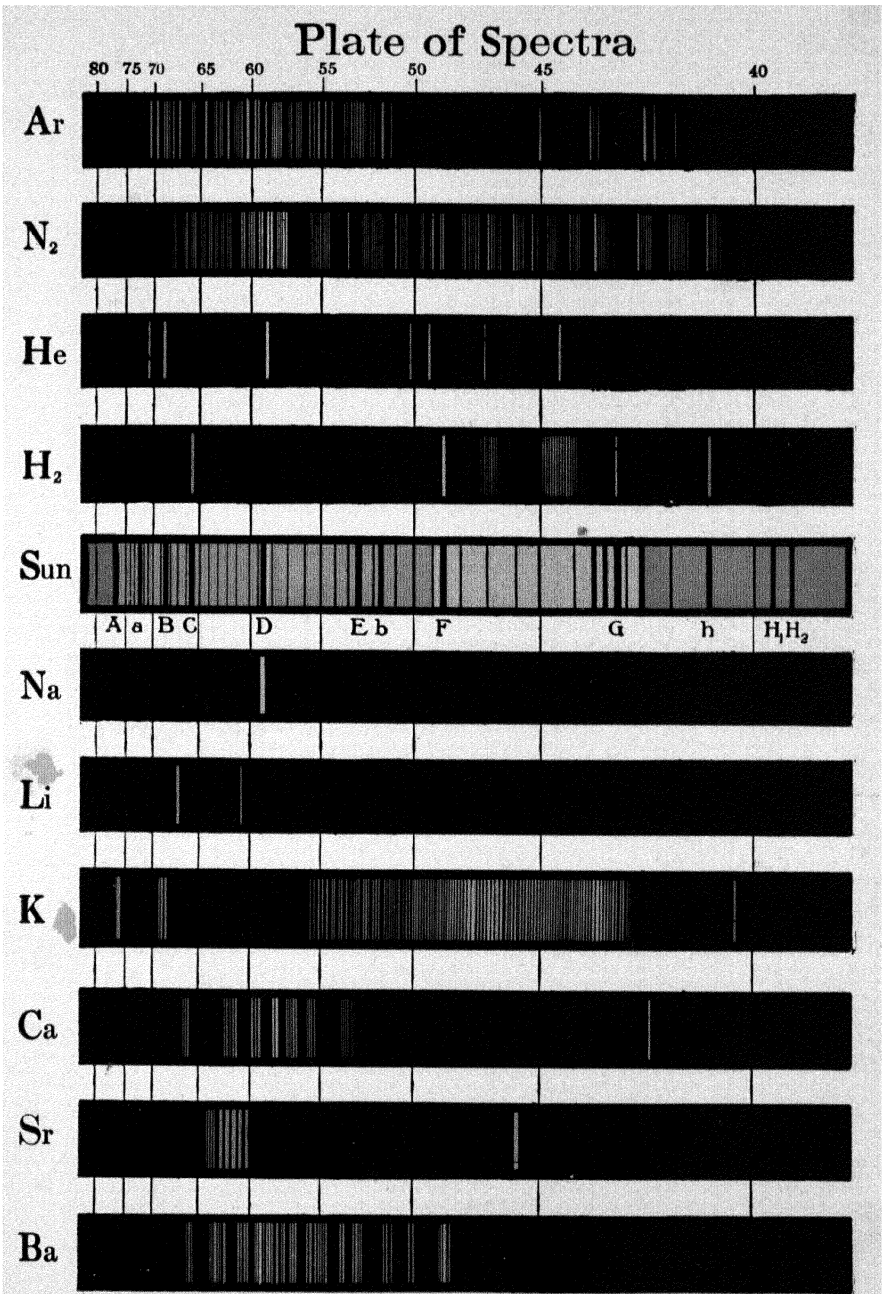

FIG. 129. (From *Inorganic Chemistry*, by H. P. Cady, by permission of McGraw-Hill Book Co., Publishers.)

narrow band of light from the source to be examined is allowed to pass through a prism by which it is diffracted. Light waves of the shorter wave lengths are bent at a sharper angle than those of the longer wave lengths. Consequently, if the light is composite, being made up of rays of several wave lengths, these are separated and appear as bright lines on a scale reflected from one of the faces of the prism. In this way the spectrum of the flame is obtained. The sodium flame is monochromatic, in that it gives a single bright line in the yellow part of the spectrum. There are characteristic spectra for each of the elements, specific lines being observed at definite positions on the scale when the flame of the volatilized compound is examined. Some of these spectra are shown by the plate of spectra, Fig. 129. The use of the spectroscope is an important means of detecting substances. The electric arc may be used to volatilize compounds which are not volatile at the temperature of the Bunsen burner.

EXERCISES

1. What general method is commonly employed for the production of metals of high activity? Why is this the method which is used?
2. Illustrate by equations the reactions of the alkaline earth metals which are characteristic of the group.
3. Account for the similarities in the properties of these metals and for the differences in their activities.
4. Discuss the importance of magnesium in the field of transportation.
5. Explain the separation of magnesium ions from the ions of barium, strontium, and calcium.
6. Why must the solution be weakly basic for the precipitation of magnesium ammonium phosphate in the test for magnesium ions?
7. Explain the separation of barium ions from those of strontium and calcium.

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CHAPTER XXIV

THE PRODUCTION OF METALS FROM ORES

The metallic elements occur in a number of different compounds and some of them occur in the uncombined state. The naturally occurring materials from which the metals are produced are known as *ores*. The ores containing uncombined metals are *native ores*. Only the metals of low activity occur in native ores. The most important classes of compound ores are the *oxide*, *sulfide*, and *carbonate ores*. Chlorides and sulfates are also used as ores of some of the metals. The most abundant of the naturally occurring minerals are silicates; but these substances are not usually important as ores because of difficulties involved in the decomposition of complex silicates to produce compounds from which metals may be liberated readily.

The Extraction of Metals from Their Ores. Different procedures are followed in the extraction of metals, depending on the nature of the ore. The name, *metallurgy*, may be employed to designate the processes used in the production and refining of metals, although this science deals also with the preparation of many products of a metallic nature and the principles which are involved in the treatment and study of such products.

In order to obtain metals from *native ores* it is necessary to separate them from the rock with which they are mixed in their natural deposits. This material is known as *gangue*. Separation from the gangue is accomplished through the use of a *flux*, a material which reacts with these foreign substances when they are strongly heated together in a furnace, forming a molten product which is not miscible with the melted metal. This product is known as a *slag*. The production of metals from *compound ores* requires the liberation of the metal from the compound in addition to the separation from the gangue. *Oxide ores* are usually reduced with carbon, although other good reducing agents, such as hydrogen and aluminum, are also used in special procedures. *Sulfide*

and carbonate ores are first heated strongly in air, a process called the roasting of the ore. The sulfides burn to form oxides and the carbonates are decomposed with the formation of oxides, which are then reduced as in oxide ores. In a number of instances the roasting of the sulfide is incomplete and the process is more complicated than this.

The metal product of these furnace operations is usually impure, so that it requires *refining* to form a suitable commercial material. The presence of impurities in the metal product is due to three main causes: *viz.*, incomplete separation of the slag; combination of carbon, the reducing agent, with the metals to form carbides which are soluble in the molten metal; and the presence in the ore of other reducible substances. The refining of the metal is frequently accomplished in an electrolytic process.

The Production of Metals of High Activity. There are a number of the metals which are not satisfactorily prepared by the reduction of their oxides with carbon, because they are active enough to combine with the excess of carbon used in the process. The most satisfactory method of producing these metals is by the electrolytic reduction of their ions at the cathode of a cell. The activity of these metals is so great, however, that they cannot be reduced in a practical manner by the electrolysis of aqueous solutions of their salts because hydrogen is deposited preferentially. For each metal there is a minimum electrical potential which is required to cause the discharge of its ions. The required potential varies somewhat depending on the concentration of the ions and the temperature. The standard for the measurement of these potentials will be discussed in Chapter XXXII. For the present it is sufficient to note that the ions of a particular metal are not discharged unless the difference in potential between the electrodes is great enough. The discharge of hydronium ions occurs at a potential which is so much lower than that required for the ions of the active metals, such as the alkali metals, the alkaline earth metals, and aluminum, that these ions cannot be discharged from aqueous solution. The production of these metals, consequently, is accomplished by the electrolysis of fused electrolytes containing the ions of the metals.

The first step in the production of these metals is the preparation of the fused electrolyte. The fused chlorides are most gen-

erally employed. No difficulty is encountered in the preparation of the fused chlorides of the most active metals of the group, such as sodium, potassium, barium, and calcium. The hydrated ions of these metals are easily decomposed. Sodium and potassium chlorides crystallize from solution without water of hydration. The hydrated chlorides of barium and calcium crystallize from solution; but they may be decomposed by moderate heating with the evaporation of the water, leaving the anhydrous chlorides. The hydrated chlorides of beryllium, magnesium, and aluminum separate from their concentrated solutions; and these salts hydrolyze when they are heated, leaving a residue of the oxide. Therefore, special procedures are required for the preparation of the anhydrous chloride to serve as the fused electrolyte. The electrolyte used for the preparation of aluminum is not a single substance, but is an electrolytic solution of aluminum oxide in the anhydrous fused salt, cryolite, Na_3AlF_6.

The Electroformation of Magnesium. In the United States, magnesium is produced by the electrolysis of magnesium chloride which is obtained from the brine of salt wells, such as those in Michigan and from sea water. The salt well brines contain sodium, calcium, magnesium, chloride, and bromide ions, with varying small per cents of other ions. The proportions of these ions are equivalent to approximately 14% of sodium chloride, 9% of calcium chloride, 3% of magnesium chloride, and 0.15% of bromine. The steps in the procedure for the preparation of anhydrous magnesium chloride from these brines are shown in the flow sheet, Fig. 130. Bromine, an important product of the process, is first displaced by the action of chlorine. The ions of iron and other metals which are less active than magnesium are precipitated in the form of their hydroxides by the addition of a suspension of magnesium hydroxide. The solution is then partially evaporated so as to crystallize a large proportion of the common salt, which is separated for use as a raw material for the preparation of many substances. By the further evaporation of this solution and the proper control of the ion concentrations, a double salt, $(MgCl_2)_2CaCl_2(H_2O)_{12}$, separates from a mother liquor in which the magnesium and calcium ions remain in the ratio 1 : 10. The double salt is dissolved in hot water and the hexahydrate, $MgCl_2(H_2O)_6$, is crystallized, leaving a solution which contains

the two ions in a 1 : 1 ratio. This solution contains approximately 50% of the magnesium ions in the original brine, so that it is returned to the process as indicated. The hexahydrate may be converted to the dihydrate by heating it in air, if the temperature is carefully controlled. Complete dehydration to produce anhydrous magnesium chloride is brought about by heating the dihydrate in a current of hydrogen chloride.

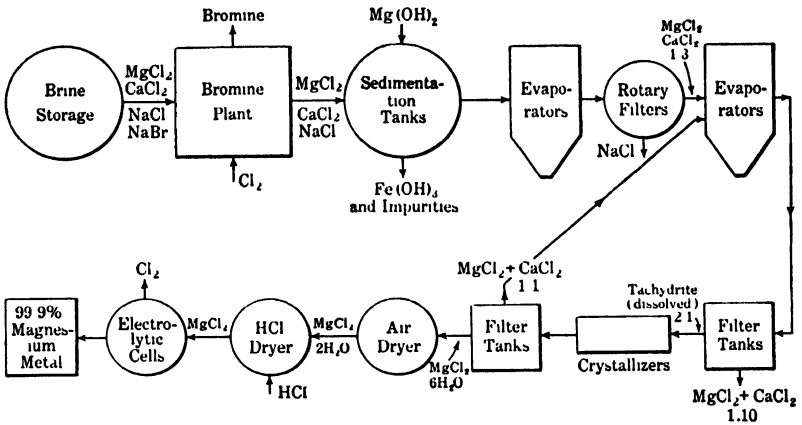


FIG. 130. — Flow Sheet of Magnesium Metal Production. (Courtesy of The Dow Chemical Company.)

The electrolysis of the fused chloride takes place in an iron cell which is heated to maintain the necessary temperature, Fig. 131. Graphite anodes project downward into the cell. Iron cathodes are placed on opposite sides of the row of anodes. Magnesium is liberated at the cathode and chlorine at the anode. The cathodes are so constructed that small drops of the metal are deflected, as they rise, and pass through openings in the cathode into the space back of it, where the liquid metal collects. Contact with chlorine is avoided in this manner. The metal in the reservoir is protected from atmospheric oxidation by a film of the electrolyte. The direct product of the cells has a purity of approximately 99.5%, and subsequent refining is not necessary.

A virtually unlimited source of magnesium compounds which is now being employed as a source of the metal is sea water, which contains only a small percentage of magnesium ions. The chloride may also be produced from the natural minerals, *magnesite*, $MgCO_3$, and *dolomite*, $MgCO_3CaCO_3$.

Magnesium may also be produced by the reduction of the oxide with a limited proportion of carbon in an electric furnace at a temperature of approximately 2000°. In this process, which was developed in Austria, the gaseous metal evaporates from the furnace and is condensed to give a product containing magnesium oxide and other impurities. This product is purified by distillation from a second furnace. New installations of this process were scheduled to start production in 1939.

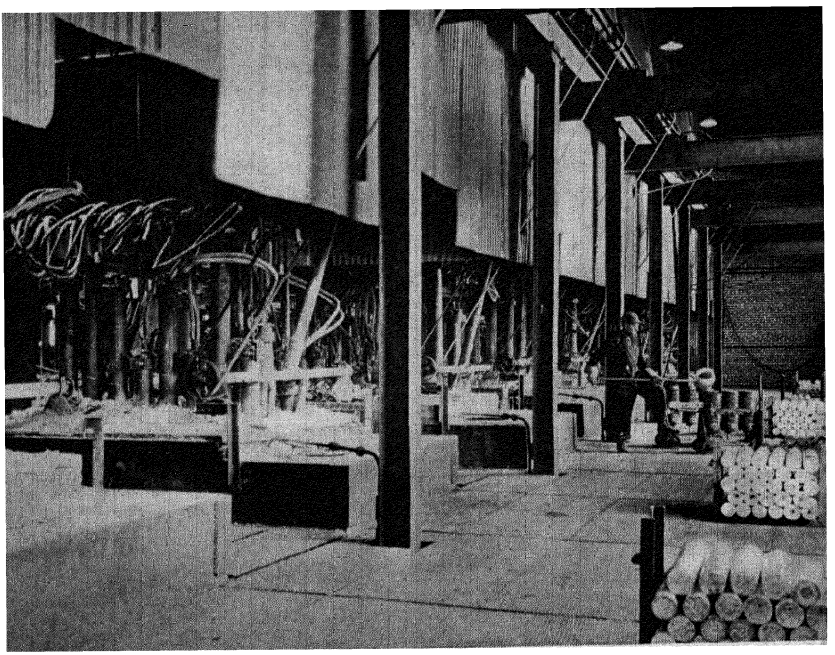


FIG. 131. — Cells for the Electrolytic Production of Magnesium. (Courtesy of The Dow Chemical Company.)

The Production of Beryllium. Beryl is not easily decomposed by acids. Nevertheless, the product formed when the mineral is melted and then suddenly cooled by pouring it into water does react with sulfuric acid. The sulfates of beryllium, aluminum, and such other metals as may be present in the ore are produced. Beryllium sulfate may be recovered from the solution and decomposed by heating it in a rotary kiln. The oxide is then heated with carbon in an atmosphere of chlorine to produce the anhydrous chloride. Metallic beryllium may be prepared from

the anhydrous chloride by reduction with sodium or magnesium and by electrolysis. Metallic beryllium is often prepared in the form of a master alloy with copper by the reduction of the mixed oxides with carbon or with hydrogen.

The Electroformation of Aluminum. Although aluminum was first prepared by the reduction of its fused chloride with potassium and later with sodium, it was not found possible to produce it at low enough cost for general industrial use by this method. Even with improvements in the production of sodium and of the fused chloride, the price was still $4 per pound in 1886. The discovery by Hall in America and by Heroult in France of the method of producing the metal by the electrolysis of the oxide dissolved in fused cryolite has made it possible to market the metal at prices ranging below twenty cents per pound.

Purification of the Bauxite. Since most of the impurities in bauxite are compounds of metals of lower activity than aluminum, these metals would be liberated along with aluminum if the impure bauxite were put directly through the electrolytic process, so that a highly impure metal product would be obtained. It is therefore necessary to purify the ore before adding it to the electrolytic cells. The crude ore is dried and ground to a powder. It is then digested with a sodium hydroxide solution heated under pressure to a temperature of 160–170°. Most of the aluminum oxide is dissolved under these conditions, but iron oxide is not dissolved.

$$Al_2O_3 + 3\ H_2O + 2\ OH^- \longrightarrow 2\ Al(OH)_4^-.$$

After removal of the undissolved substances, aluminum hydroxide is precipitated from the solution by seeding it with the crystalline material and allowing it to cool.

$$Al(OH)_4^- \rightleftharpoons Al(OH)_3\downarrow + OH^-.$$

The precipitate is heated to produce anhydrous aluminum oxide which has a purity of approximately 99.5%. This refined oxide is now ready for use in the electrolytic cell. It is reported that aluminum is now being produced from clay at a large experimental plant in Germany. This source of the oxide is at present said to be more costly than the bauxite ores; but it can be relied upon in an emergency.

The Production of Aluminum. The electrolytic reduction of aluminum by *the Hall process* is carried out in a strong steel cell, Fig. 132, lined with a relatively thick layer of carbon, prepared by baking a mixture of coke and tar in position on the inside walls

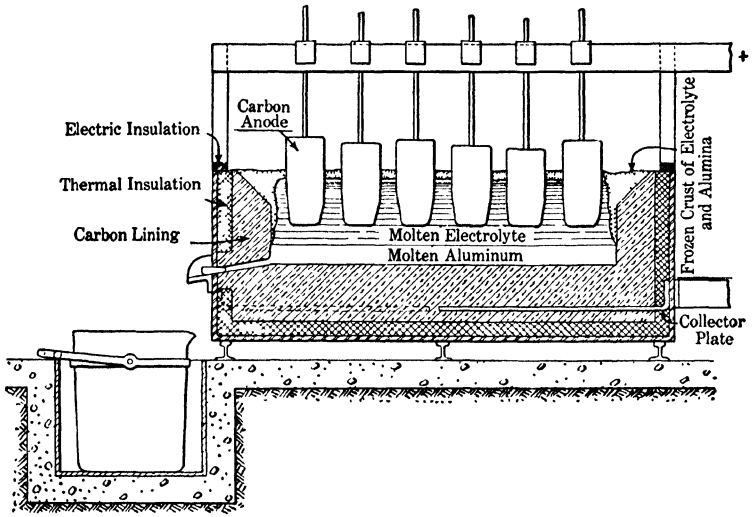
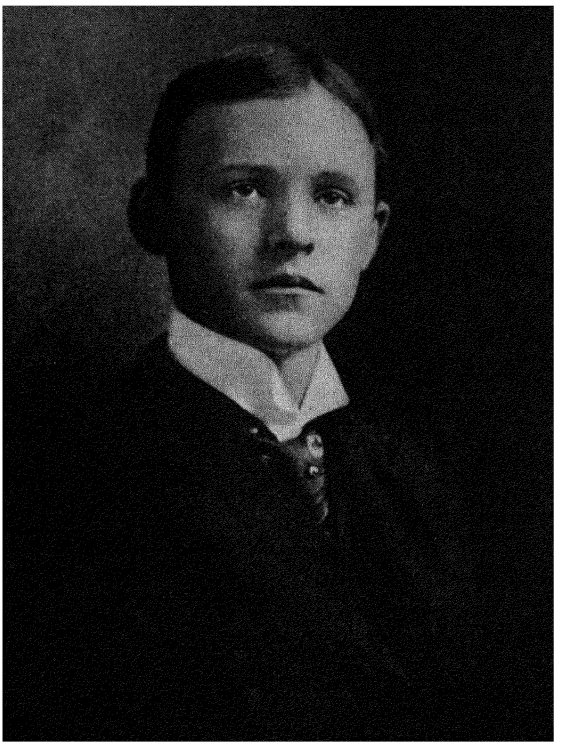


FIG. 132. — Cell for the Electrolytic Production of Aluminum. (Courtesy of Aluminum Company of America.)

of the cell. The lining must be a good conductor of electricity because it serves as the cathode of the cell; and it must be strong enough to prevent cracking which would allow the molten aluminum to come in contact with the metal walls of the cell and to become contaminated with iron. The anodes are large carbon rods which extend down into the cell. In order to start the operation of the cell, the anodes are lowered until an arc is formed between the anodes and the carbon lining of the cell. Cryolite is introduced and is melted by the heat of the arc. When a sufficiently large quantity of melted cryolite is present in the cell, the purified aluminum oxide is added and the anodes are raised and adjusted at the proper height for the current to flow through the solution of the oxide in molten cryolite. The temperature is maintained at approximately 1000° by the resistance to the passage of the current. The voltage is not high, the drop per cell being about six volts. Forty to one hundred cells are connected in series and the amperage for each line of cells is from 10,000 to 30,000 amperes.



CHARLES MARTIN HALL (1863–1914).

While still an undergraduate student at Oberlin College, Hall became interested in the problem of developing a cheap method for the production of the metal, aluminum. Although it is the most abundant of the metals, at that time aluminum could be prepared only by a process so costly that its extensive use was out of the question. While still a very young man, he achieved success where many investigators had failed. In 1886, the year after his graduation, at the age of 22 Hall obtained the metal by the electrolysis of its oxide dissolved in an anhydrous solvent, melted cryolite. This discovery furnished the basis for the production at low cost and in large quantity of a metal which possesses properties rendering it suitable for a great many uses.

During the operation of the cell, aluminum is discharged at the cathode and collects at the bottom of the cell, since it is more dense than the electrolyte. It is drawn off from time to time and cast into bars and ingots. Oxygen is liberated at the anode, where it immediately combines with carbon to form the monoxide and dioxide. The anodes are gradually consumed and must be replaced. A crust of the solidified electrolyte forms over the surface of the cell liquid. The oxide is introduced through this crust from time to time, without interrupting the process. The purity of the metal product is 99–99.5%. This is pure enough for most of the uses of the metal; but a procedure for the further refining of this product has been developed, and is discussed in a later paragraph in this chapter.

The Production of Metals from Native Ores. Several of the metals occur in important native ores: *e.g.*, copper, silver, gold, and the platinum metals. These metals occur in small percentages in veins in rock and in sands with which they are mixed. Two different procedures are employed in the production of *copper*, for example, from its native ores. In one process, the ore is crushed in stamp mills; and a large proportion of the finely divided siliceous material is washed away from the coarser and denser metal by a stream of water. The concentrated product is then mixed with the proper proportions of limestone as a flux and coke as a fuel and smelted in a blast furnace. In this process, a blast of hot air is blown in near the base of the furnace; and the coke burns fiercely, generating the heat necessary for the process. The silicate impurities react with the flux to form a fusible slag, and the copper melts. The two liquids collect in separate layers in the crucible at the base of the furnace and are "tapped" from the furnace at different levels. In the other procedure, the metal is extracted from its low grade ores by leaching the crushed ore with an ammoniacal solution of cupric ammonia carbonate. Soluble cuprous ammonia carbonate is formed.

$$Cu(NH_3)_4^{++} + Cu \longrightarrow 2\,Cu(NH_3)_2^{+}.$$

When ammonia is boiled out of the solution, a precipitate containing copper hydroxy carbonate and copper hydroxide is formed, which is then smelted by the same procedure as is used for a naturally occurring oxidized ore.

Silver may be separated from native ores by amalgamation and by leaching with cyanide solutions. In the amalgamation process, the crushed ore is washed over plates of amalgamated copper. The dense particles of the metal settle and are dissolved in the mercury. The amalgam is then removed and heated to distil the mercury. When the crushed ore is leached with cyanide solutions, silver is dissolved with the formation of the complex silver cyanide.

$$4\,Ag + 8\,CN^- + O_2 + 2\,H_2O \longrightarrow 4\,Ag(CN)_2^- + 4\,OH^-.$$

Silver is then displaced from this solution by the action of zinc.

$$Zn + 2\,Ag(CN)_2^- \longrightarrow 2\,Ag\downarrow + Zn(CN)_4^{--}.$$

A large proportion of the silver produced in the United States in 1939, nearly 64 million troy ounces, was a by-product of the refining of copper and lead.

Gold occurs primarily in the free condition. It is not abundant, but is widely distributed in veins of quartz and in alluvial sands and gravel. In placer mining the alluvial sands are agitated with water, the heavier particles of gold settling to the bottom of the container and the sand being washed away. These operations have been performed extensively by hand in shallow pans. The same operation is performed on a large scale by washing the sands containing gold down a trough across which cleats are fastened. Gold in quartz veins is extracted by crushing the ore and washing it over amalgamated copper plates. The larger particles of gold form an amalgam which is scraped off and distilled, leaving gold as a residue. The more finely divided particles are extracted by a cyanide solution, forming the soluble complex salt $NaAu(CN)_2$, from which gold is precipitated by the use of zinc. Gold is also recovered in the electrolytic refining of silver. The world production of gold in 1939 was 39,818,000 troy ounces. The Union of South Africa produced nearly one third of this total; and the production in the continental United States was 4,620,000 ounces.

The Production of Metals from Oxide Ores. The production of tin from the dioxide is mentioned in a preceding chapter. Zinc oxide is an important ore and the oxide is produced by the roasting of the sulfide and carbonate ores. There are a number of metal oxides which either occur naturally or are prepared in the

first step in the metallurgy of the metal. The usual procedure for obtaining metals from these ores involves reduction by carbon in a blast furnace. In such ores, the coke serves as both the fuel and the reducing agent. A number of the metals are liberated from oxides by the use of a restricted proportion of carbon in an electric furnace. Some of the metals which are active enough to combine with carbon are produced by the reduction of the oxides with aluminum so as to obtain the carbon-free metals. Iron is the most important of the metals. Because of its important position and the special nature of the problems involved, the metallurgy of iron and the metals which go into the formation of special steels is the subject of the following chapter.

The Production of Metals from Carbonate Ores. Copper is produced from the oxidized ores containing the hydroxy carbonates, *malachite*, $Cu_2(OH)_2CO_3$, and *azurite*, $Cu_3(OH)_2(CO_3)_2$. These ores are decomposed by heat to form the oxide, which is then reduced by heating it with coke and a flux in a furnace. Other oxidized ores of copper, such as *cuprite*, Cu_2O, are reduced in a similar manner. Low-grade oxidized ores of copper may be leached with dilute sulfuric acid, forming a solution of cupric sulfate. Copper is recovered from this solution by electrolysis and by displacement with iron. *Smithsonite*, $ZnCO_3$, is an important ore of zinc. It is decomposed to form the oxide, which is reduced by heating it with coke in a retort. *Magnesite*, $MgCO_3$, is becoming increasingly important as a source of magnesium. The carbonate may be converted into the chloride which is fused and electrolyzed, or into the oxide which may be reduced by carbon in an electric furnace.

Production of Metals from Sulfide Ores. A number of the metals occur as sulfides. The extent to which the metals in the transition series occur in such ores is noteworthy. The sulfides are important ores of such metals as copper, zinc, cadmium, lead, mercury, silver, antimony, and bismuth. The metallurgy of zinc and cadmium, mercury, copper, and lead will now be discussed in greater detail to illustrate some of the differences in the procedures for the treatment of sulfide ores.

The Concentration of Sulfide Ores. The oil flotation process is now used extensively for the concentration of sulfide ores, and also for some of the other classes of ores. The ore is

crushed to a fine powder and added to a large volume of water to which suitable oils and emulsifying agents are also added. The mixture is agitated in a flotation machine, Fig. 133, and air is blown through the mixture. An oily froth which adsorbs the

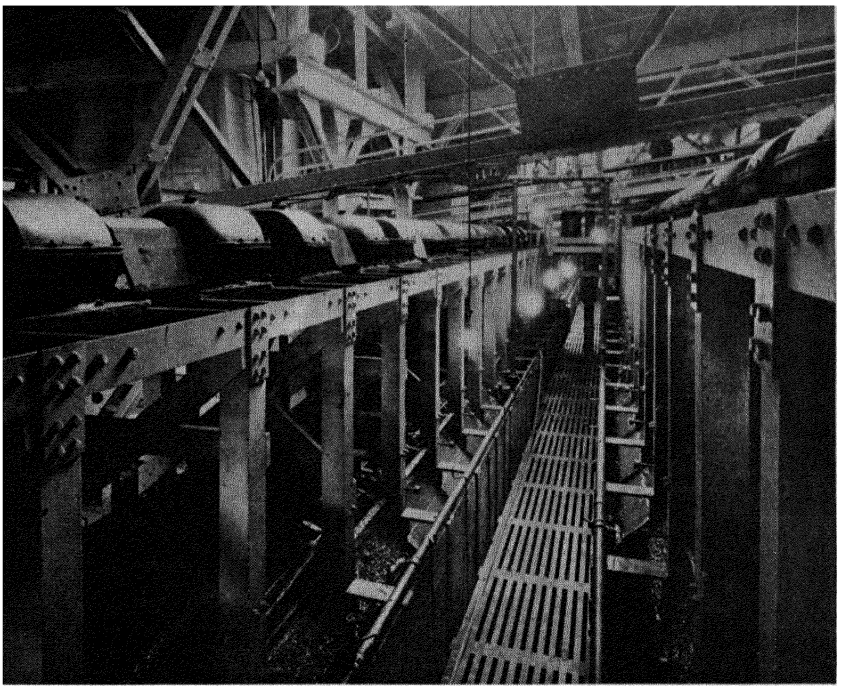


FIG. 133. — Flotation Machine. (Courtesy of Anaconda Copper Company.)

sulfide mineral is produced in this manner, while the silicate minerals are selectively wet by water and remain in the water layer. The oil froth is separated from the water and the oil is distilled, leaving the concentrated sulfide ore for the smelting process.

The Metallurgy of Zinc and Cadmium. The ores of zinc frequently contain small percentages of cadmium compounds, so that the two metals are produced together in the smelting of such ores. Two processes are in general use for the production of zinc from sulfide ores: *viz.*, the retort process and the electrolytic process.

The Retort Process. The concentrated ore is roasted in air to form zinc oxide and sulfur dioxide.

$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2.$$

An important by-product is sulfuric acid made from the sulfur dioxide. A mixture of zinc oxide with an excess of coke is charged into a tube-shaped retort made of fire clay, Fig. 134; and an earthenware receiver is attached to the end of the retort. A

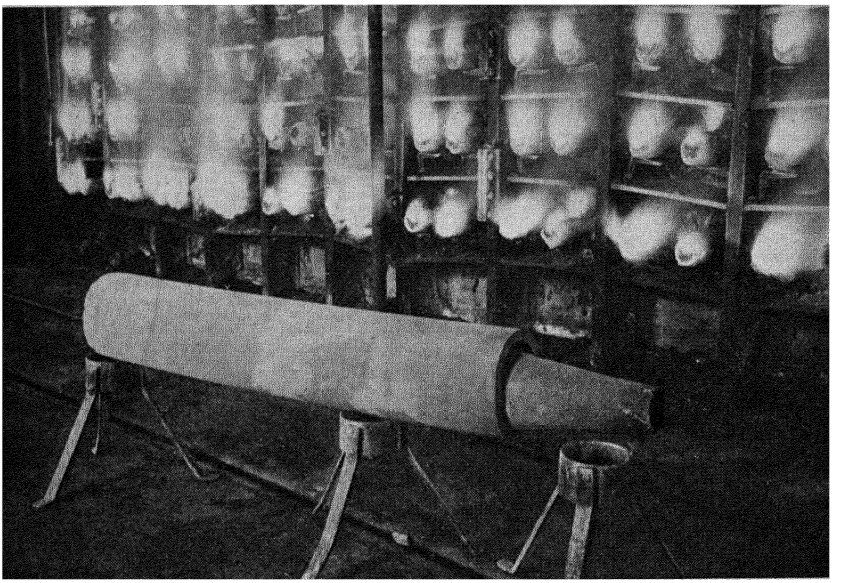


FIG. 134. — Zinc Retort and Condenser in Front of Retort Furnace. (Courtesy of New Jersey Zinc Company.)

number of these retorts are heated simultaneously in a gas-fired furnace. The reduction takes place at approximately 1200°. An excess of coke is used so that carbon monoxide is produced, because zinc is oxidized to the oxide by carbon dioxide as the materials cool.

$$ZnO + C \longrightarrow Zn + CO.$$

The boiling point of zinc is 907°. Consequently, zinc is distilled from the retorts and is condensed in the receivers. While the receiver is cold, a finely divided solid, called *zinc dust*, is formed by the condensation of the gaseous metal directly to the solid state. A large proportion of the zinc dust escapes from the receiver, being carried along by the carbon monoxide. Consequently, the temperature of the receiver is maintained above the melting point of zinc, 432°; and a liquid product is obtained. The liquid is poured into molds to solidify, yielding a solid known as

spelter. The metal produced in this way contains small per cents of lead and cadmium.

The Electrolytic Process. The concentrated ore is roasted at a more moderate temperature to form a mixture of the oxide and sulfate.

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2.$$
$$ZnS + 2\,O_2 \longrightarrow ZnSO_4.$$

The roasted product is leached with sulfuric acid to dissolve the sulfate directly and to convert the oxide into the soluble sulfate.

$$ZnO + 2\,H_3O^+ + SO_4^{--} \longrightarrow Zn^{++} + SO_4^{--} + 3\,H_2O.$$

A small amount of zinc dust is added to the solution, which is now nearly neutral, to precipitate metals of lower activity than zinc.

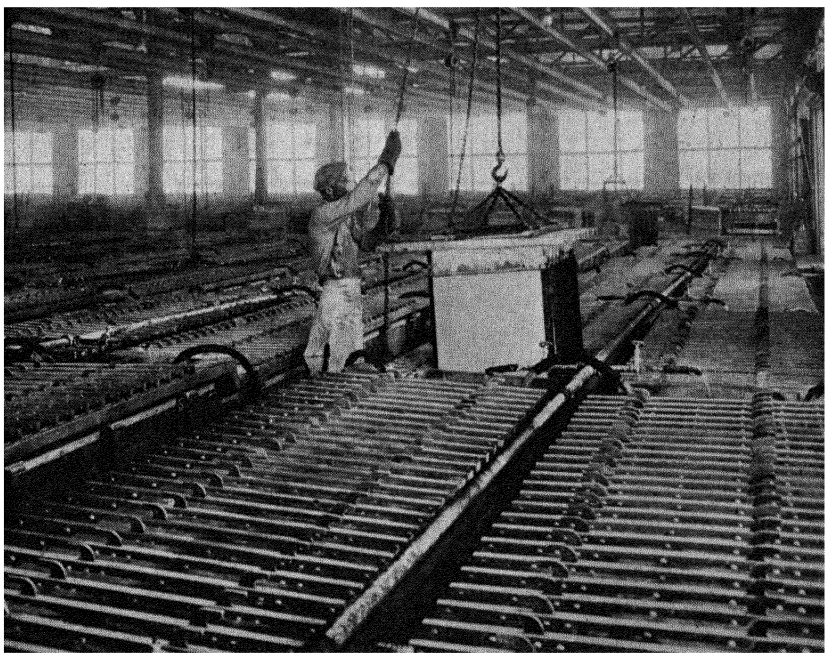


FIG. 135. — Electrolytic Production of Zinc. (Courtesy of Anaconda Copper Company.)

The solution is then electrolyzed, Fig. 135, and zinc is deposited at the cathode. Sulfuric acid is regenerated by the anode reaction and the solution after electrolysis is used again for the leaching of a fresh portion of the roasted ore. The zinc deposited at the

cathode has a purity of approximately 99.95%. The production of zinc in 1939 in the United States was approximately 507,000 tons, 25% by the electrolytic process.

Cadmium is obtained solely as a by-product of the production of other metals. Cadmium oxide is reduced at lower temperatures than zinc oxide and the boiling point of cadmium, 767°, is lower than that of zinc. Consequently, cadmium distils from the retorts along with the first portion of the zinc. This portion may be condensed separately and redistilled to concentrate the cadmium. The metal may also be produced from dusts deposited in the flues of the furnaces in which the sulfide ores of zinc, copper, and lead are roasted; but it is obtained primarily from the precipitated metals formed in the purification of the zinc sulfate solutions before electrolysis. Cadmium and the excess of zinc dust in these residues are dissolved by diluted sulfuric acid, thus effecting separation from copper and other less active metals. Cadmium is reprecipitated by the use of zinc dust and the metal product is refined by electrolysis. It is estimated that the production of cadmium in the United States in 1939 was about 1900 metric tons.

The Metallurgy of Mercury. The important ore of mercury is *cinnabar*, *HgS*. The production of metallic mercury requires merely the heating of the sulfide ore in air, producing the metal and sulfur dioxide.

$$HgS + O_2 \longrightarrow Hg + SO_2.$$

Mercury vapor is condensed from the gaseous products. Mercury may be purified by washing it with dilute nitric acid, which oxidizes the more active metallic impurities likely to be present, especially zinc and cadmium. Redistillation serves to effect further purification. The production of mercury in the United States in 1939 was 18,633 flasks of 76 pounds each.

The Metallurgy of Copper. Nearly 70% of the copper produced in the United States is from sulfide ores. The procedure for the extraction of the metal from these ores is complicated by the fact that they always contain iron and the separation of copper from iron offers difficulties. The per cent of copper in most of the ores which are now secured is small, averaging 1–2%. There are several steps in the process: *viz.*, (1) the concentration of the ore; (2) the partial roasting of the ore; (3) the formation of the matte; (4) the formation of "blister copper"; and (5) the refining of blister copper.

The ores are concentrated by the oil flotation process, already described. The concentrated ore is then roasted so as to burn out a portion of the sulfur, but to leave enough sulfur in the partially roasted product to hold all of the copper and a portion of the

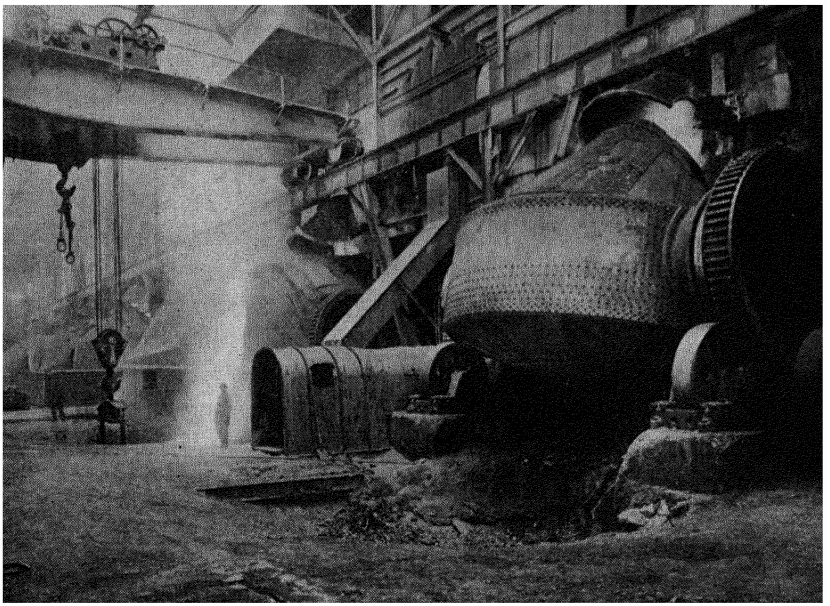


FIG. 136. — Copper Converter. (Courtesy of Anaconda Copper Company.)

iron in combination. The partially roasted ore is next fused with limestone as a flux in a furnace. In this step, silica is removed by reaction with the ferrous oxide formed during the roasting, and with the flux.

$$SiO_2 + FeO \longrightarrow FeSiO_3.$$
$$SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2.$$

Cuprous and ferrous sulfides melt, forming a product known as *matte*. The molten matte and slag separate into two layers which are tapped from the furnace.

The formation of blister copper from the matte takes place in a copper converter, Fig. 136, in which a blast of air is blown through the molten charge. The calculated amount of sand is added with the matte to serve as a flux for the removal of the iron. Since ferrous sulfide is more active than cuprous sulfide, it burns

first when a blast of air is blown through the matte; and the iron oxide reacts with silica to form a ferrous silicate slag.

$$2\,FeS + 3\,O_2 \longrightarrow 2\,FeO + 2\,SO_2.$$
$$FeO + SiO_2 \longrightarrow FeSiO_3.$$

When all of the ferrous sulfide is oxidized, the air blast is interrupted and the converter is tipped to pour out the slag. The converter is then turned back to the upright position and the air blast is renewed. Cuprous sulfide now burns to form copper and sulfur dioxide.

$$Cu_2S + O_2 \longrightarrow 2\,Cu + SO_2.$$

During this part of the process, some of the sulfide is oxidized to cuprous oxide; but most of the oxide formed in this manner is reduced by unchanged sulfide to form the metal.

$$2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2.$$
$$2\,Cu_2O + Cu_2S \longrightarrow 6\,Cu + SO_2.$$

The converter handles a charge of about 65 tons of matte and the "blow" requires approximately five hours. The metal is poured into molds to solidify. The escape of sulfur dioxide gives the metal a blistered appearance. The metal product contains 1–3% of impurities.

Low-grade copper sulfide ores may be leached with a solution of sulfuric acid containing ferric sulfate as an oxidizing agent. The solution obtained in this manner contains cupric and ferrous sulfates.

$$CuS + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 2\,FeSO_4 + S\downarrow.$$

Copper may be deposited electrolytically or may be displaced by iron from this solution. The world production of copper from all types of ores was approximately 2,190,000 metric tons in 1939, the production in the United States being about 698,325 tons.

The Metallurgy of Lead. There are three different processes which are used for the production of lead from its sulfide ore. The sulfide may be roasted to form lead oxide and the oxide reduced by carbon.

$$2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2.$$
$$PbO + C \longrightarrow Pb + CO.$$

A portion of the ore may be burned to form a mixture of the oxide and sulfate. When the oxidized ore is heated with the unchanged sulfide, lead is produced.

$$PbS + 2\,PbO \longrightarrow 3\,Pb + SO_2.$$
$$PbS + PbSO_4 \longrightarrow 2\,Pb + 2\,SO_2.$$

The sulfide may be reduced directly by heating it with scrap iron or a mixture of iron oxide and carbon.

$$PbS + Fe \longrightarrow Pb + FeS.$$

In the United States, the procedure frequently involves a combination of these three reactions. A mixture containing the proper proportions of roasted ore, raw ore, iron oxide, coke, and a flux to react with acidic impurities in the ore, is heated in a blast furnace. Silver and gold dissolve in the molten lead, if they are present in the ore.

The crude furnace product may be refined by several methods. Easily oxidized substances may be removed by melting the lead and stirring it frequently to insure contact with air. The oxidized impurities rise to the surface and may be skimmed off. Silver and gold may be extracted from the molten lead by zinc, in a procedure known as the *Parkes process*. Gold and silver are much more soluble in zinc than in lead, and zinc is not soluble in molten lead. When a small proportion of zinc is stirred into the molten lead, and then allowed to separate, it rises to the surface, bringing most of the silver and gold with it. The silver and gold are recovered from the zinc alloy by skimming it from the surface of the lead and distilling out the zinc. If the lead contains much bismuth it is usually refined in an electrolytic process.

The Metallurgy of Nickel and Cobalt. The most important nickel ore is the double sulfide, $NiS(FeS)_2$, which occurs mixed with additional iron sulfide and copper sulfide, in Ontario. Cobalt occurs in arsenides and sulfides. Cobalt is obtained primarily from the arsenide ores containing silver, nickel, and cobalt, which also occur in Ontario. The production of nickel in 1938 was approximately 127,000 tons, 105,000 tons being produced in Canada. The world production of cobalt in this same year was about 6000 tons, Northern Rhodesia and Morocco being important producers.

The production of nickel and cobalt from the complex arsenide ores involves a number of steps. The ore is smelted in a small blast furnace, separating most of the silver and forming a *speiss*, a mixture of the arsenides of nickel, cobalt, iron, and copper. The speiss is roasted, first with silica to remove the iron as a silicate; next with sodium nitrate and sodium carbonate to remove the arsenic as the arsenate; and then with sodium chloride to form the chlorides of the remaining metals. The chlorides of cobalt, nickel, and copper are leached out with water and the copper is displaced by a more active metal. Cobalt and nickel hydroxides are precipitated, heated to remove water, and the oxides are reduced to the metals. Nickel may be separated from cobalt by heating the metal product to a temperature of 50°–100° in a current of carbon monoxide gas, with the formation of gaseous *nickel carbonyl*, $Ni(CO)_4$. This compound is decomposed to form nickel and carbon monoxide at higher temperatures.

Nickel is produced from the complex sulfide ores which contain approximately 3% of nickel by first burning out a part of the sulfur. The ore is then heated in a blast furnace with a flux; and a matte, containing all of the nickel and copper and about half of the iron in the ore is formed. This material is oxidized in a converter, like the Bessemer converters, with silica as a flux, and most of the iron is removed, leaving a matte which contains approximately 37% of nickel and 42% of copper. There are several processes for producing nickel from this matte. In the Orford process, the matte is fused with carbon and sodium sulfate, or with sodium sulfide, and two layers are formed. Most of the nickel is in the lower layer as a nickel sulfide. This sulfide is oxidized to form the oxide, which is reduced with carbon in an open-hearth furnace. The crude product is refined electrolytically by making it the anode in a cell with nickel sulfate as the electrolyte. Platinum is obtained as a by-product from the material which fails to go into solution at the anode during the refining.

Nickel is used extensively in the production of nickel steel and other nickel alloys. *Monel metal* contains 60% of nickel, 36% of copper, 3.5% of iron, and 0.5% of aluminum; *nickel coins*, 25% of nickel and 75% of copper; *german silver*, 20% of nickel, 55% of copper, and 25% of zinc; and *illium*, an acid resistant alloy, contains 62% of nickel, 7% of copper, 22% of chromium, 8% of

molybdenum, and 1% of iron. *Cobalt* is used in the production of the alloy, *stellite*, containing varying proportions of cobalt, chromium, tungsten, and molybdenum, and in high-grade steels, such as metal-cutting and magnet steels.

The Refining of the Metals. Some of the impurities in the metal products from the smelting processes have sufficient value to justify the cost of separating them from the metal. In other instances the value of the metal is greatly increased by the removal of the impurities because they impart objectionable properties. The production of gold and silver in connection with the refining of other metals is an important source of these two costly metals. The presence of arsenic in copper greatly decreases the conductivity of this metal. Special methods may be employed for the separation of certain specific impurities, as in the extraction of silver and gold from lead. Some of the metals which have relatively low boiling points are refined by distillation, as in the refining of mercury. The usual method for the refining of the metals is an electrolytic process.

The electrorefining of a metal involves the use of the crude metal as the anode, a solution of a suitable salt of the metal as the electrolyte, and the pure metal or an inert material as the cathode. *The refining of copper* illustrates the principles which are involved.

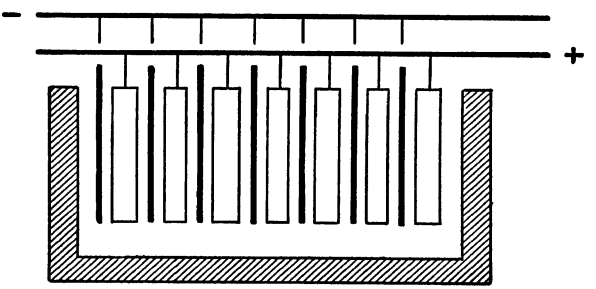


FIG. 137. — Diagram of Copper Refining.

The anodes are large plates of crude copper, such as blister copper, about three feet square and two inches thick. The cathodes are thin sheets of pure copper which have themselves been prepared electrolytically. The anodes and cathodes are placed alternately in large cells, Figs. 137 and 138. The electrolyte is a solution of cupric sulfate which is acidic with sulfuric acid. During the pas-

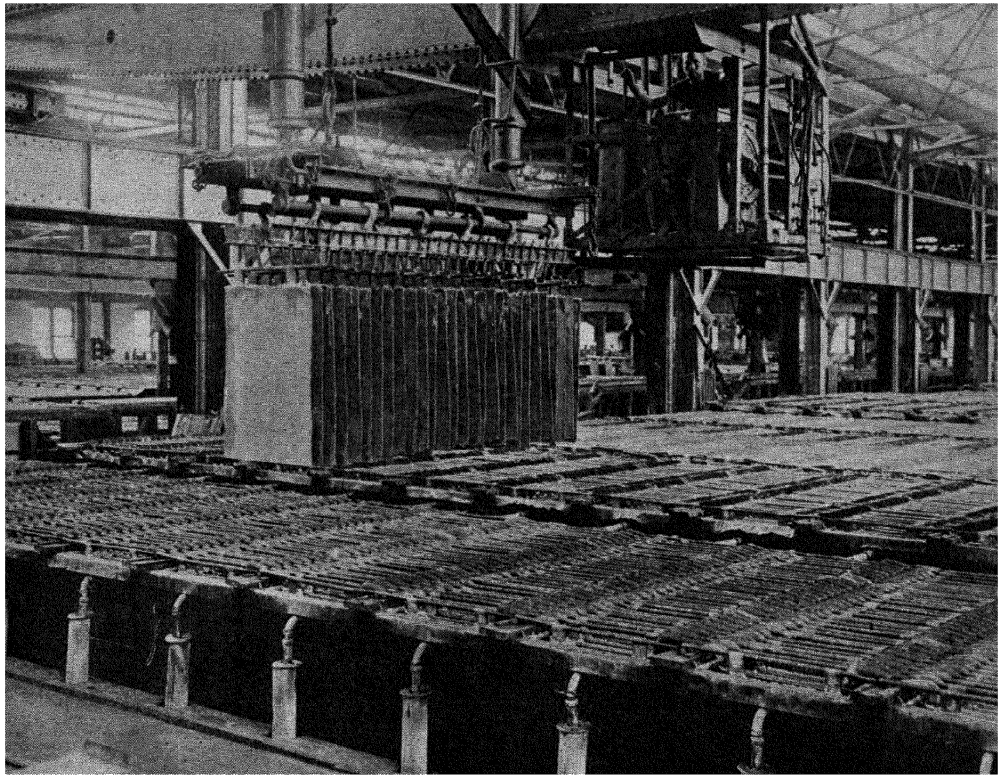


FIG. 138. — Lifting Cathodes from Electrolytic Bath. (Courtesy of Raritan Copper Works.)

sage of the current, cupric ions gain electrons and are deposited on the cathode, so that the cathodes gradually build up.

$$Cu^{++} + 2\,\epsilon \longrightarrow Cu.$$

Simultaneously, an equivalent number of positive ions, chiefly cupric ions, are formed at the anode, so that the concentration of the solution is not greatly changed.

$$Cu \longrightarrow Cu^{++} + 2\,\epsilon.$$

Metals more active than copper, such as iron and nickel, also dissolve at the anode, but they are not deposited at the cathode.

$$Fe \longrightarrow Fe^{++} + 2\,\epsilon.$$

Lead also dissolves and is removed from the solution by the precipitation of lead sulfate.

$$Pb + SO_4^{--} \longrightarrow PbSO_4\downarrow + 2\,\epsilon.$$

The oxidation of arsenic at the anode yields arsenious acid which partly precipitates in the form of arsenites in the anode mud and partly remains in the solution. Gold and silver, being less active than the copper, do not dissolve at the anode, but settle to the bottom as they are dislodged by the wearing away of the anode; and they are present in the anode mud. The purity of the electrolytically refined copper is 99.94–99.98%. Gold, silver, and other substances of value, such as arsenic, selenium, and tellurium, are obtained from the anode mud.

In the electrolytic refining of copper, only a low potential difference is required. The composition of the vat liquid is not materially changed during the process, and the composition of the crude anode differs so little from that of the pure cathode that there is but little reverse potential to be overcome.

Other metals may be refined in a similar manner, through the application of these principles. The electrolyte used in the *electrorefining of silver* is silver nitrate. Silver deposits at the cathode and also dissolves from the anode. Metals of greater activity dissolve also; but the potential required for their deposition is higher than that required for silver and the ions of these metals remain in solution. Metals which are less active than silver, as gold, do not dissolve and are recovered from the anode

mud. In the *electrolytic refining of lead*, the crude metal is the anode; a sheet of pure lead is the cathode; and the vat liquid is a solution of lead fluosilicate, $PbSiF_6$. This salt is used instead of some of the more familiar salts because the oxidation of lead to form the dioxide takes place at the anode during electrolysis of a salt solution containing oxyanions. The successful operation of the electrolytic refining processes demands that the simple ions of the metal be formed at the anode as they are discharged at the cathode.

The electrorefining of aluminum introduces difficulties because its ions are not deposited from aqueous solution. It is necessary to

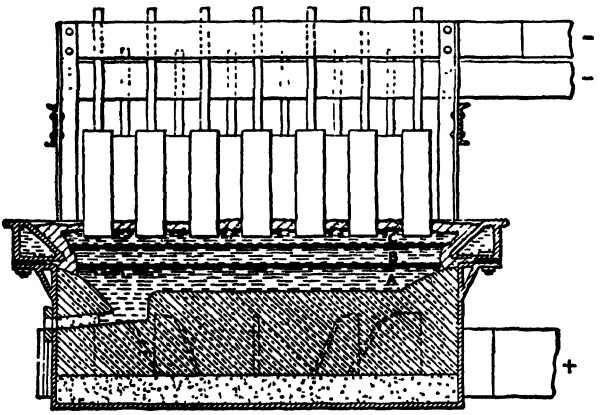


FIG. 139. — Electrolytic Refining of Aluminum.

use an anhydrous electrolyte similar to that employed in the production of the metal from its ore. However, metallic aluminum is itself a liquid at the temperature necessary to fuse the salt electrolyte; so that the arrangement of the materials in the cell requires the separation of a liquid anode, a liquid cathode, and a liquid electrolyte, all at high temperature. This is accomplished in *the Hoopes process*, Fig. 139, by the use of three layers of different density. Since the electrolyte used in the Hall process is less dense than aluminum, it is necessary to increase the density of the fused salt by dissolving other salts in the fluoride mixture. The electrolyte, which is the middle layer in the cell, is a fused mixture containing fluorides of sodium, aluminum, and barium, nearly saturated with aluminum oxide. The upper layer of pure aluminum is the cathode. In order that the anode may be made

dense enough to serve as the lowest layer, an alloy of aluminum, copper, and silicon is prepared. The passage of the current causes aluminum ions from the fused salt mixture to discharge at the cathode, the layer of pure melted aluminum at the top of the cell. An equivalent quantity of aluminum goes into solution in the fused salt mixture from the crude anode, the aluminum alloy at the bottom of the cell. The metals selected to increase the density of the aluminum in the preparation of the alloy for use as the anode are less active than aluminum. Consequently, they do not dissolve at the potential at which the cell is operated. Likewise, the metal ions in the salts selected to prepare a fused electrolyte of the proper density are more active than aluminum, so that they are not deposited at the cathode. Under these conditions, aluminum is the only metal which forms ions at the anode and is deposited at the cathode; and thus only aluminum is transported from the anode to the cathode.

ALLOYS

The refining of a metal is required if the impurities which are present alter the properties in an objectionable manner. In many instances, the presence of certain specified impurities alters the properties of the metal in a desirable manner; and these ingredients are intentionally introduced. Many of the metal products which find extensive use are not single metals but are alloys containing two or more metals. By the formation of alloys it is possible not only to modify the properties of metals, but also, in many instances, to prepare metallic products possessing properties not exhibited by any single metal. In this way, a much wider range of choice is provided in the selection of a metallic material for a specific use, than if one were restricted to the use of pure metals.

Types of Alloys. Alloys are usually prepared by melting metals together and allowing the melt to cool. There are several different types of alloys, some being homogeneous and others heterogeneous. The simplest type is that in which the two metals do not separate when the melt solidifies. The crystals of the product contain both of the component metals in a homogeneous structure known as a *solid solution*. A second type is that in which the cooling of the melt gives a homogeneous product which is not

a true solid. Such products are amorphous and are *supercooled liquids.* A third type of homogeneous alloy is that in which the two metals combine to form a *binary compound* which contains the two metals in a definite ratio.

Many of the alloys do not fall into any single homogeneous type, but are *heterogeneous* in structure. During the cooling of a liquid solution of two metals in each other, the solution usually becomes saturated with one of the metals before the other and that metal begins to crystallize as further cooling proceeds. This causes an increase in the concentration of the other metal in the liquid phase. After a time, the concentration and temperature become adjusted so that both metals crystallize together to give a mixture of small crystals of the two components. These heterogeneous alloys may appear to be homogeneous because the particles are so finely divided; but they actually consist of one material embedded in a deposit of the other. The differences in the crystal structure of an alloy may be made apparent by etching a polished surface of the alloy with a suitable reagent and examining it under the microscope. The magnified surface may also be photographed, producing a photomicrograph, Fig. 140. Photomicrographs are used extensively in the study of the structure of alloys and the effects of heat treatment in altering this structure.

FIG. 140. — Photomicrograph of Bismuth and Cadmium Alloy. (From Holmes, *General Chemistry.*)

Two-Component Systems. The simplest type of heterogeneous alloys is that in which the components form no compounds with each other; yield no amorphous, supercooled liquids which are solid-like in appearance; are miscible in the liquid state; and are immiscible in the solid state, that is, do not yield solid solutions. The crystallization of a substance from an aqueous solution in which the above conditions are applicable and the crystallization of an alloy are similar processes, merely occurring at widely different temperatures. Although different methods of studying the composition of the solid and liquid phases in equilibrium with each other at the different temperatures are neces-

sary, the systems may be represented in a similar manner by the use of fusion diagrams.

The Solidification of Solutions of Salt in Water. Such systems serve to illustrate general principles involved in those cases in which the components yield no chemical compound, supercooled liquid, or solid solution. If a dilute solution of salt in water is cooled sufficiently, at some temperature below zero degrees, depending on the concentration of the solution, ice begins to separate. The freezing out of water increases the concentration

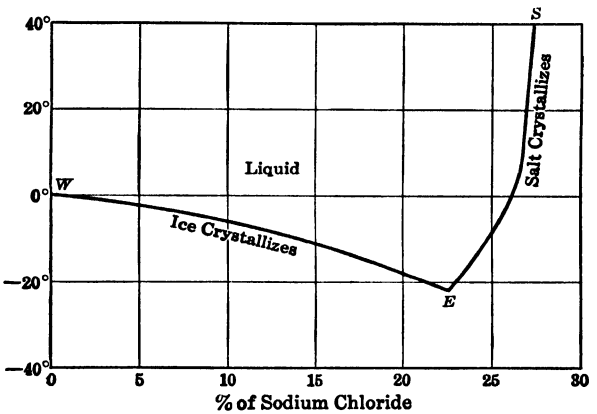


FIG. 141. — Fusion Diagram, Sodium Chloride and Water.

of salt in the remaining solution and the freezing temperature drops to a lower degree. The processes of separation of ice and depression of the freezing point continue until the solution of minimum freezing temperature remains. This solution then solidifies, depositing both ice and solid salt in the same proportions as in the solution. This minimum freezing temperature is known as the *eutectic point*. In the case of a solution of salt and water, the eutectic temperature is − 22.4°. The mixture of crystals which separates at this temperature, *the eutectic mixture*, contains 23% by weight of common salt. If a solution containing more than 23% of salt is cooled, salt begins to crystallize from the solution, causing an increase in the relative concentration of liquid water. This continues until the temperature and composition are those for the solidification of the eutectic mixture, when the entire mass solidifies without further change in temperature or composition as one continues to remove heat. In the diagram, Fig. 141,

the depression of the freezing point of water by increasing concentrations of salt is shown by the curve *WE*. The depression of the freezing point of salt is only partially represented by the curve *SE*. Along the curve *WE*, the solid in equilibrium with the solution is ice. Along the curve *ES*, the solid phase is salt. All points above the curve *WES* are in the liquid phase. The point *E* represents the intersection of the fusion curve of water with increasing per cents of salt and the fusion curve of salt with increasing per cents of water. This is the eutectic point of this system and shows the composition and solidifying temperature of the eutectic mixture.

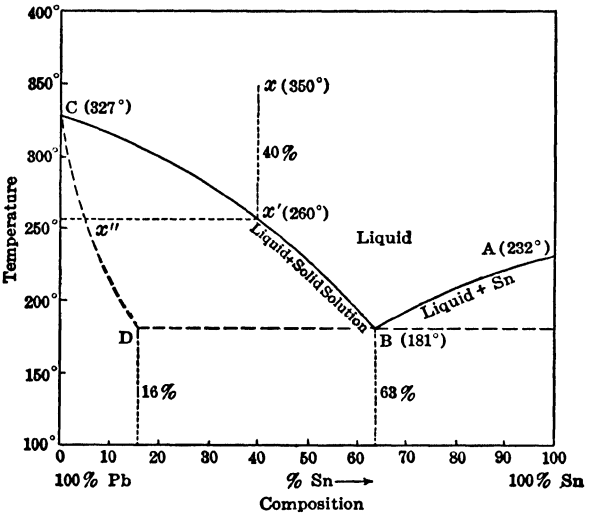


FIG. 142. — Tin-Lead Alloys.

Alloys of Tin and Lead. The solidification of most alloys involves changes which are much more complex than those of the simple type discussed in the preceding paragraph. Alloys of tin and lead illustrate the type in which a *solid solution* is formed. The melting point of tin is 232° and of lead 327°. The freezing point of tin is lowered by the presence of lead in the melt, as shown by the curve *AB*, Fig. 142. Similarly, the freezing point of lead is depressed by the presence of dissolved tin, as shown by the curve *CB*. At all temperatures and concentrations represented by points on the curve *AB*, the solid phase separating from the melt is pure tin. But the solid phase separating at the points represented by the

curve *CB* is a solid solution containing lead and tin. The composition of the solid phase in equilibrium with the liquid melt at each temperature is shown by the curve *CD*. The point *X* represents a solution containing 40% of tin at a temperature of 350°. When this solution is cooled to the point *X'*, at approximately 260°, a solid solution of the composition represented by the point *X''* separates. The composition of the solid solution separating at any temperature is shown by drawing the horizontal line to intersect the curve *CD*, as shown in the figure. The solid solution contains a larger proportion of lead than the solution from which it separates, so that the concentration of tin in the melt increases as crystallization proceeds. This causes a further depression of the freezing point and the separation of crystals of solid solution which are increasingly rich in tin. These changes continue until the melt of the composition of the eutectic mixture is reached at the point *B*, the intersection of the freezing point curves of lead and tin. At the eutectic point, the entire melt solidifies without further change in the proportions of lead and tin, or in the temperature. The solid product formed at this point consists of the solid solution and tin in a heterogeneous mixture. This mixture contains 63% of tin and solidifies at 181°. When larger proportions of lead, such as 50% or 70%, are used in the alloy, the solidification of the melt commences at a temperature above the eutectic point. During the time the melt is cooling from the temperature at which the separation of the solid commences to the temperature at which the eutectic mixture solidifies, there is a mixture of solid material with the remaining liquid solution. Consequently, the partially solidified alloy can be shaped as it solidifies and it is possible to produce the plumber's "wiped joints."

Compound Formation. If the two metals in a two-component system yield a binary compound, the fusion diagram is somewhat more complicated. It may, however, be considered to be two adjacent curves, each being similar to the systems just studied. In one part of the fusion diagram, the behavior of one of the components and the binary compound is shown; and in the other part, that of the other component and the binary compound. The freezing point of each component is depressed by the presence of the compound dissolved in it; and the freezing point of the com-

pound is depressed by each of the components. There are, consequently, two eutectic mixtures.

Magnesium and tin yield a binary compound of the composition Mg_2Sn. The fusion diagram of the magnesium-tin alloys, consequently, serves to illustrate the case in which the metals are miscible in the liquid state, but form a binary compound. In

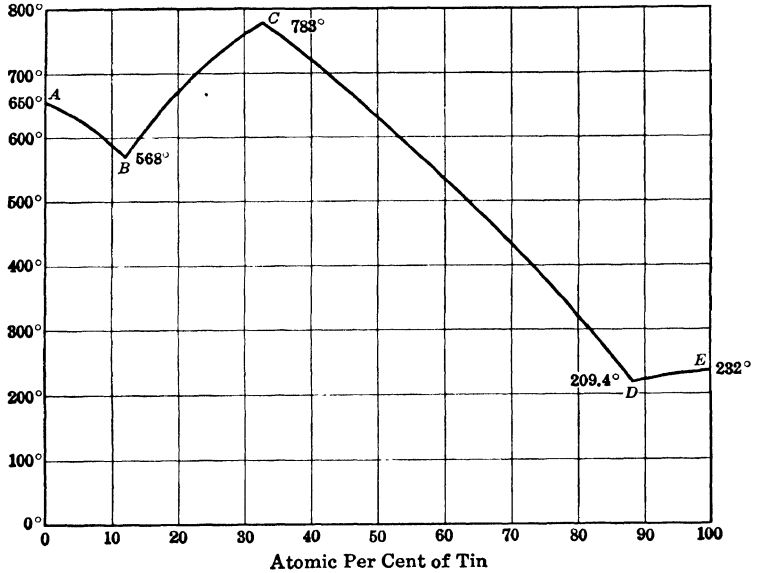


FIG. 143. — Fusion Diagram, Magnesium and Tin.

Fig. 143, the composition of this system is represented in terms of atomic percentages in preference to weight percentages. The melting point of magnesium is 650°; of tin, 232°; and of the compound, Mg_2Sn, 783.4°. At temperatures above those represented by the freezing point curve for solutions of these metals in all concentrations, the system persists in the liquid state. Along the branch *AB* of this curve, the solid which separates is pure magnesium; and along the curve *DE*, pure tin as in the case already considered. Along the curve *BCD*, however, the pure compound Mg_2Sn crystallizes. The point *B* represents the composition and freezing temperature of the eutectic mixture of magnesium with the compound. This mixture contains 11.6 atomic per cent of tin and solidifies without change in composition at 568°. The other eutectic mixture, separating at *D*, 209.4°, contains 11.13 atomic per cent of magnesium.

Commercial Alloys. Most of the alloys of industrial importance are complex systems, frequently involving a number of components. The formation of supercooled liquids, in addition to the solid solutions, heterogeneous mixtures, and compounds, adds to the complexity of the solidified product. The phase diagram is one of the important means of investigating the constitution of alloys. Alloys having the composition of the eutectic mixture or of a binary compound have a fixed melting point; but alloys in general do not have definite melting points. The properties of alloys cannot be predicted with certainty from a knowledge of the properties of the component metals. The alloy containing 25% of nickel and 75% of copper shows none of the color of copper. An alloy containing 82% of copper,15% of manganese, and small percentages of nickel and iron is a very poor conductor of electricity, so that it has uses based on its high electrical resistance. The alloy containing 50% of bismuth (melting point 271°), 25% of lead (melting point 327.4°), 12.5% of cadmium (melting point 320.9°), and 12.5% of tin (melting point 232°) melts sharply at 71°. The composition of some of the alloys of tin and lead is shown in Table 32 (p. 424), and of some alloys of copper in Table 37 (p. 504).

EXERCISES

1. What is an ore of a metal? Name the common classes of ores and give examples of metals produced from each of these classes.
2. What procedure is employed for the production of the metals of high activity? Why? Describe the production of magnesium and of aluminum from naturally occurring materials.
3. What two methods are used for the extraction of a metal from its native ores?
4. What method is commonly employed for the concentration of the sulfide ores?
5. Describe the retort process for the production of zinc.
6. Describe the electrolytic production of zinc.
7. What is the chief source of cadmium? How is it separated from zinc?
8. Outline the production of copper from a sulfide ore containing much iron; and give reasons for each step.
9. What procedure may be followed for the production of copper from low-grade sulfide ores?
10. Why is the metal product of a furnace operation usually impure? What two objectives lead to the refining of metals?
11. Describe the electrorefining of copper, of lead, and of aluminum; and account for the elimination of different varieties of impurities which are likely to be present.

12. What are alloys? How are they usually prepared?
13. What is meant by the eutectic point? the eutectic mixture?
14. Describe the changes which occur during the cooling of a system involving substances which yield a binary compound.
15. Why are the alloys of metals important?

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CHAPTER XXV

IRON AND STEEL

Iron is the most important of the metals. It is not found in the uncombined state in natural deposits near the surface of the earth, except in meteoric iron, which contains approximately 90% of iron; but it is believed that the interior of the earth is composed largely of this element. Iron is fourth in abundance among the

FIG. 144. — The Sagamore Mine, Minnesota. (Courtesy of John A. Savage and Company.)

elements in the outer portion of the earth. Its most important ore is (1) *hematite*, Fe_2O_3. Other oxide ores are (2) *limonite*, $Fe_2O_3(H_2O)_3$, and (3) *magnetite*, Fe_3O_4; the carbonate, (4) *siderite*, is also useful.

The most important iron ore deposits in the United States are hematite ores in the Lake Superior region in Minnesota and Michi-

gan. The principal producing mines in this region are open pits, Fig. 144; but underground mines are also operated. A second large producing area of hematite ore is in Alabama. The magnetite ore is mined in New York and in Pennsylvania. Iron ore is mined in sixteen of the states. Ores of this metal occur widely distributed in many nations, other leading producers being Russia, Germany, France, Great Britain, and Sweden.

The Iron of Commerce. Pure iron has only limited commercial importance, since it is too soft and malleable to hold its shape under great strain. The pure metal cannot be tempered. The industrial importance of iron is due largely to the fact that the presence of small proportions of specified ingredients in the iron, particularly carbon, modifies the properties of the metal to a great extent. The most familiar of the varieties of commercial iron are *steel* and *pig iron*. These names do not signify substances of specific composition; but apply to the products of particular furnace processes. The composition of steel, for example, may be varied over wide limits to develop the properties which are desired for the particular use to which the steel is to be applied.

The production of the finer grades of commercial iron requires more than one furnace operation. The purpose of each of these operations can be understood most clearly by a consideration of the following facts. Iron is obtained from its ore, an impure oxide, by reduction in the presence of an excess of carbon. The ore contains other reducible substances and the reduction products of some of these contaminate the metal product. At the temperature of the furnace, carbon not only dissolves in molten iron, but also combines with it to a considerable extent. The properties of iron are greatly modified by the presence of these absorbed substances. Hence, the operations subsequent to the reduction of the oxide are for the purpose of eliminating as completely as possible those impurities which impart objectionable properties, and regulating the proportions of the impurities which are desirable.

The Reduction of the Ore. The Blast Furnace. The reduction of the ore is carried out in the blast furnace, Fig. 145. In the iron industry, the furnaces vary in height from fifty to one hundred and twenty-five feet, with a maximum diameter of approximately twenty-five feet. They are constructed of steel plates and are lined with firebrick. The furnaces taper, as shown

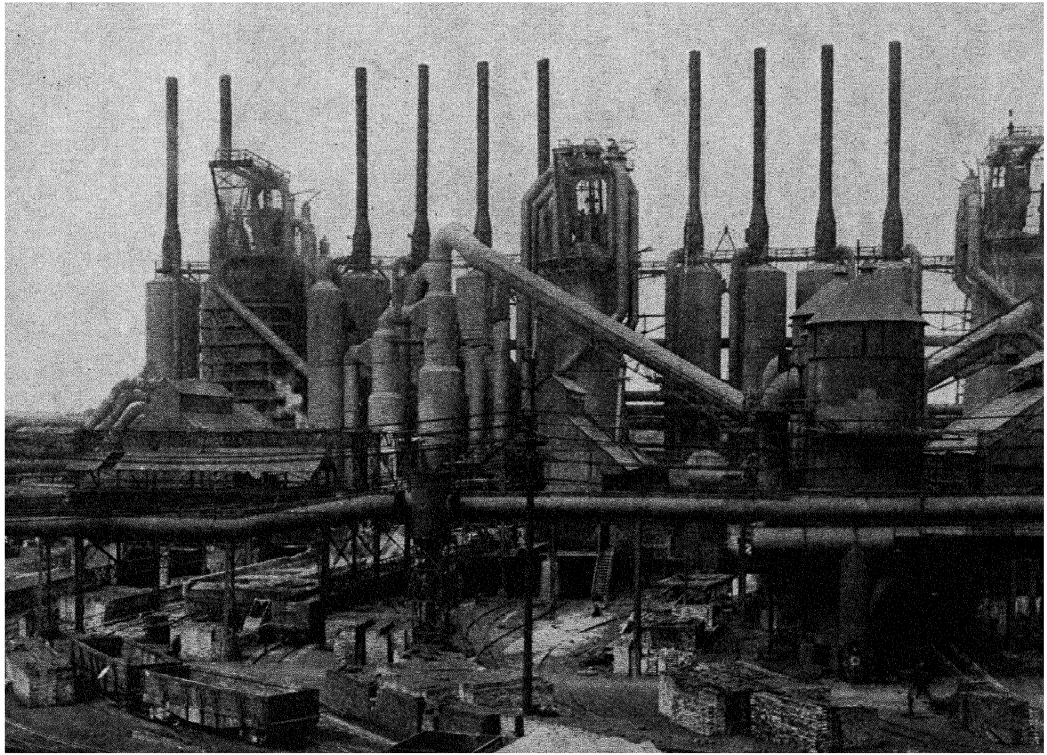

FIG. 145. — Blast Furnaces and Stoves. (Courtesy of United States Steel Corporation.)

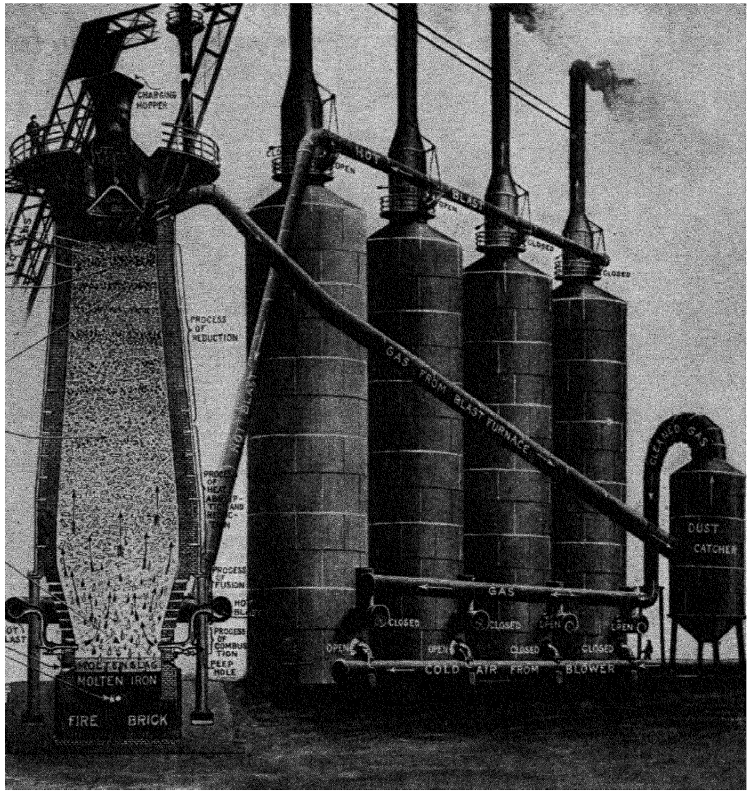

FIG. 146. — Blast Furnace with Stoves. (Courtesy of the *Scientific American*. Copyright.)

in the diagram, Fig. 146, so as to minimize frictional wear of the solids on the furnace walls in the upper part and to aid in the formation of an arch just above the fusion zone, so that the solid charge is supported. The liquid products collect in the *crucible* at the base of the furnace. There are two outlets from the crucible, the *metal tap* and the *cinder notch*. The metal and the slag may be tapped from the furnace through these outlets by the removal of the plugs which close them at other times. A large iron pipe encircles the furnace near the top of the crucible; and a number of water-jacketed nozzles, tuyères, lead through the furnace wall to admit the blast of hot air. The charging hopper at the top of the furnace is so constructed that the solid charge may be introduced without undue loss of the gaseous products. The gas outlet is just below the charging hopper. Each furnace is provided with a series of stoves for heating the air blast.

The solid charge consists of the proper proportions of ore, coke, and flux. The ore is impure iron oxide containing siliceous matter and small proportions of compounds of sulfur, phosphorus, and manganese. The coke is the fuel and the source of the carbon monoxide which is the active reducing agent. The function of the flux is the elimination of highly infusible substances by reacting with them to form a slag which is liquid at the temperature of the furnace. If the ore contains an excess of silica and complex silicates, the usual condition, the flux is limestone; but if the impurities are basic, the flux is sand. All of the products of the furnace are liquid or gaseous at the working temperatures so that the furnaces may be operated continuously.

The reactions which take place during the operation of the furnace fall into four groups: *viz.*, the combustion of the fuel and the reactions of its combustion products; the reduction of the ore; the formation of the slag; and the formation of impurities in the metal product. Coke burns fiercely under the forced draft of preheated air, with the formation of carbon dioxide. This reaction is the source of the heat for the process; and the hottest part of the furnace, about 1500°, is just above the tuyères. As the carbon dioxide rises through the charge coming in contact with heated coke, it is reduced to carbon monoxide, which serves as the reducing agent and is itself again converted into carbon dioxide. These changes may occur a number of times as the gases rise through the

charge; but toward the top of the furnace, in the presence of an excess of coke and at a temperature as low as 300°, carbon monoxide is the stable product.

The oxides of iron are reduced by the action of carbon monoxide, forming successively magnetic oxide, ferrous oxide, and iron, as the charge settles into the hotter parts of the furnace. The reactions are reversible; but the reduction is completed in the furnace because of the large excess of carbon monoxide maintained.

$$3\,Fe_2O_3 + CO \longrightarrow 2\,Fe_3O_4 + CO_2.$$
$$Fe_3O_4 + CO \longrightarrow 3\,FeO + CO_2.$$
$$FeO + CO \longrightarrow Fe + CO_2.$$

Slag formation involves a number of complex reactions between impurities of an acidic nature and the basic flux. The type of change is represented by the reaction of silica. Limestone in the charge decomposes to form calcium oxide and carbon dioxide. Calcium oxide reacts with silica and with complex silicates to form a fusible slag.

$$CaCO_3 \longrightarrow CaO + CO_2.$$
$$CaO + SiO_2 \longrightarrow CaSiO_3.$$

The introduction of impurities into the metal product results from a number of reactions. Carbon dissolves in iron and also reacts with iron to form a carbide, *cementite*, Fe_3C. The oxysalts of silicon, sulfur, and phosphorus may be reduced in part to form binary compounds with iron. Thus, calcium phosphate in the ore may be reduced to the phosphide or may yield phosphorus, which in turn combines with iron.

$$Ca_3(PO_4)_2 + 8\,C \longrightarrow Ca_3P_2 + 8\,CO.$$
$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \longrightarrow 3\,CaSiO_3 + 5\,CO + 2\,P.$$
$$3\,Fe + P \longrightarrow Fe_3P.$$

These binary compounds dissolve in iron, lowering its melting point, so that it melts in the hottest part of the furnace. The liquid metal and slag collect in separate layers in the crucible, and are tapped from the furnace at suitable intervals, Fig. 147.

The products of the blast furnace are pig iron, slag, and blast furnace gas. *Pig iron* varies in composition, but usually contains 2–5% of carbon, 1–3% of silicon, and smaller percentages of sulfur, phosphorus, and manganese, and other substances, depending on

the composition of the ore and the operation of the furnace. It melts sharply at temperatures between 1150° and 1250°, depending on its composition, while pure iron melts at 1535°. Pig iron is a hard and brittle product. It is coarsely crystalline and has little tensile strength. Pig iron is used directly in the manufacture of castings, such as parts of stoves, radiators, window weights, and many other objects which are not to be subject to great

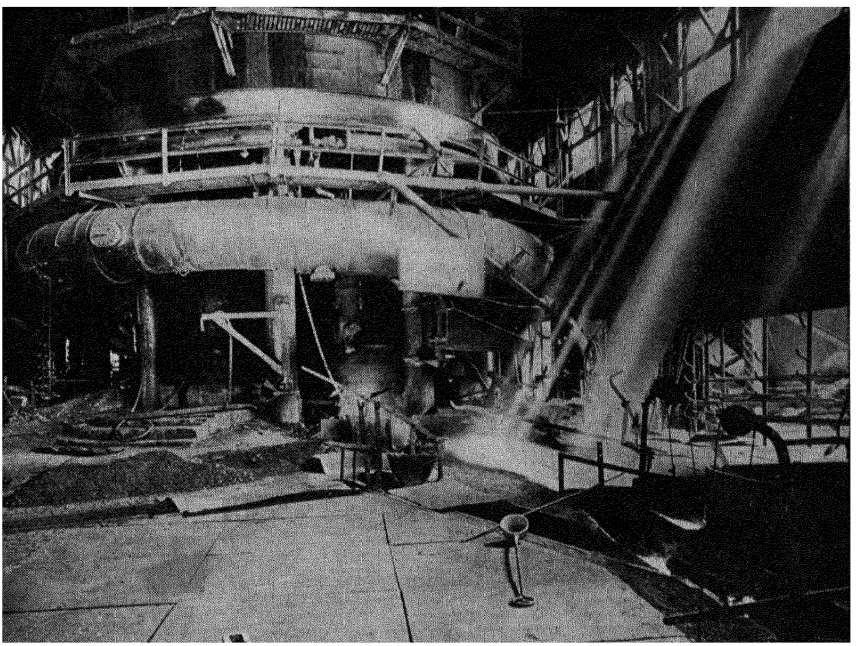

FIG. 147. — Tapping Molten Iron from a Blast Furnace. (From Ewing Galloway, New York.)

strain or sudden shock. Castings are made by remelting pig iron with scrap iron in a furnace and pouring the molten metal into the mold of the object. There are two varieties of cast iron. White cast iron is produced when the product is cooled suddenly. In this variety, most of the carbon remains in combination with iron as cementite. Gray cast iron results from the slow cooling of the product. When the metal cools slowly from a high temperature, the carbide decomposes to a large extent, giving a mixture containing finely divided graphite crystals interspersed throughout the metal. This product is softer and somewhat stronger

than the white variety. The most extensive use of pig iron is in the production of steel. The world production of pig iron in 1938 was approximately 82,500,000 tons, a large decrease from that of 1937. The production of 20,000,000 tons in the United States was a little more than one half of the 1937 production and was the lowest proportion of the total in more than half a century. More than 32,000,000 tons of pig iron were made in the United States in 1939, while the world production was 102,000,000 tons.

The slag is essentially a mixture of silicates, containing aluminates, phosphates, and sulfates, in small proportions. It has no important industrial uses. The solid may be crushed and used as ballast for railroads and for filling in embankments; and some grades of slag may be used in making Portland cement.

Blast furnace gas contains all of the nitrogen in the air blast, some carbon dioxide, and proportions of carbon monoxide up to approximately 20% by volume. Because of its carbon monoxide content, blast furnace gas is used as a fuel in the stoves for preheating the air blown into the furnaces and to develop power in the plant.

Steel. Simple carbon steel contains carbon in proportions ranging up to 1.5%, depending on the type of steel, but contains very small proportions of silicon, sulfur, and phosphorus. The procedures by which the undesirable impurities are removed usually lead to the removal of carbon also, so that the required proportions of carbon must be introduced into the refined metal. The two most extensively used processes for the production of steel from pig iron are the open-hearth process and the Bessemer process. The amount of steel produced in the United States in 1939 was approximately 47,150,000 tons, 91.7% in open-hearth furnaces, 6.4% in Bessemer converters, and 1.9% in electric furnaces.

The Open-Hearth Process. The great expansion in the steel industry in the past sixty years has been due to the development of the basic open-hearth process, by which it is possible to produce a high-grade steel in large quantities from pig iron containing sulfur and phosphorus. The open-hearth furnace, Fig. 148, is a reverberatory furnace; *i.e.*, a furnace in which the flames from the burning fuel are reflected by a low roof upon the charge on a shallow hearth. The hearth is approximately forty feet long by twelve feet wide and two feet deep. It is lined with a basic material such

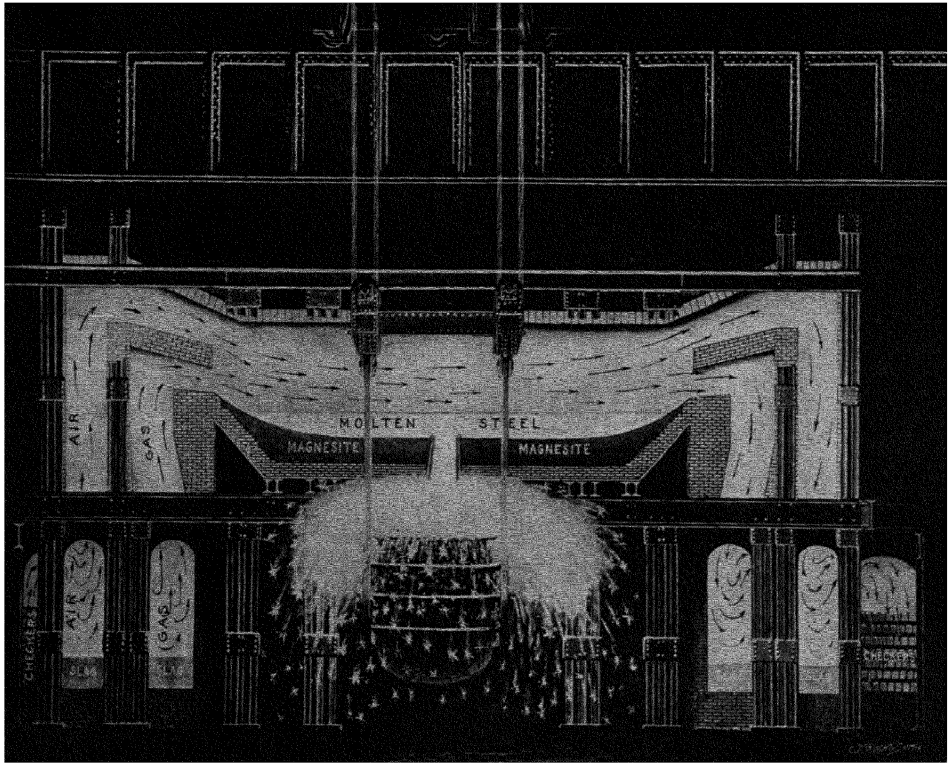

FIG. 148. — Open-Hearth Furnace. (Courtesy of the *Scientific American*. Copyright.)

as magnesite. The furnace is heated by the combustion of oil or a fuel gas in a blast of air. High temperatures are maintained by preheating the gases. This is accomplished most efficiently by the Siemens-Martin process. The entering gases are blown through a checker work of hot brick; and the emerging gases pass through a similar checker work on the opposite side of the furnace, so that the brick becomes strongly heated. The direction of flow of the gases is reversed at suitable intervals.

The charge consists of fifty to one hundred tons of pig iron, with the proper proportion of iron oxide from high-grade ore or oxidized scrap iron to oxidize the impurities in the pig iron. The oxides of silicon and phosphorus are acidic in nature and are not readily volatilized from the furnace. Hence, a basic flux is introduced. Carbon monoxide escapes as a gas and the oxides of sulfur, silicon, and phosphorus react with the basic flux to form a slag. Typical reactions are represented by the following equations.

$$3\ Fe_3C + Fe_2O_3 \longrightarrow 11\ Fe + 3\ CO.$$
$$6\ Fe_3P + 5\ Fe_2O_3 \longrightarrow 28\ Fe + 3\ P_2O_5.$$
$$P_2O_5 + 3\ MgO \longrightarrow Mg_3(PO_4)_2.$$

The process is complete in eight to ten hours and samples are removed from time to time to determine by analysis the completion of the reactions. The required percentage of carbon and other alloying materials is now added. Deoxidizers, known as "scavengers," are also added to remove entrapped gases which would produce flaws and weaken the steel. Aluminum, titanium, ferrosilicon, and ferromanganese are commonly used for this purpose.

The open-hearth process is under chemical control, and it employs an outside source of heat so that the metal may be kept in the liquid state as long as desired. Consequently, the product has uniform composition and is suitable for the manufacture of steel rails, bridge girders, and machinery.

The Bessemer Process. A process for burning carbon out of pig iron by means of a blast of air was patented by Kelly, an American, in 1852. The patent rights were secured and the process was perfected by Bessemer, an Englishman, in 1855. The process is carried out in a large converter made of steel and lined with silica and clay. The converter, Fig. 149, is mounted on trun-

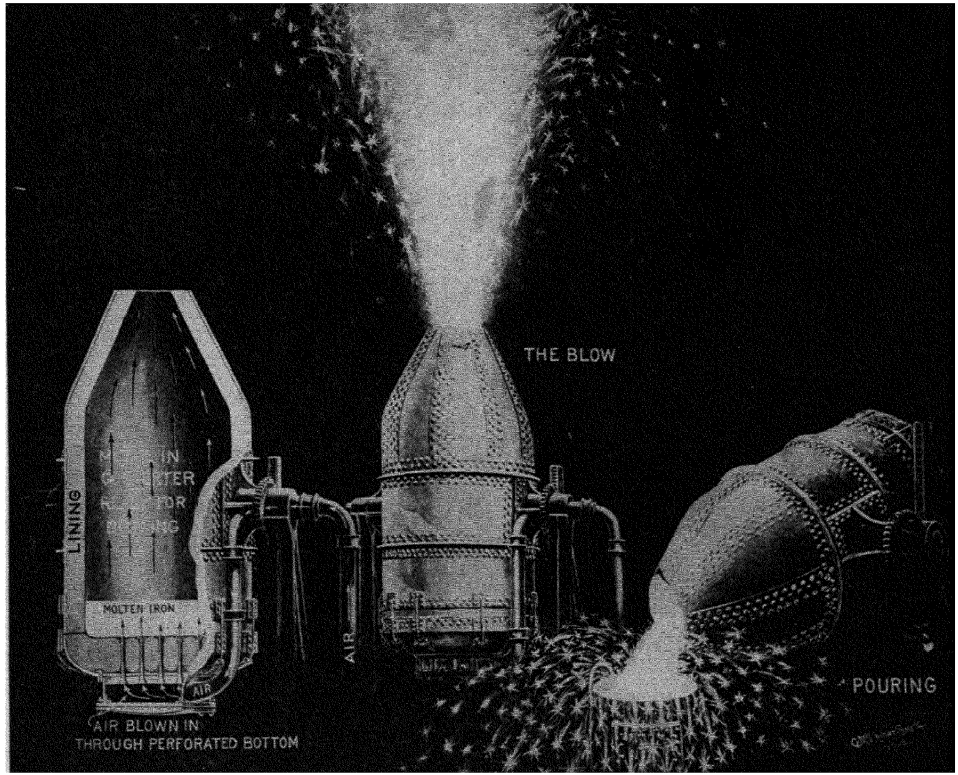

FIG. 149. — Bessemer Converter. (Courtesy of the *Scientific American*. Copyright.)

nions, so that it may be tipped to any desired angle. The charge, consisting of about 15 tons of molten pig iron, is introduced when the converter is in a nearly horizontal position. The converter is brought to the upright position and a blast of air is blown through the charge, the blast being admitted through a number of small openings in the bottom of the converter. The burning of the carbon, silicon, and manganese contained in the pig iron raises the temperature several hundred degrees, so that the charge does not solidify, although the melting point rises during the process of purification. Carbon is oxidized to carbon monoxide, which passes out as a gas and burns at the mouth of the converter. Silica unites with some of the oxidized iron to form a slag. When the flame of the burning carbon monoxide dies away, the converter is turned back to the horizontal position, cutting off the air blast; and the required amount of a high-carbon alloy is added. Scavengers are also introduced to remove entrapped gases and to reduce oxidized products. The molten steel, separated from the slag, is poured into molds to solidify. The reactions are complete in fifteen to twenty minutes. With the acidic lining of silica, the converter does not effect the removal of sulfur and phosphorus and is limited to the treatment of pig iron from ores which contain only very small percentages of these elements. It is possible to employ a lining of basic material for the Bessemer converter, as is done to some extent in British practice, thus providing for the removal of phosphorus, but the basic Bessemer process has not been extensively used in American practice. Bessemer steel is subject to certain defects due to the incomplete removal of objectionable materials and to the lack of uniformity of the product.

The development of the Bessemer process revolutionized industry by making available an adequate supply of steel. It thus made possible the rapid extension of the railroads and the development of this country during the years immediately following the Civil War. Bessemer steel is not suitable for steel rails to support the modern heavy locomotives and rapidly moving trains. It is now used primarily for machinery castings and as a structural metal.

Electric Furnace Steel. The high-grade steel required for automobile engines, axles, and wheels, and for airplane parts and tool steel must possess as exact and uniform composition as it is

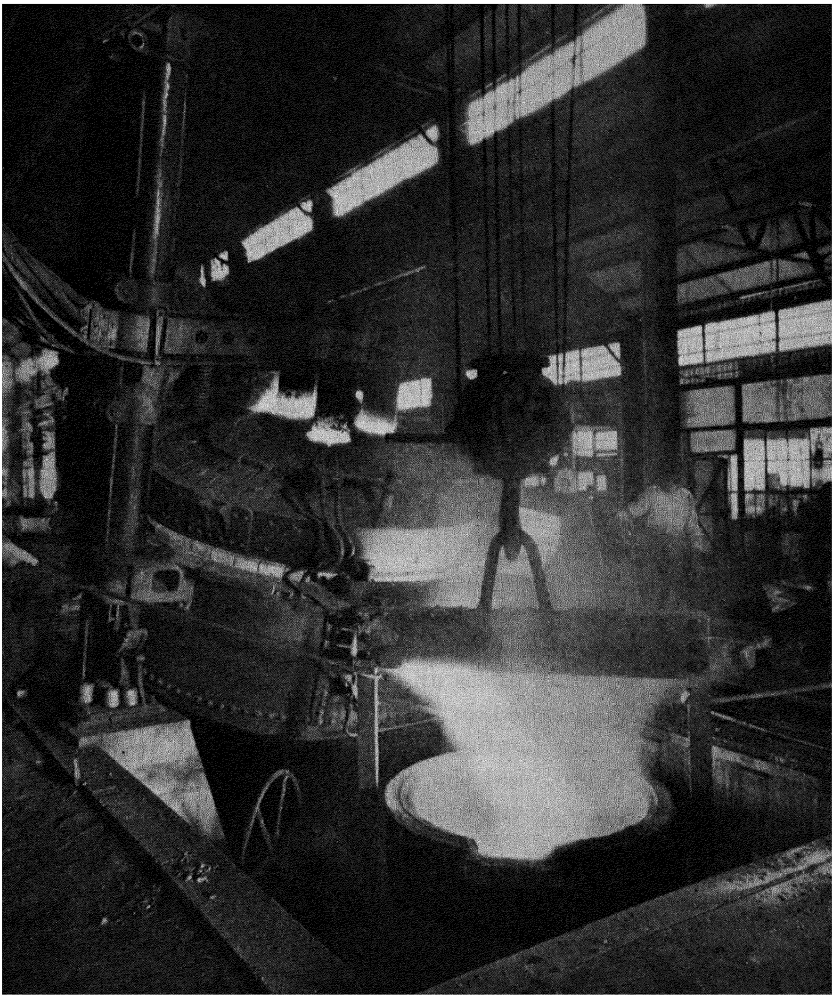

FIG. 150. — Pouring Molten Steel from Heroult Electric Furnace. (From Ewing Galloway, New York.)

possible to secure. Large quantities of this type of steel are produced in electric furnaces, which are essentially large crucibles heated by an electric arc, Fig. 151. The crucibles are provided with basic linings and the elimination of impurities in the iron is accomplished as in the open-hearth furnace. The electric furnace has the advantage over the open-hearth that high temperatures are maintained so that sulfur, silicon, and phosphorus may be removed more effectively, and the process is under more exact control. This makes possible not only a more nearly complete removal of the undesired ingredients, but also a higher degree of uniformity in the composition of the product. The charge is either the Bessemer or the open-hearth product.

A small quantity of *crucible steel* is made from wrought iron for the manufacture of tools, razors, watch springs, and other articles for which the specifications are rigid. Small quantities, 60 to 100 pounds, are produced in one batch, by heating wrought iron and carbon together in large graphite crucibles. Steel for these uses is now produced primarily in the electric furnace.

Wrought Iron. Wrought iron is a system composed of the two components, pure iron and slag. The per cent of slag in the metal varies from 1 to 3% depending on the type of product for which it is to be used. The slag is distributed throughout the iron in the form of fine fibers and films. The purification of the iron may be accomplished in a "puddling furnace," which is a reverberatory furnace having a basic lining. Iron oxide is used as the oxidizing agent, and the removal of the impurities in the iron involves a series of reactions of the same nature as those of the open-hearth process. As the impurities burn out, the melting point of the metal rises and a pasty mass is formed. The charge is "puddled" with an iron rod and blooms weighing about 100 pounds are withdrawn from the furnace and worked and rolled so as to squeeze out the excess of the slag and thoroughly to incorporate the desired proportions.

In the Aston process, molten pig iron of suitable composition is blown in Bessemer converters as in the production of steel. The purified product is then poured into a specially prepared slag maintained at a temperature several hundred degrees below the freezing point of the purified metal. The metal solidifies so quickly that the dissolved gases burst out with enough force to

shatter the metal into small solid fragments. These fragments settle to the bottom of the slag, where they cohere to form a sponge-like ball of iron impregnated with liquid slag. The excess of the slag is poured off and the sponge ball of iron, weighing 6000 to 8000 pounds, is squeezed in a press, so that the excess of the slag is forced out and the cellular mass of slag-coated particles of plastic iron is welded into a solid bloom. The bloom of wrought iron is then rolled to incorporate the slag thoroughly with the iron.

Wrought iron is tough, malleable, and has high tensile strength. It can be welded and worked under the hammer. This material is used for chains, bolts, anchors, and wire fencing. Its high melting point makes it suitable for making grate bars. The chief importance of wrought iron is due to its resistance to corrosion. This is attributed to the purity of the metal and the presence of films of slag which prevent the deep pitting of the product. Wrought iron is used on this account in making pipes and tubing, plates, sheets, and bars. Soft steel made in the open-hearth furnace has replaced wrought iron for many of these uses.

The Tempering of Steel. The properties of a carbon steel depend on the relative amount of carbon and the condition in which it exists in the steel. The system, iron-carbon, is very complex, because there are several different forms of iron; and a number of different compounds, solutions, and mixtures are possible, depending on the temperature, the concentration of the carbon, and the method applied in the heat treatment of the steel. At temperatures above 900°–1000°, the carbon, chiefly in the form of the carbide, cementite, is in stable equilibrium in solid solution in γ-iron, known as austenite. If the steel is cooled slowly from this temperature, cementite more or less completely separates from this solution and partially decomposes, as other transition temperatures are reached. The mixture thus obtained is soft steel because it contains free iron in the α-iron form mixed with graphite and cementite. If the steel is cooled quickly, there is insufficient time for equilibrium to be established at the various temperatures, and the solid solution, austenite, remains at room temperature at which further transitions occur slowly if at all. This product is very hard. If the hardened steel is reheated to some definite temperature, partial separation of the solid solution into iron and

cementite occurs, the extent of the separation depending on the temperature and the length of time allowed before suddenly cooling it to prevent further changes. The heat treatment of steel also modifies the properties by affecting the size of the minute crystals in the product.

Case-Hardened Steel. In the manufacture of certain articles, such as machine parts, it is often desirable to prepare a product which possesses the very hard surface of a high-carbon steel, but retains the toughness of a low-carbon steel in the body of the metal. This condition may be secured by manufacturing the article from low-carbon steel and then baking it, packed in carbon or in a cyanide, until the desired amount of carbon has been absorbed into the surface of the metal. Surface hardening may also be accomplished by heating the object in an atmosphere of ammonia gas. The ammonia decomposes and nitrogen combines with iron and certain of the alloying metals, such as aluminum, chromium, and molybdenum, to form nitrides of the metals.

Electrolytic Refining of Iron. The electro-deposition of iron may be applied in the refining of the crude pig iron made from iron ores containing much phosphorus. The crude iron is made the anode and the electrolytic bath is ferric chloride. It is possible in this way to cause iron to be deposited so as to form directly certain finished products, such as iron pipes. This method of refining iron may come into more extensive use as it becomes necessary to use the lower grade ores, which offer greater difficulties in the furnace processes than the ores now being used; but it is not now industrially important.

Corrosion and Protection of Iron. *The rusting of iron* exposed to moist air is due primarily to the action of carbonic acid to yield ferrous ions and the subsequent oxidation of the ferrous ions to ferric oxide by atmospheric oxygen. Pure iron does not rust appreciably, but the oxidation is favored by the presence of impurities in the iron. The rust is porous and does not adhere to the iron to protect it, as in the case of aluminum and magnesium. The painting of iron is intended to exclude moisture and other atmospheric substances. A paint which is useful for this purpose consists of a mixture of iron oxide and an oil. This is a device for covering the surface of the iron with iron oxide in a form that will stick to the metal. The paint, however, gradually wears off and

must be replaced. The different metal coatings, such as tin, zinc, chromium, aluminum, and cadmium, all have the same purpose; *viz.*, the protection of the iron by excluding the atmospheric substances which cause it to rust. Electroplating methods have been developed for the deposition of many of the metal coatings in an adherent form on the surface of iron; but methods of aluminum plating, which would make possible large savings in the upkeep costs of bridges, have not been developed to industrial success.

The Alloy Steels. Alloy steels are prepared by mixing metals in addition to, or instead of, carbon with the purified iron. Alloy steels containing relatively large per cents of the alloying metals are usually prepared in the electric furnace. Those containing relatively small proportions may be prepared in the open-hearth furnace. Machine parts which are lighter and stronger than similar parts made of carbon steel, may be manufactured through the use of alloy steels. This has been especially important in the automobile industry, in the manufacture of aircraft, and in transportation vehicles in general. Approximately 2,870,000 tons of alloy steels were produced in the United States in 1938, 670,000 tons in the electric furnace and most of the remainder in the open-hearth furnace.

The presence of some of these alloying elements affects the transitions in the iron-carbon system discussed in connection with the tempering of steel. In some instances, as in that of silicon, the effect is to increase the rate of the decomposition of the cementite and to make the steel soft. Nickel retards the transition of one of the forms of iron into another and causes the steel to retain its hardness. Tools made of carbon steel are not suitable for use in high-speed lathes, because they become heated by friction, and the metal undergoes a change in composition which results in the loss of temper. High-speed steel, such as *tungsten steel*, 10–25% of tungsten and 2–10% of chromium, and *molybdenum steel*, 6–7% of molybdenum, may be heated red hot without the loss of temper. *Manganese steel*, 10–15% of manganese, is very hard and tough and is used in safes and in machines for grinding. *Chrome steel*, 2–4% of chromium, is very hard and is suitable for files and other tools for cutting. *Chrome-vanadium steel*, 2–10% of chromium and 0.15% of vanadium, has high tensile strength and resistance to stresses and strains, and this steel finds application in automobile

parts. *Stainless steel*, containing 12–20% of chromium, small per cents of carbon, and sometimes other metals such as nickel and copper, is used in the manufacture of cutlery, valves, turbine blades, automobile parts, and in many chemical manufacturing processes. The iron alloy, known as "*Allegheny Metal*," contains 17–20% of chromium, 7–10% of nickel, and small per cents of other elements, such as manganese, silicon, and carbon, and has high resistance to corrosion. *Invar*, containing 35% of nickel, 64% of iron, and 0.5% each of carbon and manganese, has a very low coefficient of expansion. *An alloy cast iron*, containing 3.3% of carbon, 2.3% of silicon, 0.75% of manganese, 0.35% of chromium, 0.7% of nickel, and the remainder iron, is used for automobile blocks.

The Ferroalloys. The ferroalloys are alloys of iron and one or more of the other elements. Some of these are used in steel-making as deoxidizing agents and for the removal of entrapped gases. In this application, the alloy metal combines with oxygen or other impurities and the product goes into the slag. Other ferroalloys are introduced into the purified metal to form products which contain prescribed proportions of the alloying metal. The ferroalloys are commonly prepared by the reduction of a mixture of an iron oxide ore and the oxidized ore of the alloying metal in an electric furnace, or by the reduction of the oxidized alloying metal ore in a mixture with scrap iron or steel in an electric furnace. Ferromanganese, ferrochrome, and ferrosilicon may also be produced in a blast furnace process.

Ferrosilicon is prepared by the reduction of siliceous iron ore with carbon in an electric furnace. The silicon content ranges from 7–95%. This material is used in the steel industry both as a deoxidizer and for the introduction of silicon to form silicon steel and duriron.

Ferromanganese, containing 70–80% of manganese, and ***spiegeleisen,*** containing 15–30% of manganese, are prepared by the reduction of a mixture of the manganese ore, *pyrolusite*, MnO_2, and iron oxide with carbon in a blast furnace. They are used in the steel industry for the removal of oxygen and sulfur and for the introduction of manganese as an alloying metal. The pure metal may be prepared by the reduction of the oxide by aluminum.

$$3\ MnO_2 + 4\ Al \longrightarrow 3\ Mn + 2\ Al_2O_3.$$

The metal is also prepared by the reduction of the oxide with silicon in an electric furnace. The metal is used in the preparation of the alloy, *manganin*, which contains 84% of copper, 12% of manganese, and 4% of nickel. This alloy is used in electrical instruments because its resistance is affected to only a small extent by changes in temperature.

Ferrochrome is the product of the reduction of the mineral *chromite*, $Fe(CrO_2)_2$, with carbon in an electric furnace. The principal use of chromium is in the form of ferrochrome in the steel industry; but the pure metal may be prepared by the reduction of chromic oxide with aluminum or by heating it with silicon in an electric furnace. The metal is used in the production of alloys, such as "*nichrome*," containing 60% of nickel, 15% of chromium, and 25% of iron, which is used as a heating element in electric irons, stoves, toasters, and ovens. Another important chromium alloy is "*stellite*," which may be made in differing compositions, such as 60% of cobalt, 15% of chromium, 20% of tungsten, and 5% of molybdenum. This alloy may also contain 30% of cobalt, 4% of chromium, 14% of tungsten, and 52% of iron. These alloys are used in high-speed tools and in surgical instruments, which may be heated for sterilization without injury to the instrument.

Compounds of chromium are used in the chromium plating of copper, iron, and steel. A solution of chromic acid containing a small per cent of sulfates is the electrolyte; and the object to be plated is the cathode, with inert anodes.

Ferromolybdenum is made from the ore *molybdenite*, MoS_2. The ore is roasted to form molybdenum trioxide, MoO_3, and is then concentrated by leaching with ammonia, to form ammonium molybdate, which has variable composition. Ammonium molybdate is decomposed by heat, reforming the oxide in concentrated form. The oxide is mixed with scrap iron and reduced by carbon in an electric furnace. The product usually contains 50–60% of molybdenum. It is used in the production of tool steel and aircraft and automobile parts which are subject to high strain.

Ferrotungsten is produced by the reduction of the ferrous tungstate ore by carbon in the electric furnace. A familiar use of the pure metal is in the filament in electric light bulbs. To prepare the pure metal, the ore, *wolframite*, an isomorphous ferrous man-

ganous tungstate, is fused with sodium carbonate to form sodium tungstate. This compound is extracted by leaching with water. Tungstic acid is precipitated by the action of hydrochloric acid on the tungstate, and the acid is reduced by heating it with carbon. The melting point of tungsten is 3387° and the metal produced is a powder. The conversion of this powder into a metal suitable for the filament of a light bulb was found to be a difficult problem. The metal may be changed into a compact mass by passing an electric current through the powder, closely packed under great pressure. The small particles become sintered together, forming a brittle product which must be worked at low temperatures to break up the large crystals, so that it may be drawn into wire. The wire has high tensile strength and high resistance to the passage of the electric current, so that it becomes heated to incandescence. The bulbs must be filled with an inert gas, such as argon or nitrogen, to decrease the rate at which the filament evaporates.

Ferrovanadium, like most of the ferroalloys, is produced by heating a mixture of the oxide of vanadium and iron oxide with the calculated proportion of carbon in an electric furnace. The ore, *vanadinite*, $Pb_5(VO_4)_3Cl$, is leached with concentrated hydrochloric acid; and ammonium vanadate is next formed by the evaporation of the solution with an excess of ammonium chloride. The oxide is produced by heating ammonium vanadate. The pure metal may be secured by the reduction of the dichloride with hydrogen; but the pure metal has no important uses.

Ferrotitanium is valuable in the steel industry as a scavenger for the removal of nitrogen; and ***ferrozirconium*** is valuable as a scavenger for oxygen and for sulfur.

EXERCISES

1. What process is used for the reduction of iron oxide ores? Describe the furnace.
2. What is the composition of the charge and the function of each ingredient in this charge?
3. Write equations to represent typical reactions into which each ingredient of the charge enters.
4. What is the composition of each of the products of the blast furnace? For what purposes are these products used?

5. Why is it necessary to refine pig iron to produce a more valuable form of industrial iron?
6. Discuss the production of steel in the open-hearth process, showing clearly what is accomplished and how it is accomplished.
7. Compare the Bessemer process with the open-hearth process.
8. What is meant by the tempering of steel? What are some of the changes which occur during the heat treatment?
9. Discuss the corrosion of iron and steps which are taken to prevent it.
10. What are alloy steels? Give examples indicating the alteration in the properties of iron which are brought about by the use of alloying metals.
11. What are the ferroalloys? How are they commonly prepared?

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CHAPTER XXVI

THE TRANSITION ELEMENTS

The transition elements are structurally the elements composed of atoms which have an incomplete electron shell at a lower energy level than the valence shell. In each of the long periods of the elements, such a shell of electrons builds up with increasing atomic number from an intermediate complete shell of eight electrons, as the outermost shell, to a second stable configuration containing eighteen electrons in more complex atoms. The change commences with the third element following the inert gas in each of these long periods and is complete with the thirteenth element; *i.e.*, there are ten elements in each transition period. In the fifth period, there are an additional fourteen elements, the rare earths.

The elements of each B group occupy the corresponding position in the different transition series. They frequently show a greater similarity to the neighboring elements in the same period than to the corresponding elements in the group. The elements of Groups III–B and IV–B exhibit so great a similarity to the elements of Groups III and IV, respectively, that they have been discussed together in preceding chapters.

The elements in the transition series commonly exhibit more than one oxidation state, the lowest being an electrovalence, frequently 2 +. The elements of the higher numbered groups commonly exhibit positive oxidation numbers of the covalent type, in which they show the chemical characteristics of the nonmetals, and oxidation-reduction reactions are prominent. Many of these elements are at present unimportant and will receive only brief mention in this chapter. The general procedures for the production of the metals and the more important salts are discussed in other sections. Consequently, this chapter deals primarily with the relationships of the elements and the ions which they form.

GROUP I-B. COPPER, SILVER, AND GOLD

The elements of this group, like the alkali metals, are composed of atoms which have one valence electron and may form ions which have an electrovalence of 1 +. Otherwise, they differ from the alkali metals in a number of details. The outermost shell of the kernel of the atom inside of the valence shell contains eighteen electrons; and these atoms may lose electrons from this shell also under certain conditions, to form ions in higher valences. The elements have low activity and readily form complex ions.

The Properties of the Metals. Copper is a reddish-brown metal, silver a lustrous white metal, and gold a yellow metal. The metals are malleable and ductile and are excellent conductors of heat and electricity. They readily form alloys with each other and with other metals. Several of the physical properties of these metals are shown in Table 36.

TABLE 36

PROPERTIES OF COPPER, SILVER, AND GOLD

	Copper	*Silver*	*Gold*
Atomic weight . . .	63.57	107.88	197.2
Atomic number . . .	29	47	79
Isotopes	63, 65	107, 109	197
Electron structure . .	2, 8, 18, 1	2, 8, 18, 18, 1	2, 8, 18, 32, 18, 1
Oxidation numbers . .	1+, 2+	1+, 2+	1+, 2+, 3+
Melting point	1083°	960.5°	1063°
Density (20°), g. per ml. .	8.92	10.5	19.3

The Reactions of the Metals. These metals rank low in activity, and the activity decreases with increasing atomic numbers. When heated in an excess of air, copper unites with oxygen to form cupric oxide. Silver and gold do not oxidize under these conditions. Copper and silver unite with sulfur but gold does not. The product of the direct union of copper with sulfur is cuprous sulfide, even though an excess of sulfur be present. Copper and silver also unite readily with the halogens, but gold does not combine directly with them at ordinary temperatures. The metals of this group do not displace hydrogen from acidic solutions.

Copper and silver are dissolved by nitric acid, but gold does not react with nitric acid.

$$8\,H^+ + 2\,NO_3^- + 3\,Cu \longrightarrow 4\,H_2O + 2\,NO + 3\,Cu^{++}.$$

Gold is dissolved by aqua regia, on account of the increased reducing activity of gold in the presence of chloride ions, leading to the formation of the complex, chlorauric acid, $HAuCl_4$.

$$\begin{gathered} 4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO \\ Au + 4\,Cl^- + H^+ \longrightarrow HAuCl_4 + 3\,\epsilon \\ \hline 5\,H^+ + NO_3^- + Au + 4\,Cl^- \longrightarrow 2\,H_2O + NO + HAuCl_4. \end{gathered}$$

Uses of the Metals. Copper ranks high in importance. Of an estimated consumption of 800,000 tons of copper in the United States in 1939, approximately one half was used on account of its high conductivity of electricity in electrical machinery, light and power lines, and telephone and telegraph wires and cables. Large amounts of the metal are used in the production of alloys, Table 37.

TABLE 37

ALLOYS OF COPPER

Name	*Composition (Per Cents)*
Aluminum brass	Cu, 68–70; Zn, 27–31; Al, 1–3
Aluminum bronze	Cu, 90; Al, 10
Babbitt metal	Cu, 2–22; Sn, 70–90; Sb, 7–24
Bell metal	Cu, 75–80; Sn, 20–25
Brass	Cu, 60–90; Zn, 10–40
Britannia metal	Cu, 1–3; Sn, 90–95; Sb, 5–10
Bronze	Cu, 80; Sn, 15; Zn, 5
Constantan	Cu, 60; Ni, 40
Gun metal	Cu, 90; Sn, 10
Manganese bronze	Cu, 70–95; Mn, 5–30
Manganin	Cu, 82; Mn, 15; Ni, 3
Monel metal	Cu, 36; Ni, 60; Fe, 3.5; Al, 0.5
Nickel silver	Cu, 55; Ni, 20; Zn, 25

Since copper is a good conductor of heat and is not readily corroded, it is used in boilers, water heaters, and cooking utensils, and in the manufacture of roofing shingles and gutters, the sheathing of the bottoms of boats, and for a variety of similar purposes. Metals which corrode easily may be protected with a film of copper by an electroplating process, similar in principle to the

refining of copper. Electrotypes are made in a similar manner by making a cast of the object, coating it with graphite to give it conductivity, and using the prepared cast as the cathode in an electroplating cell.

Silver is a white metal of high luster. It is very ductile and malleable, and is the best conductor of heat and electricity among the metals. It reacts with sulfur and with hydrogen sulfide in the air and for this reason becomes tarnished. Silver is oxidized by nitric acid to form silver nitrate and by hot, concentrated sulfuric acid to form silver sulfate. Silver is used as an ornamental metal, for table silverware, and for coins. Pure silver is too soft for most purposes and an alloy with copper is usually used, the American coins containing 90% of silver. Sterling silver contains 92.5% of silver. Silver is used extensively for plating articles made of cheaper metals. The article to be plated is made the cathode in a bath of potassium silver cyanide with anodes of silver bars. From this bath, the silver is deposited more slowly and evenly than when the bath is a solution of silver nitrate. Mirrors may be silvered by reducing an ammoniacal solution of silver nitrate with glucose or formaldehyde. The deposit on the glass is varnished to protect it. Silver is used extensively in the preparation of its salts.

Gold has little practical value. The fixed value of gold as the basis of the American monetary system was $20.67 per troy ounce. The legal price of gold was fixed at $35 an ounce in 1934. For use in jewelry, gold is alloyed with copper. The purity of gold is expressed in carats, pure gold being 24 carat. Good jewelry is usually 14–18 carat gold. White gold may be produced by alloying the metal with nickel and zinc. A thin coating of gold is often deposited on copper in producing cheap jewelry. This may be done by electroplating through the use of a solution of the complex aurocyanide as the electrolyte. Gold is also used in dentistry.

The Ions of Copper. Copper forms ions in two oxidation states, cuprous compounds, Cu^{+}, and cupric compounds, Cu^{++}. Cupric ions result from the vigorous oxidation of copper by strong oxidizing agents, such as the halogens and nitric acid. Cuprous ions are formed by the mild reduction of cupric ions. Both cuprous and cupric ions yield a number of complex ions: *e.g.*, cuprous ammonia, $Cu(NH_3)_2^{+}$, cuprocyanide, $Cu(CN)_2^{-}$, and cupro-

chloride, $CuCl_2^-$; cupric ammonia, $Cu(NH_3)_4^{++}$, and chlorocuprate, $CuCl_4^{--}$; and the tartrate, $Cu(C_4H_6O_2)_2^{--}$, and hydrate, $Cu(H_2O)_4^{++}$. The common soluble cupric salts are the sulfate, chloride, and nitrate. Solutions of these salts are acidic because they contain the cation acid, $Cu(H_2O)_4^{++}$.

$$Cu(H_2O)_4^{++} + H_2O \rightleftharpoons Cu(OH)(H_2O)_3^+ + H_3O^+.$$

Cupric hydroxide, $Cu(OH)_2$, is precipitated as a gelatinous blue solid by the reaction of sodium hydroxide with a soluble cupric salt.

$$Cu(H_2O)_4^{++} + 2\ OH^- \rightleftharpoons Cu(OH)_2(H_2O)_2\downarrow + 2\ H_2O,$$
or
$$Cu^{++} + 2\ OH^- \rightleftharpoons Cu(OH)_2\downarrow.$$

This hydroxide reacts with an excess of hydroxide ions to form the soluble, dark-blue *cuprate ion, $Cu(OH)_4^{--}$.*

$$Cu(OH)_2(H_2O)_2 + 2\ OH^- \rightleftharpoons Cu(OH)_4^{--} + 2\ H_2O.$$
$$Cu(OH)_2 + 2\ OH^- \rightleftharpoons Cu(OH)_4^{--}.$$

The hydroxide is soluble in an excess of ammonia because of the formation of the complex ammonia ion.

$$Cu(OH)_2(H_2O)_2 + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4^{++} + 2\ OH^- + 2\ H_2O.$$

Cupric hydroxide is unstable, decomposing when heated in suspension to form the black oxide and water.

$$Cu(OH)_2 \longrightarrow CuO + H_2O.$$

Cupric oxide is formed also by the direct reaction of copper with an excess of oxygen and by the decomposition of the nitrate and carbonate.

Cuprous oxide, Cu_2O, is formed by the mild reduction of cupric compounds in alkaline solution. This reaction is used in Fehling's test for the presence of dextrose and other reducing sugars. The reaction is an important diagnostic test for the presence of sugar in urine as evidence of diabetes. When a solution of cupric sulfate containing a tartrate, to convert enough of the cupric ions into the complex tartrate to prevent the precipitation of cupric hydroxide, is made alkaline and boiled in the presence of dextrose, a red precipitate of cuprous oxide is formed.

Analytical Properties of Cupric Ions. Cupric sulfide is precipitated with the other members of the tin and copper groups by the passage of hydrogen sulfide into an acidic solution containing the ions of these metals. It is not dissolved by the dilute ammonium polysulfide solution used for the extraction of the sulfides of the tin group elements. Copper sulfide is dissolved by dilute nitric acid with the formation of the free cupric ions.

$$3\,CuS + 8\,H^+ + 2\,NO_3^- \longrightarrow 3\,Cu^{++} + 2\,NO + 4\,H_2O + 3\,S.$$

This solution gives a dark-blue coloration with an excess of ammonia. The cupric ion also yields a brown precipitate with potassium ferrocyanide.

$$2\,Cu^{++} + Fe(CN)_6^{----} \longrightarrow Cu_2[Fe(CN)_6]\downarrow.$$

Ions of Silver. The common oxidation state of silver is the electrovalence of 1 +, and silver nitrate is the most familiar of its soluble salts. The silver ion yields several complex ions: *e.g.*, silver ammonia, $Ag(NH_3)_2^+$, silver thiosulfate, $Ag(S_2O_3)_2^{---}$, and silver cyanide, $Ag(CN)_2^-$. The sulfate is only moderately soluble and the halides and sulfide are slightly soluble. The test for the silver ion is based on the formation of a white precipitate by reaction with chloride ions. This precipitate is insoluble in nitric acid and is dissolved by ammonia with the formation of the silver ammonia ion.

GROUP II-B. ZINC, CADMIUM, AND MERCURY

The atoms of these metals have two valence electrons outside of a stable shell of eighteen electrons. The metals are less active, and the hydroxides less basic, than the elements of Group II.

The Properties of the Metals. The polished surface of zinc has a white luster and of cadmium, a silvery-white luster. Mercury is a silvery-white liquid. Zinc is brittle when cast; but its malleability and ductility are high enough at temperatures between 100 and 150° to permit its being rolled into sheets and drawn into wire. Cadmium is harder than zinc, but it also has greater malleability and ductility. Mercury is the only metal which is stable in the liquid state at room temperature. Some of the common properties of these metals are shown in Table 38.

TABLE 38

PROPERTIES OF ZINC, CADMIUM, AND MERCURY

	Zinc	*Cadmium*	*Mercury*
Atomic weight . . .	65.38	112.41	200.61
Atomic number . . .	30	48	80
Isotopes	64, 66, 67, 68, 70	106, 108, 110, 111, 112, 113, 114, 116	196, 197, 198, 199, 200, 201, 202, 204
Electron structure . .	2, 8, 18, 2	2, 8, 18, 18, 2	2, 8, 18, 32, 18, 2
Oxidation numbers . .	2+	2+	1+, 2+
Melting point	419.4°	320.9°	− 33.87°
Boiling point	907°	767°	356.9°
Density (20°), g. per ml.	7.14	8.6	13.546

Reactions of the Metals. *Zinc* and *cadmium* are active enough to combine with oxygen at room temperatures; but the surface of the metals becomes coated with an adherent outer layer of the basic carbonate which protects the metal. The oxides of the metals are stable and the metals displace hydrogen ions from acidic solutions. *Mercury* does not combine with oxygen at room temperature and the oxide is easily decomposed by heat. It does not displace hydrogen ions from acidic solutions; but it does react with oxidizing acids to form mercurous ions if an excess of the metal is present, and mercuric ions if an excess of the oxidizing agent is present.

The Uses of the Metals. Approximately 275,000 of the 630,000 tons of *zinc* consumed in the United States in 1939 were used for galvanizing iron. The protective coating may be applied by dipping the cleaned metal into melted zinc, by electrolytic deposition, or by baking the metal with zinc in closed drums. Approximately 175,000 tons were used in making brass, and 62,000 tons and 89,000 tons in rolled zinc and die castings, respectively. Zinc is used in dry cells, in metallurgy for the extraction of silver from lead and for the displacement of silver and gold from the complex cyanide solutions, for the production of zinc oxide for use in paint, and for a number of other specific purposes.

One of the principal uses of *cadmium* is in bearing metals for internal combustion engines, approximately 250 tons having been used for this purpose in the United States in 1938. Cadmium is also used for the protection of iron against corrosion. The metal

is deposited electrolytically, and the plated articles are heated to cause the cadmium to alloy with the iron in the surface layer. Cadmium is used in the production of alloys, such as those of low melting point, and in the production of its compounds.

The use of *mercury* in barometers and thermometers is familiar. Mercury is used in vapor lights which are rich in rays of the shorter wave lengths, ultraviolet light. Mercury forms alloys, known as amalgams, with all of the common metals except iron and platinum. This property is applied in the amalgamation process for the extraction of gold and silver from native ores; and amalgams of tin, silver, and gold are used in dentistry. Some use is made of mercury as the liquid in heat engines, due to the high efficiency which these engines offer for the transfer of heat energy into work.

The Ions of Zinc and Cadmium. These metals yield simple divalent ions in acidic solution. The common soluble salts are the chlorides and sulfates. The nitrates also are highly soluble. Both of these ions hydrolyze in aqueous solutions of their salts, zinc ions being more highly hydrolyzed than those of cadmium.

$$Zn(H_2O)_6^{++} + H_2O \rightleftharpoons Zn(OH)(H_2O)_5^{+} + H_3O^{+}.$$
$$Cd(H_2O)_6^{++} + H_2O \rightleftharpoons Cd(OH)(H_2O)_5^{+} + H_3O^{+}.$$

Both zinc and cadmium yield slightly soluble hydroxides. Zinc hydroxide is amphoteric but cadmium hydroxide is not. Hence, the zinc hydroxide complex ion is present in basic solutions of zinc salts.

$$Zn(H_2O)_6^{++} + 4\,OH^{-} \longrightarrow Zn(OH)_4^{--} + 6\,H_2O.$$

Both zinc and cadmium ions yield complex ions with an excess of ammonia and with an excess of cyanide ions: $Zn(NH_3)_4^{++}$; $Cd(NH_3)_4^{++}$; $Zn(CN)_4^{--}$; and $Cd(CN)_4^{--}$. Cadmium also yields a complex iodide ion, CdI_4^{--}.

Analytical Properties of Zinc and Cadmium Ions. The difference in the solubilities of the sulfides of these two metals is great enough to permit the precipitation of cadmium sulfide in the acid hydrogen sulfide or copper group; while zinc sulfide is precipitated in the alkaline sulfide or nickel group. Cadmium sulfide is dissolved by dilute nitric acid and the cadmium ion produces the complex ion when an excess of ammonia is added to the solution

for the precipitation of bismuth hydroxide. Cadmium may be detected in the presence of copper, which exhibits a similar behavior, by converting the ammonia complex ions of both metals into the cyanide complex ions, followed by the saturation of the solution with hydrogen sulfide. Yellow cadmium sulfide precipitates under these conditions; but the cuprocyanide complex ion is so stable that no precipitate of copper sulfide forms to interfere with the cadmium test.

Zinc sulfide and manganous sulfide dissolve quickly when the nickel group precipitate is digested with dilute hydrochloric acid, leaving a residue of the sulfides of nickel and cobalt. The amphoteric nature of the zinc ion makes possible the separation from the manganous ion by the addition of an excess of sodium hydroxide. The test for the presence of zinc ions may be made by acidifying the solution containing the zinc hydroxide complex ions with acetic acid and passing hydrogen sulfide into this weakly acidic solution. Zinc ions yield a white sulfide.

The Ions of Mercury. The metal yields two ions, the mercurous ion, Hg_2^{++}, and the mercuric ion, Hg^{++}. The mercury atom contains two valence electrons outside of a complete shell of eighteen electrons. The mercurous ion, in which the atom has lost one valence electron and has an oxidation number of 1 +, still contains one electron in its outer shell. Two of these simple particles share electrons to form a complex ion, $(Hg : Hg)^{++}$. This complex ion exists not only in solutions of mercurous compounds, but also in the solid compounds. The stability of the ion is great enough to prevent the formation of other complex ions and to require vigorous oxidation to convert it into the mercuric ion. In the oxidation of mercury by a moderately active acidic oxidizing agent, the mercurous ion is formed if an excess of mercury is present. The mercurous ion is also formed by the mild reduction of the mercuric ion.

$$6\,Hg + 8\,H^+ + 2\,NO_3^- \longrightarrow 3\,Hg_2^{++} + 4\,H_2O + 2\,NO.$$
$$Hg^{++} + Hg \longrightarrow Hg_2^{++}.$$

The mercuric ion results from the oxidation of the metal and of the mercurous ion with an excess of an active oxidizing agent.

$$3\,Hg + 8\,H^+ + 2\,NO_3^- \longrightarrow 3\,Hg^{++} + 4\,H_2O + 2\,NO.$$
$$3\,Hg_2^{++} + 8\,H^+ + 2\,NO_3^- \longrightarrow 6\,Hg^{++} + 4\,H_2O + 2\,NO.$$

The common soluble salts of these ions are the nitrate and the sulfate. The ions hydrolyze to form acidic solutions.

$$Hg_2^{++} + 2\,H_2O \rightleftharpoons Hg_2(OH)^+ + H_3O^+.$$
$$Hg^{++} + 2\,H_2O \rightleftharpoons Hg(OH)^+ + H_3O^+.$$

The mercurous ion resembles the silver ion in many of its properties, but it does not form the complex ions which the silver ion yields. When an excess of sodium hydroxide is added to solutions of mercurous and mercuric ions, the oxides are precipitated. Mercuric ions react with chloride ions to form the slightly ionized mercuric chloride, which yields the complex ion, $HgCl_4^{--}$, with an excess of chloride ions. A similar complex iodide ion, HgI_4^{--}, known as "Nessler's reagent," is used in detecting small amounts of ammonia, by the formation of a yellow precipitate of the composition, Hg_2ONH_2I. Mercuric chloride also reacts with ammonia to form the white ammono-chloride, $HgNH_2Cl$.

Mercuric fulminate, $Hg(ONC)_2$, is formed by the reaction of ethyl alcohol with a hot solution of mercuric nitrate and nitric acid. It is insoluble in alcohol and water. It is stable when moist, but is a powerful explosive which detonates from a sharp blow, when it is dry. It is used in making percussion caps. ***Mercuric thiocyanate, $Hg(CNS)_2$,*** may be precipitated by mixing solutions of a mercuric salt and potassium thiocyanate. The solid may be mixed with enough dextrin solution to make a thick paste, and molded into small pellets, known as "Pharaoh's serpents." When these are dried and ignited, they burn, forming a very voluminous ash.

Tests for the Mercury Ions. Mercurous ions are detected by the fact that they yield a white precipitate with chloride ions. This precipitate darkens when ammonia is added, due to the formation of free mercury along with the ammono-chloride. Mercuric ions yield a black precipitate with hydrogen sulfide in acidic solution. This precipitate does not dissolve in hot, three-normal nitric acid, whereas the sulfides of the other copper group metals do dissolve in nitric acid of this concentration. Mercuric sulfide dissolves in aqua regia with the formation of mercuric chloride. After the removal of the free chlorine, the reaction of this solution with a limited amount of stannous chloride solution gives a white precipitate of mercurous chloride. With an

excess of stannous chloride, a black precipitate of finely divided mercury is obtained.

THE ELEMENTS OF GROUPS V-B, VI-B, AND VII-B

With increasing numbers of electrons in the outer shell of the kernel of the atom, the group relationships become less well defined, and the similarities between each element and those having the next lower and the next higher atomic numbers become more apparent.

The Oxidation States. These elements are characterized by a number of oxidation states, ranging upward from 2 + to the group number. The elements in Group V–B are *vanadium*, *columbium*, and *tantalum*. Vanadium yields compounds in the oxidation states 2 +, 3 +, 4 +, and 5 +. In the two lower states, the element forms simple positive ions, as represented by the salts, vanadous sulfate, VSO_4, and vanadic sulfate, $V_2(SO_4)_3$. The amphoteric nature of vanadium in the 4 + state is shown by the hydrolysis of the anhydrous chloride, VCl_4, to form vanadyl chloride, $VOCl_2$. In the 5 + state, the oxide, V_2O_5, is acidic; and the corresponding acid is metavanadic acid, HVO_3. Columbium and tantalum produce their most stable compounds as non-metallic elements in an oxidation state of 5 +. The pentachlorides of columbium and tantalum hydrolyze to produce the acids, metacolumbic acid, $HCbO_3$, and metatantalic acid, $HTaO_3$, respectively.

The elements of Group VI–B, *chromium*, *molybdenum*, *tungsten*, and *uranium*, may exhibit successive oxidation numbers from 2 + to 6 +, with some exceptions. The most important oxidation states of chromium and molybdenum are 3 + and 6 +. Chromium yields simple chromic salts which furnish the trivalent Cr^{+++} ion in acidic solution and the metachromite ion, $Cr(OH)_4^-$, in basic solution. Molybdenum forms similar simple salts in the oxidation state 3 +, but the hydroxide is not amphoteric. In the oxidation state of 6 +, these elements form compounds which are typical of the non-metals: *viz.*, chromates, such as potassium chromate, K_2CrO_4, and molybdates, such as sodium molybdate, Na_2MoO_4. The only important compounds of tungsten are in the 6 + state, represented by the tungstates, such as the normal sodium salt, Na_2WO_4. Although some uranium compounds in

the 4 + state are stable, the most important oxidation state of this element is 6 +, represented by the uranyl compounds, such as uranyl nitrate, $UO_2(NO_3)_2$.

Group VII–B contains the elements, *manganese*, *masurium* which has not yet been isolated, and *rhenium*. Manganese yields compounds in the oxidation states 2 +, 3 +, 4 +, 6 +, 7 +. The element exhibits the properties of a metal in producing the simple ions in the two lower oxidation states. In the 4 + state, manganese is weakly acidic, producing the oxide, MnO_2, and salts such as zinc manganite, $ZnMnO_3$. In the higher states, the element is distinctly non-metallic in nature, yielding the manganate ion, MnO_4^{--}, and the permanganate ion, MnO_4^-. The most stable oxidation state of rhenium is in the perrhenates, such as the acid, $HReO_4$.

Since the elements yield compounds in a number of states of oxidation, oxidation-reduction phenomena are prominently shown. The chemical nature of the element undergoes change from the metallic character in the low oxidation states to the non-metallic character in the high oxidation states. Consequently, the acidic or basic nature of the solution in which oxidation-reduction occurs affects the activity to a great extent. The general relationships will be discussed in Chapter XXXI, using the compounds of chromium and manganese as the basis of the discussion.

Properties and Reactions of the Elements. Most of these metals are hard and tough. They have high melting points, ranging from rhenium, 3440°, tungsten, 3387°, tantalum, 2850°, and molybdenum, 2620°, down to manganese, 1220°. They do not readily tarnish in air, but combine with oxygen at high temperatures. Most of these metals combine with the halogens and with sulfur. They are commonly attacked by the active oxidizing agents but do not readily displace hydrogen.

Uses of the Metals. With the exception of rhenium and uranium, the metals are used in the production of alloys, especially the alloy steels. For this use, they are prepared in the form of the ferroalloys, discussed in the preceding chapter. Tantalum has such great resistance to corrosion that it is used in chemical plant equipment. The carbides of several of these metals, vanadium, columbium, tantalum, molybdenum, and tungsten, are hard substances which may be used for cutting tools and wire-drawing dies.

The carbides of tantalum, columbium, and tungsten are particularly suited to these uses. Tantalum absorbs gases so readily that it is used in the vacuum tube industry, particularly in the production of electronic tubes.

IRON, COBALT, AND NICKEL

The atomic numbers of these elements place them between manganese in Group VII–B and copper in Group I–B. They are a natural group of elements, having similar structure and many similar chemical and physical properties. The greater similarity between elements of consecutive atomic numbers than between those of similar electronic groupings, as the number of electrons in the outer shell of the kernel of the atom increases, has been pointed out. Similar groups of three elements are in each of the long periods. In the fourth period, the elements, *ruthenium*, *rhodium*, and *palladium*, and in the fifth period, *osmium*, *iridium*, and *platinum*, bear a relation in these transition periods of elements which is similar to that of iron, cobalt, and nickel in the first of the long periods. No useful correlation can be made between iron, ruthenium, and osmium, which occupy the corresponding position in each of the three series.

Properties of Iron, Cobalt, and Nickel. The metals have a silvery luster, and are malleable and ductile. They have melting points between 1450° and 1530° and their densities differ by only a gram per milliliter. Each of the metals yields a number of important alloys. Some of the properties of the elements are shown in Table 39.

TABLE 39

PROPERTIES OF IRON, COBALT, AND NICKEL

	Iron	*Cobalt*	*Nickel*
Atomic weight . . .	55.85	58.94	58.69
Atomic number . . .	26	27	28
Electron structure . .	2, 8, 14, 2	2, 8, 15, 2	2, 8, 16, 2
Oxidation numbers . .	2+, 3+	2+, 3+	2+
Melting point	1530°	1490°	1452°
Density (20°), g. per ml.	7.86	8.9	8.9

Reactions of Iron, Cobalt, and Nickel. The pure metals do not rust in air at ordinary temperatures, but impure iron is

corroded in moist air. At elevated temperatures, these metals combine with oxygen, the halogens, sulfur, and carbon. Iron displaces hydrogen ions readily, while cobalt and nickel react only slowly with the hydrogen ions of acidic solutions. With oxidizing acids, iron yields trivalent ions, and cobalt and nickel form the divalent ions. The metals become passive in contact with concentrated nitric acid and with acid dichromate solutions. In this condition, they do not displace hydrogen ions from dilute solutions nor the ions of less active metals from salt solutions. When the passive metal is struck a sharp blow or is scratched, the passive condition is destroyed and the metal reacts normally.

The Ions of Iron. Iron forms two important series of salts, the ferrous salts and the ferric salts. The ferrous compounds are produced by the mild oxidation of the metal, as in the reaction with hydronium ions, and by the reduction of ferric ions.

$$Fe + 2\,H_3O^+ \longrightarrow H_2 + Fe^{++} + 2\,H_2O.$$
$$2\,Fe^{+++} + Sn^{++} \longrightarrow Sn^{++++} + 2\,Fe^{++}.$$

Ferric ions are formed by the oxidation of ferrous ions and by the stronger oxidation of the metal.

$$4\,H^+ + NO_3^- + 3\,Fe^{++} \longrightarrow 2\,H_2O + NO + 3\,Fe^{+++}.$$
$$2\,Fe + 3\,Cl_2 \longrightarrow 2\,FeCl_3.$$

The sulfates and chlorides are the most familiar of the soluble salts. The ions hydrolyze to form acidic solutions. In the presence of an excess of hydroxide ions, ferrous ions yield the hydroxide while ferric ions yield the hydrated oxide.

Ferric oxide reacts with acids to form ferric salts. It also reacts with the fused alkalies to form *ferrites*.

$$Fe_2O_3 + 2\,NaOH \longrightarrow 2\,NaFeO_2 + H_2O.$$

Magnetic oxide of iron is considered to be the ferrous salt of the metaferrite ion, $Fe(FeO_2)_2$. Strong oxidizing agents in basic solution oxidize ferric oxide to the ferrate in which the oxidation number of the iron is 6 +.

Analytical Properties of Ferrous and Ferric Ions. In the general analysis, the iron is in the ferrous condition in the filtrate from the precipitation of the acid hydrogen sulfide groups, regardless of its valence in the original substance.

$$2\,Fe^{+++} + S^{--} \longrightarrow 2\,Fe^{++} + S\downarrow.$$

Ferrous iron is now oxidized to the ferric condition by the action of nitric acid, because ferric iron gives a more satisfactory separation of the iron in the hydroxide precipitation than ferrous iron. Ferric hydroxide is then precipitated along with the hydroxides of aluminum and chromium by the addition of ammonium hydroxide.

$$Fe^{+++} + 3\ OH^- \longrightarrow Fe(OH)_3\downarrow .$$

Ferric hydroxide is not dissolved by the hot sodium hydroxide solution used for the separation of aluminum hydroxide, nor by the sodium peroxide which converts the chromic hydroxide into the soluble chromate. After the separation of the aluminum and chromium, the remaining precipitate may be dissolved in hydrochloric acid and a confirmatory test for iron made by the use of potassium ferrocyanide solution. The valence of iron in the original solution must be determined by direct tests made on small portions of this solution. The colors of the precipitates produced by reaction with potassium ferrocyanide and with potassium ferricyanide serve as tests for ferric and ferrous iron, respectively. Soluble ferrocyanides react with ferric iron to form the slightly soluble *Prussian blue*, $Fe_4[Fe(CN)_6]_3$. With ferrous iron, the ferrocyanides form a white precipitate of potassium ferrous ferrocyanide, $K_2Fe[Fe(CN)_6]$. A ferricyanide solution mixed with a ferric salt gives a dark brown solution containing undissociated ferric ferricyanide, $Fe[Fe(CN)_6]$; and with ferrous iron, the ferricyanide gives a dark blue precipitate, Turnbull's blue, commonly called a ferrous ferricyanide.

The Ions of Cobalt and Nickel. Cobalt yields both the cobaltous ions, Co^{++}, and cobaltic ions, Co^{+++}. The common salts are cobaltous chloride, sulfate, and nitrate. The cobaltic ion is an active oxidizing agent and its salts decompose readily. Strong oxidizing agents in alkaline solution convert cobalt hydroxide into the dioxide, CoO_2. Nickel yields the divalent ion, Ni^{++}. No salts are known containing trivalent nickel ions. Nickel also yields a dioxide which is important in the Edison storage cell, where it is produced by the oxidation of the nickelous compound at the anode in an alkaline solution.

Both cobalt and nickel ions yield complex ions with ammonia and with cyanide ions: $Co(NH_3)_6^{++}$, $Co(CN)_6^{----}$, $Ni(NH_3)_6^{++}$, $Ni(CN)_4^{--}$. Cobalt, especially, shows to a high degree the prop-

erty of forming coördinate bonds to build up a number of complex addition compounds which are more stable than the simple cobaltous ions. The cobaltinitrite ion, $Co(NO_2)_6^{---}$, is sometimes employed as a laboratory reagent in a test for potassium ions. A yellow precipitate is formed when a solution of sodium cobaltinitrite is added to a potassium salt in weakly acidic solution.

$$2\ K^+ + Na^+ + Co(NO_2)_6^{---} \rightleftharpoons K_2NaCo(NO_2)_6\downarrow .$$

Ammonium ions give a similar precipitate. The cobaltinitrite is prepared by the reaction of cobaltous nitrate with sodium nitrite and acetic acid.

$$Co^{++} + 5\ NO_2^- + 2\ HNO_2 \longrightarrow Co(NO_2)_6^{---} + NO + H_2O.$$

Analytical Properties of the Ions of Cobalt and Nickel. The sulfides of these metals are not precipitated from acidic solutions under the conditions used for the precipitation of the copper group. Since they yield ammonia complex ions, they do not precipitate in the iron group of hydroxides. The sulfides are precipitated from ammoniacal solution and remain as a residue when the group precipitate is digested with dilute hydrochloric acid. The presence of cobalt in the residue may be shown by the borax bead test. Cobalt borate gives a dark blue bead.

$$2\ CoS + 3\ O_2 \longrightarrow 2\ CoO + 2\ SO_2.$$
$$CoO + Na_2B_4O_7 \longrightarrow Co(BO_2)_2 + 2\ NaBO_2.$$

The precipitate may then be dissolved in aqua regia, the excess of chlorine removed by evaporation, and the presence of nickel shown by the formation of a scarlet precipitate when dimethyl glyoxime is added to the ammoniacal solution.

$$Ni^{++} + 2\ HON{=}C(CH_3)C(CH_3){=}NOH + 2\ OH^- \longrightarrow Ni(ON{=}C(CH_3)C(CH_3){=}NOH)_2\downarrow + 2\ H_2O.$$

The presence of cobalt does not interfere in this test since it forms a complex ion with dimethyl glyoxime instead of a precipitate.

EXERCISES

1. What is meant by the transition elements? In terms of the structures of the atoms, how are the elements of successive atomic numbers related to each other in the transition series?
2. How do the atoms of each B group resemble those of the main group? How do these groups differ structurally?

3. Mention points of similarity and difference between the elements of Group I–B and those of Group I.
4. Represent by equations the reactions (if any occur) of copper, silver, and gold with oxygen, sulfur, chlorine, and acids.
5. List the common complex ions of copper and silver, and give the conditions under which each is formed.
6. Discuss the relationships of the metals in Group II–B to those in Group II and to the metals in Group I–B.
7. What similarities and differences are shown by the metals of Group II–B with respect to each other?
8. Represent by equations the reactions which show the behavior of the metals of Group II–B with acids.
9. How may the ions in the low oxidation state be produced from the ions of the same metal in a higher oxidation state? Illustrate by equations for the formation of cuprous, mercurous, and ferrous ions.
10. How may ions in the high oxidation state be produced from those of the metal in a lower state? Illustrate by equations.
11. Explain the acidity of solutions of the ions of the elements in the transition series.

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CHAPTER XXVII

SALTS I. THE NITRATES

The most important of the naturally occurring substances are salts. The outer crust of the earth is composed chiefly of silicates, although large amounts of calcium carbonate occur as limestone and marble in various localities. There are also many salt deposits which are less abundant, such as the sulfates, sulfides, phosphates, nitrates, chlorides, and others.

Salts are compounds which contain the positive ions of basic substances and the negative ions of molecular acids. In the solid state they have crystalline structures in which the unit particles are ions. These particles exert strong forces of attraction and repulsion upon one another on account of the nature of the electric charges which they bear, and the crystal lattice is determined by these forces.

Properties of Salts. Most of the salts dissolve to a greater or less extent in water, becoming dispersed into ions by the action of water molecules on the ions in the solid salt. The crystalline structure is also broken down by melting the salts. Consequently, aqueous solutions of salts and fused salts are, in general, good conductors of the electric current. Aqueous solutions of salts exhibit great deviations from Raoult's law in the effects which they produce on the vapor pressure of water. The distinguishing properties of salts in solution are the properties which result from dispersion into ions; but there is no single set of properties which is characteristic of all salt solutions. Each salt in solution exhibits two series of reactions, one due to positive ions and the other to negative ions, and the properties of salt solutions are additive.

There are also some substances which exhibit the general properties of salts, but are not highly ionized even in dilute solution. Mercuric chloride is a substance of this type. The depression of the vapor pressure caused by this substance is nearly the same as that caused by non-electrolytes in the same molal concentra-

tion. Zinc and cadmium chlorides show the effects of higher ion concentrations than mercuric chloride, but their behavior also indicates incomplete ionization. Bjerrum has proposed the name "acidate" for substances which are derived from acids by the replacement of hydrogen ions by metals or other radicals without regard to their ionic nature. If this system is adopted, salts are a special class of acidates.

Types of Salts. Salts which contain neither replaceable hydrogen ions nor replaceable hydroxide ions are called *normal salts.* Sodium sulfate, Na_2SO_4, and sodium phosphate, Na_3PO_4, are normal salts. They become dispersed in solution into one variety of positive ion and one variety of negative ion. Salts which yield two different varieties of positive ions or two different varieties of negative ions are *mixed salts.* Sodium potassium carbonate, $NaKCO_3$, and calcium chloride hypochlorite, $CaCl(OCl)$, are mixed salts. Mixed salts which contain replaceable hydrogen ions are called *acid salts,* because the negative ion of the salt is an acid. These salts yield hydronium ions by interaction with water. Salts containing radicals which may take up protons are basic salts. Since the negative ions of all acids may add a proton, all salts are basic in nature. The name, basic salt, however, usually signifies a salt which contains hydroxide radicals or oxide radicals in a form which may neutralize acids. In this sense, the salts represented by the formulas $Pb(OH)NO_3$ and $BiOCl$ are basic salts. In order to avoid confusion, it is preferable to call these salts lead hydroxynitrate and bismuth oxychloride, respectively, rather than basic lead nitrate and basic bismuth chloride.

Many of the salts crystallize from aqueous solution as hydrated solids. The molecules of water of hydration are held by coördinate bonds to the positive ion or to the negative ion or to some particular atom in the ions of the salt. Thus, copper sulfate yields a pentahydrate, $CuSO_4(H_2O)_5$, in which four molecules of water are associated with each cupric ion and one with the sulfate ion, $Cu(H_2O)_4SO_4(H_2O)$. The dehydrating action of some salts is due to the low pressure of water vapor permitted by the system involving the hydrated salt, the anhydrous salt, and water in equilibrium.

The Formation of Salts. There are a number of reactions which may be carried out so as to produce salts. Many of these

reactions are unimportant as sources of the salt, and usually only one or two of the possible reactions are of practical importance. The method actually used in the preparation of any salt depends on the chemical nature and availability of the raw materials and on the relative simplicity of the procedure. The most abundant of the naturally occurring compounds of potassium is the complex silicate, $KAlSi_3O_8$, but this salt is insoluble and is not easily decomposed. Therefore, it is not a practical source of other potassium salts under ordinary conditions; and these salts are commonly prepared, directly or indirectly, from the much less abundant chloride.

The formation of a salt usually involves procedures by which its ions are brought together in solution in such concentrations that the pure solid may be separated from the solution. If the salt is *slightly soluble*, no particular difficulty is encountered. It is necessary merely to mix solutions of soluble substances which furnish the required ions in moderately high concentrations. The slightly soluble salt precipitates and is separated by filtration. The preparation of *a soluble salt* usually requires the removal of other ions, so that the ionic reactions may be virtually complete, leaving the ions of the desired salt together in solution. The solid is then recovered by evaporation. Reactions which may be selected for this purpose fall into two groups: *viz.*, *the formation of volatile weak electrolytes*, as in the reaction of a metal oxide, hydroxide, or carbonate with an acid; and *the formation of a precipitate*, leaving the soluble salt in solution. The ions of some of the salts are formed from the elementary materials by *oxidation-reduction*. Silver nitrate is commonly prepared by the reaction of silver with nitric acid.

THE NITRATES

Sodium nitrate is the only one of these salts which occurs in high enough concentration in natural deposits to serve as an industrial source of the salt. Such deposits are found, as already mentioned, in arid regions in Chile, Turkestan, and Egypt. Small proportions of potassium nitrate are found in all fertile soils. The nitrates, being soluble, are usually prepared in solution by the reaction of nitric acid with the oxide, hydroxide, or carbonate of the metal or with the metal itself. Consequently, the most important source of the nitrates is now atmospheric nitrogen.

Chemical Reactions of the Nitrates. The nitrates react with the acids of high boiling point, and nitric acid is distilled from the mixture, when the substances are heated together.

$$NaNO_3 + H_2SO_4 \longrightarrow HNO_3 + NaHSO_4.$$

Acidic solutions of the nitrates exhibit the same oxidizing activity as nitric acid itself. These reactions are due to hydrogen ions and nitrate ions, so that neutral solutions of nitrates are not active oxidizing agents. The reaction of concentrated hydrochloric acid with sodium nitrate yields free chlorine and nitrosyl chloride.

$$\begin{aligned} 4\,H^+ + NO_3^- + Cl^- + 2\,\epsilon &\longrightarrow 2\,H_2O + NOCl. \\ 2\,Cl^- &\longrightarrow Cl_2 + 2\,\epsilon. \\ \hline 4\,H^+ + NO_3^- + 3\,Cl^- &\longrightarrow 2\,H_2O + NOCl + Cl_2. \end{aligned}$$

The solid nitrates are unstable toward heat. The nitrates of sodium and potassium decompose to form the nitrite and oxygen.

$$2\,NaNO_3 \longrightarrow 2\,NaNO_2 + O_2.$$

When ammonium nitrate is heated gently it decomposes to form water and nitrous oxide.

$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O.$$

The nitrates of the remaining common metals decompose to form the oxide of the metal, nitrogen dioxide, and oxygen, except that the metal itself is the product if the oxide also is unstable.

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2.$$
$$2\,AgNO_3 \longrightarrow 2\,Ag + 2\,NO_2 + O_2.$$

The nitrates, consequently, exhibit oxidizing properties at high temperatures. The fusion of sulfur with sodium nitrate and sodium carbonate produces sodium sulfate. The equation representing the reaction may be derived in terms of the changes in oxidation numbers.

$$\begin{array}{c} N^{5+}\text{——————}(-2)\text{——}N^{3+} \\ 3\,NaNO_3 + S + Na_2CO_3 \longrightarrow 3\,NaNO_2 + Na_2SO_4 + CO_2. \\ S^{0}\text{——————}(+6)\text{——————}S^{6+} \end{array}$$

Sodium Nitrate. Chile Saltpeter. $NaNO_3$. Sodium nitrate occurs extensively in an arid region in Chile. The deposits are not uniform in composition, but they contain sodium nitrate in percentages varying from an unimportant proportion to as much as 40–50%. The nitrate is in a stratum containing a large proportion of earthy matter and varying percentages of sodium chloride, sodium sulfate, and other salts. This stratum is covered by a compact top layer. After digging out this material, it is sorted and the material containing 20–50% of sodium nitrate, known as *caliche*, is leached with hot water to extract the soluble sodium nitrate. As the hot solution cools, sodium nitrate crystallizes and the solid is separated. The cold saturated solution is reheated and is used again in the extraction of fresh caliche. The solid product obtained by this extraction process contains 95–98% of sodium nitrate, and is suitable for most of the industrial demands. Sodium nitrate is now prepared commercially on an extensive scale by the reaction of synthetic nitric acid, produced from atmospheric nitrogen, with sodium hydroxide or sodium carbonate.

Sodium nitrate is used in the production of sodium nitrite, potassium nitrate, nitric acid, and other substances. Sodium nitrate is also used extensively as a plant fertilizer. Although there is an abundant supply of nitrogen in the atmosphere, most plants cannot utilize the elementary substance to fill their nitrogen requirements, but secure their combined nitrogen from compounds in the soil. Peas, beans, clover, and other leguminous plants convert elementary nitrogen into nitrogen compounds through the action of beneficent bacteria on the root nodules. The proteins thus formed are converted successively into ammonia, nitrous acid and nitrites, and nitric acid and nitrates, through the action of other bacteria, when these plants decay.

The growth of these plants, therefore, serves to enrich the soil with nitrogen compounds; but additional large quantities of chemical fertilizers are required to maintain the proper balance of nitrogen compounds required for a fertile soil, because of the removal of nitrogen compounds by the harvesting of agricultural produce.

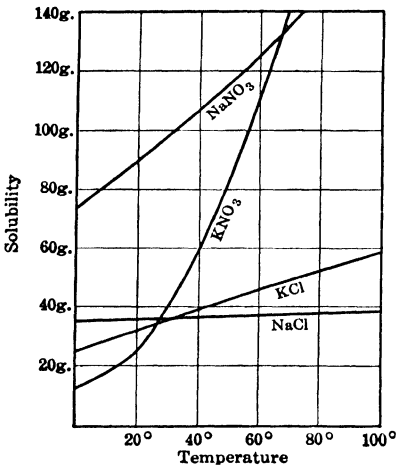

FIG. 151

Potassium Nitrate. Saltpeter. KNO_3. This salt is prepared from sodium nitrate and potassium chloride, both of which are readily secured from natural sources. The solubilities of potassium chloride, sodium nitrate, and potassium nitrate in water increase rapidly with rise in temperature; but the solubility of sodium chloride increases to only a small extent, as shown in Fig. 151. Hence, sodium chloride precipitates when hot, saturated solutions of potassium chloride and sodium nitrate are mixed, leaving a high concentration of potassium and nitrate ions in solution but only a low concentration of sodium and chloride ions.

$$K^+ + Cl^- + Na^+ + NO_3^- \rightleftharpoons NaCl\downarrow + K^+ + NO_3^-.$$

The hot solution is filtered to remove the sodium chloride, and potassium nitrate crystallizes as the solution cools because its solubility decreases greatly with the temperature.

Potassium nitrate is an active oxidizing agent at elevated temperatures. Formerly, the chief use of potassium nitrate was in the manufacture of gunpowder. *Black gunpowder* is a mixture containing 75% of potassium nitrate, 15% of sulfur, and 10% of carbon. When this mixture is ignited, a large volume of gaseous products, consisting principally of nitrogen and the oxides of carbon, is formed at high temperature. The reaction takes place rapidly and the gaseous products occupy a very large volume relative to that of the powder. Hence, this material is suitable for use as a propelling explosive. Potassium sulfide is formed as a

finely divided solid during the reaction, so that a cloud of smoke accompanies the explosion. Potassium nitrate was used in gunpowder in preference to sodium nitrate, because it takes up moisture much less readily. This type of gunpowder is no longer important, and the nitrocellulose powders are now used for propellent explosives. Potassium nitrate is used in preserving meat and in some high-grade plant fertilizers.

Ammonium Nitrate. NH_4NO_3. This white crystalline salt is prepared by the reaction of ammonia with nitric acid. When it is heated gently to a temperature somewhat above the melting point, 169.6°, ammonium nitrate decomposes into nitrous oxide and water. This salt is a high explosive, decomposing when detonated into nitrogen, oxygen, and water in a highly exothermic reaction.

$$2\ NH_4NO_3 \longrightarrow 2\ N_2 + O_2 + 4\ H_2O + 56{,}000\ \text{cal.}$$

The detonation is not easily brought about, but a mixture of ammonium nitrate and trinitrotoluene is used in shells as a military high explosive, called amatol; and ammonium nitrate is used in dynamite.

Silver Nitrate. Lunar Caustic. $AgNO_3$. The preparation of this salt is accomplished by the reaction of silver with nitric acid.

$$4\ H^+ + 4\ NO_3^- + 3\ Ag \longrightarrow 3\ Ag^+ + 3\ NO_3^- + NO + 2\ H_2O.$$

The solid salt is obtained by the evaporation of the solution. Silver nitrate melts at a temperature of 209°. The salt is used in the preparation of germicidal solutions; and thin sticks of the solid are used surgically as a cauterizing agent. Silver nitrate is an active oxidizing agent and it is reduced by organic matter to elementary silver, so that it leaves a stain on the hands and clothing. This salt is the most important of the soluble silver salts. It is used extensively in the laboratory as a source of silver ions. Large amounts of the salt are required industrially in the preparation of silver halide emulsions for use in photography.

Other Nitrates. Nitrates of most of the metals may be prepared by the reactions already discussed. They are useful in the laboratory as sources of the metal ions. Calcium nitrate may be prepared by the reaction of dilute nitric acid with limestone or with slaked lime. It is one of the products prepared from syn-

thetic nitric acid for use as a plant fertilizer. Barium nitrate and strontium nitrate are used as oxidizing agents in fireworks and in signal flares, because these metal ions impart characteristic colors to the flame: barium green, and strontium crimson. Mercurous nitrate and mercuric nitrate are prepared by the reaction of the metal with nitric acid, as already discussed. Lead nitrate is one of the important soluble lead salts. The ions of the metals of low activity hydrolyze to give acidic solutions, and a small excess of nitric acid is usually added to solutions of these nitrates to prevent extensive hydrolysis.

The Nitrites. The nitrites of the alkali metals are prepared by the thermal decomposition of the nitrates. The temperature required for the conversion may be decreased by heating the nitrate with carbon or with lead as a reducing agent.

$$2\ KNO_3 + C \longrightarrow 2\ KNO_2 + CO_2.$$

Sodium nitrite, with an equivalent amount of the nitrate, is produced by the absorption of nitrogen dioxide in sodium hydroxide.

$$2\ Na^+ + 2\ OH^- + 2\ NO_2 \longrightarrow 2\ Na^+ + NO_3^- + NO_2^- + H_2O.$$

Sodium nitrite is used extensively as a source of nitrous acid in the synthesis of organic products, such as some of the intermediate compounds in the production of dyes. Nitrous acid reacts with ammonia to form nitrogen and water. Hence, solutions containing ammonium and nitrite ions yield free nitrogen when heated.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+.$$
$$NO_2^- + H_3O^+ \rightleftharpoons HNO_2 + H_2O.$$
$$NH_3 + HNO_2 \longrightarrow N_2 + 2\ H_2O.$$

The Test for Nitrates. A delicate test for the presence of nitrates is based on the oxidizing action of the nitrate ion in acidic solution. The reduction product, nitric oxide, reacts with ferrous ions to form a highly colored, dark-brown addition product, $Fe(NO)^{++}$. The substance to be tested is dissolved in concentrated sulfuric acid in a test tube or cylinder. The tube is now inclined and a freshly prepared solution of ferrous sulfate is poured slowly down the side of the tube so as to form a separate layer above the more dense acid. In the presence of nitrates a brown ring is formed at the juncture of the two liquids. The reduction of nitric acid is represented by the following equation.

$$4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO.$$
$$[Fe^{++} \longrightarrow Fe^{+++} + 1\,\epsilon.] \times 3.$$
$$4\,H^+ + NO_3^- + 3\,Fe^{++} \longrightarrow 2\,H_2O + NO + 3\,Fe^{+++}.$$

Nitric oxide combines with the excess of ferrous ion in the solution to form the visible product. This is an indirect test for nitrates, since the final observation is based on a property of nitric oxide. Nitrites may be reduced to nitric oxide by ferrous ions in acidic solution, so that they also give a brown coloration under the conditions prescribed for the nitrate test. Nitrites, however, oxidize ferrous ions in weakly acidic solutions, such as acetic acid solutions, while the nitrate ion is more stable and requires a higher concentration of hydrogen ions. Nitrous acid and the nitrites decolorize dilute, acidic solutions of potassium permanganate, but the nitrates do not. Nitrous acid is a weak and unstable acid which decomposes at room temperature to form nitric oxide and nitrogen dioxide. Hence, nitrites may be removed from solution before applying the nitrate test, by heating the solution which has been acidified with dilute sulfuric acid. However, a portion of the nitrous acid decomposes to form nitric oxide and nitrate ions; and the brown ring test is not fully satisfactory if it is necessary to distinguish the presence of nitrates and nitrites in the same solution.

EXERCISES

1. What units of structure are characteristic of the solid salts? What is the nature of the binding force in a solid salt?
2. What general properties are shown by the solutions of the salts? What determines the specific properties of a salt solution?
3. What are normal salts? mixed salts? Explain the acidic properties of sodium hydrogen sulfate, and the basic properties of lead hydroxynitrate and bismuth oxychloride.
4. What general conditions must be met to produce any solid salt by the reaction of substances in solution?
5. What specific types of reactions may be used for the preparation of the soluble salts?
6. What is now the most important source of the nitrates? Write equations to represent the reactions involved in the preparation of three nitrates, using this source material and such other substances as may be required. Use a different final reaction in each example.
7. Represent by equations four reactions exhibited by sodium nitrate.

8. Explain the necessity for the use of chemical fertilizers to maintain soil fertility. What compounds may be used to supply the required nitrogen?
9. Explain the production of potassium nitrate by the reaction of sodium nitrate with potassium chloride.
10. Describe the nitrate test and represent the reactions by equations. Explain the interference caused by nitrites and tell how the two may be distinguished if they are present in different solutions.

SUPPLEMENTARY READINGS

Reichart and Schilz, "Nitrate Fields of Chile," *Chem. Met. Eng.* **46,** 464 (1939).
"Technology of the Chilean Nitrate Industry," *Ind. Eng. Chem.* **23,** 456 (1931).
Curtis, *Fixed Nitrogen.*

For the discussion of specific nitrates, reference should be made to a general treatise, such as:

Roscoe and Schorlemmer, *Treatise on Chemistry.*
Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry.*

CHAPTER XXVIII

SALTS II. THE HALIDES, CYANIDES, AND SULFIDES

The halides and sulfides of the metals are binary salts. These substances differ structurally from the halides and sulfides of non-metals in which the binding of the atoms is due to shared electrons. The binary salts are composed of ions in the solid state and they become dispersed into free ions in aqueous solution. With few exceptions, such as the sulfides of metals which yield weakly basic and slightly soluble hydroxides, the binary salts are incompletely hydrolyzed in the presence of an excess of the hydroacid; while the binary compounds of the non-metals with the halogens and with sulfur are generally completely decomposed by water.

THE HALIDES

The chlorides are the most abundant and important of the halides and attention will be devoted primarily to these salts. Chlorides, bromides, and iodides occur in similar compounds in sea water and in salt beds; and they exhibit similar properties and reactions. The fluorides are obtained from different sources, and they exhibit marked differences from the other halides.

Salt Beds. Sodium chloride constitutes two thirds of the soluble material present in sea water; and great salt beds composed largely of this salt occur in different parts of the world. These salt beds were formed by the evaporation of water from inclosed portions of the sea and from great inland salt lakes. Soluble salts leached from the soil gradually accumulate in these lakes until the water becomes saturated with one after another of the salts; and the deposition of the solids occurs as further evaporation takes place. Consequently, the composition of the deposit varies in different strata. The bottom layer in such deposits is a comparatively thin stratum of calcium sulfate. Above this, there is a relatively thick layer composed chiefly of

sodium chloride; and the upper strata contain other more soluble salts deposited during the final stages of the evaporation of the lake. In the Stassfurt deposit, Fig. 152, there is a layer of common salt approximately one-half mile thick. The thinner upper strata contain *sylvite*, potassium chloride, *carnallite*, a double chloride of potassium and magnesium, $KClMgCl_2(H_2O)_6$, and other salts. It is only in the thick salt deposits that the relative amount of potassium chloride is sufficiently large to be economically important.

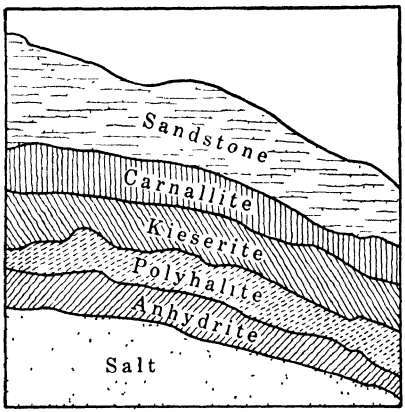

FIG. 152. — Stassfurt Salts.

Reactions of the Halides. The halides, with the exception of those which are only very slightly soluble, react readily with acids of high boiling point, with the formation of the gaseous hydrogen halides.

$$H_2SO_4 + 2\,NaCl \longrightarrow 2\,HCl + Na_2SO_4.$$

However, acids of strong oxidizing power, such as hot, concentrated sulfuric acid, oxidize hydrogen bromide and hydrogen iodide more or less completely to the free elements.

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

Solutions of chlorides, bromides, and iodides react with strong oxidizing agents in the presence of hydronium ions to form the free halogens.

$$2\,Cl^- + MnO_2 + 4\,H^+ \longrightarrow Cl_2 + Mn^{++} + 2\,H_2O.$$

The reducing activity of the halides increases with the atomic number of the halogen, and the fluorides are not oxidized by chemical oxidizing agents to form fluorine and water. The chlorides, bromides, and iodides of silver, mercurous, cuprous, and lead ions are only slightly soluble, and mercuric iodide also has low solubility. Hence, these metal ions react with the halide ions to precipitate the corresponding crystalline solid. These three reactions are dependent on the presence of the halide ions. In addition, each halide has a series of reactions which are due to

its metal ions. These reactions serve to distinguish one halide from another.

The Halides of Sodium and Potassium. ***Sodium chloride*** is mined from salt deposits which are near the surface of the earth, and is leached by water from deposits which lie at some distance beneath the surface, forming a brine which is pumped out from salt wells. The impure salt, obtained by the evaporation of sea water and from salt deposits, may be purified by recrystallization from aqueous solution. Pure salt may be precipitated from its saturated solution by the addition of concentrated hydrochloric acid or by passing hydrogen chloride gas into the solution. This is due to the great increase in the concentration of chloride ions. Sodium chloride crystallizes in cubes. The pure salt is not deliquescent under normal conditions, because its solubility is not sufficiently great to produce the requisite lowering of the vapor pressure. The presence of small amounts of impurities such as magnesium chloride causes the caking of table salt in damp weather. Salt is an essential ingredient of animal food. It is the source of all our manufactured sodium and chlorine compounds; and more than 9,000,000 tons of this salt were produced in the United States in 1939. The chart, Fig. 153, indicates the industrial importance of common salt.

Potassium chloride is the source of most of the prepared compounds of potassium; but its most extensive use is as a fertilizer to furnish the potassium compounds required by growing plants. Before the great war of 1914 to 1918, the demand for potassium salts was met largely by production from the salt deposits in Germany. Potassium chloride is obtained from carnallite, the double salt of potassium chloride with magnesium chloride, by heating it with a limited proportion of water. Most of the potassium chloride precipitates because it is less soluble than magnesium chloride. Since this source was unavailable in the United States during that war, it was impossible to obtain potassium compounds in sufficiently large quantities to meet the demands. The supply of potassium salts to fill the requirements of American chemical and agricultural industries is now assured, even though the war in Europe has again interrupted the importation of these compounds. The production of potassium compounds is now carried out extensively at Searles Lake in California and in the

Carlsbad region in New Mexico. The production of potassium salts in the United States in 1939 was approximately 450,000 tons, calculated in terms of the potassium oxide equivalent.

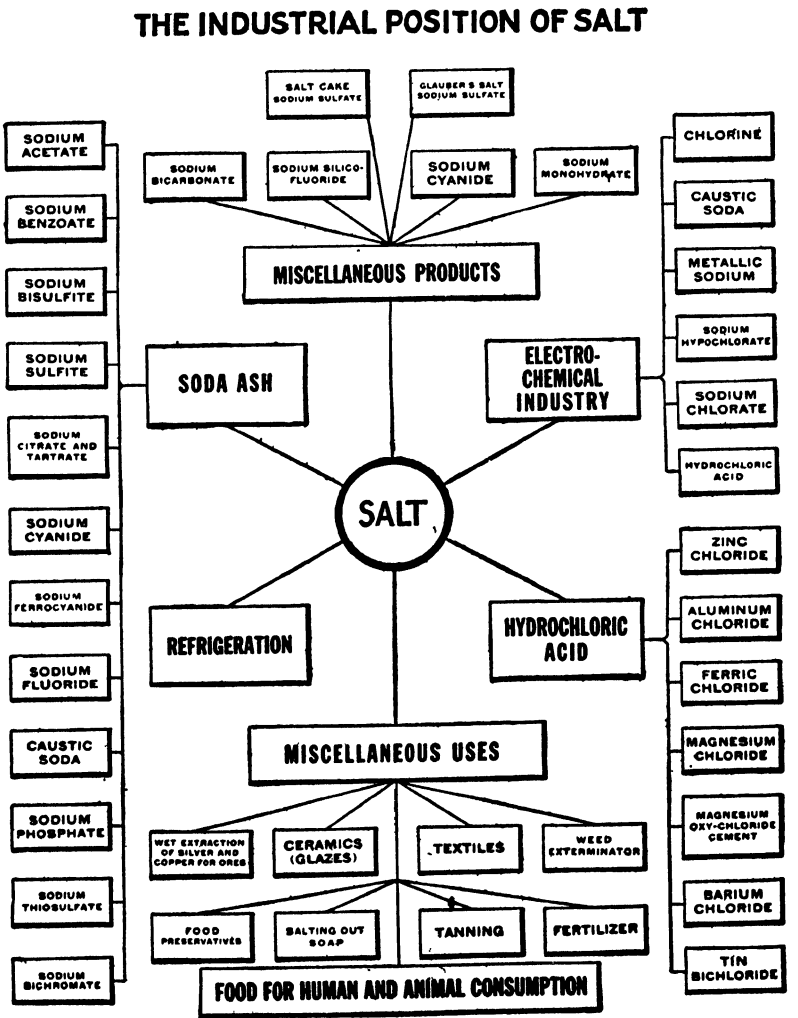

FIG. 153. — (Courtesy of International Salt Company, Inc. Copyright 1922.)

The production of potassium chloride from the Searles Lake brines has resulted from the application of the laws of chemical equilibrium to a complex system containing many components. The Searles Lake deposit consists of an extensive bed of solid salts

in a very complex mixture. The spaces between the crystals are filled with a saturated brine containing K^+, Na^+, Cl^-, CO_3^{--}, SO_4^{--}, $B_4O_7^{--}$, PO_4^{---} ions, and small percentages of other ions. The brine is pumped out and concentrated in evaporators until the solution is saturated with potassium chloride at the temperature employed. During this evaporation, large amounts of sodium chloride and the salt, $Na_2CO_3(Na_2SO_4)_2$, separate. When the solution has become saturated with respect to potassium chloride, it is also nearly saturated with borax. If the solution cools slowly, a mixture of potassium chloride and borax separates; but the borax crystallizes very slowly and it is possible to secure a crop of nearly pure potassium chloride crystals by cooling the solution quickly. After separating the potassium chloride, the mother liquor is kept in storage tanks for a few days and the borax crystallizes from its supersaturated solution. The crude product is separated, dissolved in hot water, and recrystallized.

The solution from which the crude borax has been separated is mixed with the brine from the lake before evaporation, thus making it possible to control the sulfate and carbonate concentrations so that the salt, sodium carbonate-sodium sulfate, separates instead of the slightly soluble mixed salt, potassium sodium sulfate. The precipitation of the latter substance during the evaporation would prevent the success of the process, since it would carry potassium ions out of the solution.

The Bromides of Sodium and Potassium. Small proportions of bromides are present in sea water and in the brines from the salt wells in Michigan and in other localities. The direct crystallization of sodium and potassium bromides from these brines is not practicable, on account of the large proportions of other ions in the concentrated brines. Bromine is prepared from the brines by displacement with chlorine and the salts are prepared from the element.

$$2\,Br^- + Cl_2 \longrightarrow 2\,Cl^- + Br_2.$$

Sodium and potassium bromides are prepared by the same method, the reaction of the halogen with hot solutions of the respective alkali hydroxides to form a mixture of the bromide and bromate.

$$3\,Br_2 + 6\,OH^- \longrightarrow BrO_3^- + 5\,Br^- + 3\,H_2O.$$

The solution is evaporated to dryness and the bromate is reduced to the bromide by heating the mixture with carbon.

$$KBrO_3 + 3\,C \longrightarrow KBr + 3\,CO.$$

The bromide is extracted and purified by recrystallization. These salts are used medicinally in the treatment of nervous disorders, and in the laboratory to furnish bromide ions; but their most extensive industrial application is in the preparation of silver bromide for use in photography.

The Iodides of Sodium and Potassium. These salts are prepared in the same manner as the bromides. Potassium iodide is the more common of the two salts and its principal use, as in the case of the bromide, is in the production of silver iodide. Potassium iodide is used medicinally to cause the absorption of blood clots. Thyroxine, an organic compound containing a large per cent of iodine, is secreted in the thyroid gland, and a deficiency of iodides interferes with the proper production of this compound and results in a type of goiter. Iodine compounds to supply this need are generally obtained in sufficient amounts from water and from the mineral matter in vegetables; but, in sections of the country where the supply is inadequate, iodide solutions and common salt prepared to contain sodium iodide are prescribed.

Ammonium Chloride. NH_4Cl. This salt is also known as sal ammoniac. It is prepared by the reaction of ammonia with hydrochloric acid.

$$NH_3 + HCl \longrightarrow NH_4Cl.$$

It is also formed in the reaction of ammonium bicarbonate with sodium chloride in the Solvay process for the production of soda. Ammonium chloride volatilizes when it is heated and it is partially decomposed. At 338°, 62% of the substance is present in the gaseous state as ammonia and hydrogen chloride. The equilibrium is displaced with the reformation of ammonium chloride as the gases cool, so that ammonium chloride may be purified by sublimation. A familiar use of ammonium chloride is in the manufacture of dry cells. It is also used as a flux in soldering to clean the oxide from the surface of the metal. This is due to the acidic properties of the ammonium radical.

$$CuO + 2\,NH_4^+ \longrightarrow Cu + 2\,NH_3 + H_2O.$$

Calcium Chloride. $CaCl_2$. The reaction of calcium hydroxide with ammonium chloride to recover ammonia in the Solvay process for soda yields calcium chloride.

$$2\,NH_4^+ + 2\,Cl^- + Ca^{++} + 2\,OH^- \longrightarrow 2\,NH_3 + 2\,H_2O + Ca^{++} + 2\,Cl^-.$$

The most important uses of calcium chloride depend on its high solubility in water. The freezing point of water from the saturated solution is $-55°$, and the solution is useful as a refrigerating brine in cold storage plants. The solid is deliquescent and absorbs enough moisture to make it useful on dirt roads to keep down the dust. Calcium chloride yields several hydrates. The anhydrous salt and the dihydrate are used extensively as drying agents. Since calcium chloride combines with ammonia, it is used as an absorbent for this gas in the absorption type of refrigerating machines previously discussed.

Magnesium Chloride. $MgCl_2$. The occurrence of magnesium chloride in sea water and in salt beds has been discussed. The salt crystallizes from solution as the hydrate, $MgCl_2(H_2O)_6$. This salt hydrolyzes in hot water to form magnesium hydroxy ions and hydronium ions.

$$Mg(H_2O)_6^{++} + H_2O \rightleftharpoons Mg(OH)(H_2O)_5^+ + H_3O^+$$

Consequently, water containing this salt is not suitable for use in steam boilers on account of the corrosion and scale formation which it causes. Magnesium chloride combines with magnesium oxide to produce the oxychloride, Mg_2OCl_2, which is very stable and is used under the name "Sorel cement" in the preparation of a substitute for tile. Magnesium chloride is deliquescent and its presence in table salt causes the salt to cake in damp weather. The anhydrous chloride is prepared for use in the production of the metal by heating the hexahydrate in air to form the dihydrate, which is then completely dehydrated in an atmosphere of hydrogen chloride gas.

Chlorides of Copper. There are two chlorides of copper, *cupric chloride*, $CuCl_2$, and *cuprous chloride*, $CuCl$. Anhydrous cupric chloride may be formed as a yellow solid by the direct union of the elements. The evaporation of solutions of cupric chloride yields the dihydrate, $CuCl_2(H_2O)_2$. Dilute solutions of cupric chloride are blue because of the presence of cupric ions.

The more concentrated solutions have a green color due to the presence of the complex ion, $CuCl_4^{--}$. Cuprous chloride may be formed by boiling an acidic solution of cupric chloride with metallic copper. The complex ion, $CuCl_2^-$, first formed, is decomposed to form the white cuprous chloride, CuCl, when the solution is diluted.

$$Cu^{++} + 4\,Cl^- + Cu \longrightarrow 2\,CuCl_2^-.$$

$$CuCl_2^- \rightleftharpoons CuCl\downarrow + Cl^-.$$

Chlorocuprous acid, $HCuCl_2$, absorbs carbon monoxide, so that it may be used in gas analysis for this purpose.

Chlorides of Mercury. Mercury yields chlorides in its two common oxidation states. *Mercuric chloride, corrosive sublimate, $HgCl_2$,* is usually prepared by subliming it from a mixture of mercuric sulfate and sodium chloride.

$$HgSO_4 + 2\,NaCl \longrightarrow Na_2SO_4 + HgCl_2.$$

It is a white crystalline salt which is only moderately soluble in water, but is slightly ionized in solution. Mercuric chloride in dilute solution is used as a germicidal solution for the irrigation of wounds. Mercuric chloride is highly poisonous and care must be exercised to avoid taking it internally. Tablets for the preparation of the germicidal solutions are generally colored blue by the presence of an inactive coloring material. Mercuric chloride forms insoluble compounds with proteins, so that the white of eggs is used as an antidote in cases of bichloride poisoning. The reduction of mercuric chloride with mild reducing agents yields mercurous chloride, and with stronger agents, free mercury.

Mercurous chloride, calomel, Hg_2Cl_2, is prepared commercially by heating mercuric chloride with mercury, or by heating a mixture of mercuric sulfate, salt, and mercury. Mercurous chloride is sublimed from the mixture.

$$HgSO_4 + 2\,NaCl + Hg \longrightarrow Na_2SO_4 + Hg_2Cl_2.$$

Calomel is used medicinally to stimulate the organs which produce secretions, notably the liver. When exposed to light, mercurous chloride slowly decomposes, forming mercuric chloride and free mercury. The properties of these compounds which are due to the metal ions have been discussed more fully elsewhere.

Other Soluble Chlorides. Since the chloride ion is the anion of a strong acid, the chlorides are stable toward hydrolysis when

an excess of hydrochloric acid is present in the solution. Many of these salts have extensive laboratory applications as sources of metal ions; *barium chloride*, for example, is the common source of barium ions in the laboratory test for the sulfates. *Zinc chloride* converts cellulose into a gelatinous mass which hardens to form a product that is almost impervious to water. It is used on this account as a timber preservative to form a coating to keep out moisture.

Tin and *iron* yield chlorides in two oxidation states. Both metals yield the ion in the lower oxidation state as the result of the reaction of the metal with hydrochloric acid.

$$Fe + 2\,H_3O^+ \longrightarrow Fe^{++} + H_2 + 2\,H_2O.$$
$$Sn + 2\,H_3O^+ \longrightarrow Sn^{++} + H_2 + 2\,H_2O.$$

The moderately strong reduction of the ions in the high state also produces the ion having the lower oxidation number.

$$2\,Fe^{+++} + Fe \longrightarrow 3\,Fe^{++}.$$
$$2\,Fe^{+++} + H_2S + 2\,H_2O \longrightarrow 2\,Fe^{++} + 2\,H_3O^+ + S\downarrow.$$

Vigorous oxidation of the metals and of the divalent ions produces the ions in the high state of oxidation.

$$2\,Fe^{++} + Cl_2 \longrightarrow 2\,Fe^{+++} + 2\,Cl^-.$$
$$Sn + 2\,Cl_2 \longrightarrow SnCl_4.$$

The reaction of chlorine with tin may be used for the detinning of scrap tinplate and for the preparation of stannic chloride. These metal ions react with water to form acidic solutions. The ions in the higher oxidation states are more highly hydrolyzed than in the lower state.

$$Fe(H_2O)_6^{+++} + H_2O \rightleftharpoons Fe(OH)(H_2O)_5^{++} + H_3O^+.$$

Stannic chloride is a colorless liquid which fumes strongly in moist air on account of the formation of the hydrated oxide of tin and hydrochloric acid. The compound is almost completely hydrolyzed in solution, but yields the complex chlorostannate ion, $SnCl_6^{--}$, in the presence of an excess of hydrochloric acid. The hydrate having the composition, $SnCl_4(H_2O)_5$, may be crystallized from acidic solutions. This substance is used as a mordanting and fireproofing agent for cotton goods. It reacts with sodium hydroxide to produce sodium stannate which may be converted

to the hydrated oxide in contact with the fiber, to which it adheres firmly.

Insoluble Halides. The chlorides, bromides, and iodides of the silver, lead, mercurous, and cuprous ions are only slightly soluble in water. Mercuric iodide is also virtually insoluble. These salts may be prepared by precipitation. Lead chloride is the most soluble of these slightly soluble halides, and its solubility increases rapidly with rise in temperature. The solubilities of the fluorides differ greatly from those of the other halides. Silver fluoride is a highly soluble salt; and sodium fluoride is much less soluble than the other alkali halides. The fluorides of the alkaline earth metals are only slightly soluble.

Silver Halides. These salts are precipitated by the reaction of soluble chlorides, bromides, and iodides with silver nitrate. Silver chloride is white, the bromide is pale yellow, and the iodide is distinctly yellow. Silver chloride dissolves readily in ammonia with the formation of the silver ammonia ion; silver bromide dissolves in solutions containing a high concentration of ammonia; but silver iodide does not dissolve appreciably in aqueous solutions of ammonia. The silver halides dissolve in cyanide solutions and in solutions of sodium thiosulfate with the formation of complex ions.

$$AgBr\downarrow + 2\,CN^- \rightleftharpoons Ag(CN)_2^- + Br^-.$$
$$AgI\downarrow + 2\,S_2O_3^{--} \rightleftharpoons Ag(S_2O_3)_2^{---} + I^-.$$

In each instance, the formation of the complex ion so greatly reduces the concentration of silver ions that the product of the molar concentrations of the ions becomes less than the solubility product of the silver halide.

$$[Ag^+] \times [Br^-] < S_{AgBr}.$$
$$[Ag^+] \times [I^-] < S_{AgI}.$$

The bromides and iodides of silver are used extensively in photography, because they are affected by white light, which causes the decomposition of the salts. The sensitized film or plate is prepared by coating a transparent film of nitrocellulose or cellulose acetate, or a glass plate, with a gelatin emulsion containing the colloidally dispersed salt. The film is protected from white light until the exposure is made in taking the picture. During

the exposure of the film, the silver salt partially decomposes with the formation of minute particles of uncombined silver, the decomposition being greatest at the points where the most intense light strikes the film. The exposed film is developed by immersing it for the proper length of time in a solution of a mild reducing agent, such as pyrogallol or an alkaline solution of hydroquinone. The rate of reduction is greatest in the part of the film where the incipient change, caused by the exposure to the most intense light, is greatest. Therefore, the thickness of the deposit of metallic silver formed on the film during the developing process depends on the intensity of the light striking the film during the brief time of the exposure. When the reaction has proceeded far enough, the unchanged silver salts are removed by a fixing bath, which is a solution of sodium thiosulfate. The film may now be exposed to white light without harmful result. The film is washed and dried after the completion of the fixing, and is a negative in that the light objects are dark and the dark objects light. A print is made by placing the negative over sensitized printing paper and making an exposure to light for the proper length of time. The exposed print is developed, fixed, and washed, as in the treatment of the negative.

Tests for the Chloride, Bromide, and Iodide Ions. Tests for the three common halide ions in the presence of each other may be based on the preferential oxidation of these ions. If hypochlorous acid, or sodium hypochlorite in acid solution, is added in successive small portions to a dilute solution containing chlorides, bromides, and iodides, the iodide is first oxidized to free iodine.

$$HClO + 2\,H^+ + 2\,I^- \longrightarrow H^+ + Cl^- + H_2O + I_2.$$

If a small quantity of carbon disulfide is added to the solution, the iodine is extracted by shaking the suspension and remains in the carbon disulfide layer when it settles from the solution. Iodine imparts a characteristic purple color to this layer. After the iodide is completely oxidized to free iodine, the bromide is next oxidized to elementary bromine by the further addition of the hypochlorite. Bromine is also largely extracted from the water layer by the carbon disulfide; but its color cannot be detected with certainty in the presence of the free iodine. Still further

addition of the hypochlorite, however, causes the oxidation of elementary iodine to iodic acid.

$$5\ HClO + I_2 + H_2O \longrightarrow 5\ H^+ + 5\ Cl^- + 2\ H^+ + 2\ IO_3^-.$$

Iodine is thus removed from the carbon disulfide layer; and, if the test is carried out by the use of properly regulated amounts of the hypochlorite added in successive small portions, the red color of the bromine dissolved in the carbon disulfide layer distinguishes the presence of bromine.

When a mixture of a soluble chloride, potassium dichromate, and concentrated sulfuric acid is heated in a distilling flask, *chromyl chloride*, CrO_2Cl_2, is distilled out of the mixture and may be condensed.

$$K_2Cr_2O_7 + 4\ NaCl + 6\ H_2SO_4 \longrightarrow 2\ CrO_2Cl_2\uparrow + 4\ NaHSO_4 + 2\ KHSO_4 + 3\ H_2O.$$

This substance is red in color and reacts with water with the formation of hydrochloric acid and chromic acid.

$$CrO_2Cl_2 + 6\ H_2O \longrightarrow 4\ H_3O^+ + CrO_4^{--} + 2\ Cl^-.$$

If this solution is made only weakly acidic and a soluble lead salt is added, a yellow precipitate of lead chromate is formed.

$$Pb^{++} + CrO_4 \rightleftharpoons PbCrO_4\downarrow.$$

Since the chromium compound distills over only in the presence of chlorides, these reactions may be employed in a test for chlorides. Bromides do not interfere in this test for chlorides, but iodides do. Consequently, if iodides have been found to be present, they must be removed before making the test. This may be accomplished by displacing the iodide ions with bromine.

Fluorides. Calcium fluoride occurs in nature as the mineral *fluorspar*, CaF_2, which is the chief source of the fluorine compounds. *Cryolite*, Na_3AlF_6, is the fused solvent employed in the electrolytic production of aluminum from its oxide. Calcium fluoride has a low melting point and is used to some extent as a flux. The fluoride ion forms complex ions, such as SiF_6^{--} and AlF_6^{---}, with several of the atoms of low atomic weight. In addition to the simple fluorides, there are acid salts, such as KHF_2. The structure of these substances indicates that the hydrofluoride complex ion is formed by the addition of hydrogen

fluoride to the fluoride ion, as shown by the following electron structure.

CYANIDES

Calcium cyanide may be prepared by fusing a mixture of calcium cyanamide and carbon with sodium chloride, which serves as a flux.

$$CaNCN + C \longrightarrow Ca(CN)_2.$$

Sodium cyanide is prepared by fusing a mixture of calcium cyanamide and carbon with sodium carbonate.

$$C + CaNCN + Na_2CO_3 \longrightarrow 2\,NaCN + CaCO_3.$$

The cyanides react with acids to form the highly poisonous prussic acid, HCN.

$$CN^- + H_3O^+ \rightleftharpoons HCN + H_2O.$$

Soluble cyanides are hydrolyzed to give basic solutions, because hydrocyanic acid is a very weak acid. Sodium cyanide reacts with gold and silver in contact with air to form complex cyanides; and it is used to leach these metals from some of their ores.

Complex Cyanides. The complex cyanide ions of silver, gold, copper, cadmium, zinc, iron, and a number of other metals may be formed by the addition of an excess of a solution of a cyanide to solutions containing the ions of these metals. The precipitate of the insoluble cyanide first formed dissolves in an excess of the cyanide ion solution. Complex cyanides of iron have several uses of importance. Both ferrous and ferric ions yield complex cyanides; ferrocyanide, $Fe(CN)_6^{----}$, and ferricyanide, $Fe(CN)_6^{---}$, respectively. The ferrocyanides of sodium and potassium are usually prepared as by-products of the destructive distillation of coal. Hydrogen cyanide, which is present in low concentration in the gaseous products, is absorbed when the gases are passed over iron oxide, with the formation of a cyanide of iron. Calcium ferrocyanide is formed from this product by reaction with lime; and the sodium and potassium salts are prepared from calcium ferrocyanide. The ferricyanides may be prepared by the electrolytic oxidation of ferrocyanide ions at the anode.

$$Fe(CN)_6^{----} \longrightarrow Fe(CN)_6^{---} + 1\,\epsilon.$$

Blue print paper is prepared by soaking the paper in a solution of ammonium ferricyanide and ferric citrate, in the dark. When the paper is exposed to light, the ferric ion is reduced to the ferrous condition by the citrate. The exposed paper is now placed in water and the ferrous and ferricyanide ions yield a blue precipitate which remains in the paper; but the unchanged salts are dissolved and washed out in the parts of the paper which were protected from light during the exposure.

THE SULFIDES

Sulfides occur extensively in nature and serve as important ores from which some of the metals are obtained. The natural sulfides are important also as sources of other sulfur compounds, such as sulfuric acid. Many of the sulfides are binary salts.

Reactions of the Sulfides. The sulfides burn when they are heated in air, to form sulfur dioxide and, usually, the oxide of the metal. Soluble sulfides are highly ionized in solution and are hydrolyzed to give basic solutions.

$$S^{--} + H_2O \rightleftharpoons OH^- + HS^-.$$

The soluble sulfides react with solutions of the metal ions which yield insoluble sulfides. Most of the sulfides, except those which are very slightly soluble, react with hydrochloric acid and with dilute sulfuric acid to form hydrogen sulfide. The common sulfides, with the exception of mercuric sulfide, react with nitric acid to form sulfur, nitric oxide, and the free ions of the metal in solution.

$$3\,CuS + 8\,H^+ + 2\,NO_3^- \longrightarrow 3\,Cu^{++} + 3\,S + 2\,NO + 4\,H_2O.$$

These reactions of sulfides are properties of the sulfide ion.

Soluble Sulfides. The common soluble sulfides are those of sodium, potassium, and ammonium. These compounds are usually prepared in solution by the reaction of hydrogen sulfide with the appropriate metal hydroxide. Since hydrogen sulfide is a weak acid which is only slightly soluble, the hydrosulfide is usually formed as the first product by saturating the solution of the base with hydrogen sulfide.

$$H_2S + OH^- \rightleftharpoons HS^- + H_2O.$$

The normal sulfide may be prepared by the addition of an equimolar amount of the hydroxide to the solution of the hydrosulfide.

$$HS^- + OH^- \rightleftharpoons S^{--} + H_2O.$$

These reactions are reversible so that solutions of the hydrosulfides of sodium and potassium are mildly alkaline, while solutions of the normal sulfides are strongly alkaline. The sulfides of sodium and potassium may also be prepared by the reduction of the sulfates with carbon at moderately high temperatures.

$$Na_2SO_4 + 4\,C \longrightarrow Na_2S + 4\,CO.$$

These salts are used in the laboratory to furnish a high concentration of sulfide ions.

Polysulfides. Sulfur dissolves in solutions of the alkali sulfides with the formation of the polysulfides. The polysulfides vary in composition, the simplest being the disulfides, as Na_2S_2. When acid is added to a solution of a polysulfide, a precipitate of finely divided sulfur, known as "milk of sulfur," is formed and hydrogen sulfide gas is evolved.

$$S_2^{--} + 2\,H_3O^+ \longrightarrow H_2S\uparrow + S + 2\,H_2O.$$

Calcium polysulfide, prepared by the reaction of sulfur with lime, is extensively used as "lime-sulfur" spray in vineyards and orchards.

Insoluble Sulfides. The normal sulfides of all of the metals except sodium and potassium are only slightly soluble. Nevertheless, the sulfide ion concentration in aqueous solution is not great enough to cause the precipitation of the sulfides of barium, strontium, calcium, magnesium, aluminum, and several other metals.

$$[Mg^{++}] \times [S^{--}] < S_{MgS}.$$

These sulfides may be prepared by the direct union of the metals and by the reduction of the sulfates with carbon at high temperature.

$$2\,Al + 3\,S \longrightarrow Al_2S_3.$$
$$CaSO_4 + 4\,C \longrightarrow CaS + 4\,CO.$$

The sulfide of aluminum hydrolyzes to form aluminum hydroxide and hydrogen sulfide.

$$Al_2S_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3\downarrow + 3\,H_2S\uparrow.$$

The sulfides of the alkaline earth metals are hydrolyzed to form the hydrosulfides in solution.

$$CaS + H_2O \longrightarrow Ca^{++} + OH^- + HS^-.$$

A second group of sulfides includes those having solubilities of such magnitude that they may be precipitated from basic solutions but not from acidic solutions, because of the low ionization of hydrogen sulfide in the acidic solutions. This group includes the sulfides of iron, zinc, manganese, nickel, and cobalt.

$$Fe^{++} + H_2S + 2\,OH^- \rightleftharpoons FeS + 2\,H_2O.$$
$$[Fe^{++}] \times [S^{--}] > S_{FeS}.$$

The sulfides of the cations of the copper and tin analytical groups are so slightly soluble that they may be precipitated from acidic solutions of the metal ions.

$$Cu^{++} + H_2S + 2\,H_2O \rightleftharpoons CuS + 2\,H_3O^+.$$
$$[Cu^{++}] \times [S^{--}] > S_{CuS}.$$

The analytical applications of hydrogen sulfide, based on differences in the solubilities of the metal sulfides, have been considered in the discussion of hydrogen sulfide. The reactions of these sulfides with hydrochloric and with nitric acid have been discussed in a preceding paragraph. Mercuric sulfide, which is not dissolved by nitric acid, is dissolved by aqua regia, due to the oxidizing action of nitric acid and the removal of simple mercuric ions to form the complex ion, $HgCl_4^{--}$.

$$[4\,H^+ + NO_3^- + 3\,\epsilon \longrightarrow 2\,H_2O + NO.] \quad \times 2.$$
$$[HgS + 4\,Cl^- \longrightarrow HgCl_4^{--} + S + 2\,\epsilon.] \quad \times 3.$$
$$8\,H^+ + 2\,NO_3^- + 3\,HgS + 12\,Cl^- \longrightarrow$$
$$4\,H_2O + 2\,NO + 3\,HgCl_4^{--} + 3\,S.$$

The reaction of the sulfides of arsenic, antimony, and tin with ammonium polysulfide to form complex thiosalts is applied analytically in the separation of the tin and copper groups.

EXERCISES

1. Illustrate by equations four reactions by which each of the following salts may be prepared: potassium chloride; ferric chloride; zinc chloride; lead chloride. How may the solid product be isolated in each case? What three general types of reactions are involved in the preparation of chlorides?

2. What reactions are shown in common by solutions of chlorides? Write equations to represent these typical reactions of chlorides.
3. Show by equations the reactions which may be used to produce the following successive changes: magnesium bromide to bromine to a mixture of potassium bromide and bromate to potassium bromide to silver bromide.
4. Account for the fact that silver chloride reacts readily with a solution of ammonia to form the complex silver ammonia ion. Silver bromide does this only when a high concentration of ammonia is present, and silver iodide does not react to an appreciable extent with ammonia in solution.
5. Discuss the use of the silver halides in photography.
6. Employing the solubility product principle, account for the solution of silver cyanide in a solution of potassium cyanide.
7. Explain the fact that magnesium hydroxide does not precipitate when ammonium chloride and ammonium hydroxide are added to a solution of magnesium chloride, although magnesium hydroxide is precipitated by the addition of ammonium hydroxide alone to a solution of a magnesium salt.
8. What four reactions may be applied for the preparation of sulfides? What conditions govern the choice of the method to be used in any specific case?
9. Compare the concentration of sulfide ions produced by the passage of hydrogen sulfide into each of the following solutions: concentrated hydrochloric acid; dilute hydrochloric acid; acetic acid; acetic acid containing sodium acetate; ammonium hydroxide and ammonium chloride; ammonium hydroxide; and sodium hydroxide.
10. What tests may be used for the identification of chloride, bromide, and iodide ions when they are present in a solution containing salts of these three ions? Explain the principle upon which the separations depend and write equations for all reactions involved.

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CHAPTER XXIX

SALTS III. SULFATES AND PHOSPHATES

The normal salts of sulfuric and phosphoric acids with the active metals are stable toward heat but are decomposed when they are heated with non-volatile acidic oxides, such as silicon dioxide, with the displacement of the oxides of sulfur and phosphorus, respectively. Both of the acids yield, in addition to the normal salts, salts which contain acidic anions. These hydrogen sulfate and hydrogen phosphate ions are unstable toward heat and decompose with the evolution of water.

THE SULFATES

The most abundant of the naturally occurring sulfates is calcium sulfate, which occurs in two forms, *anhydrite*, $CaSO_4$, and *gypsum*, $CaSO_4(H_2O)_2$. *Barite*, $BaSO_4$, and *celestite*, $SrSO_4$, are the natural sources of most of the barium and strontium compounds. The sulfates of sodium, potassium, and magnesium are also found to varying extents in salt deposits, and in salt lakes, wells, and springs.

Preparation of Sulfates. Sulfuric acid is a strong acid. Hence, the soluble sulfates may be prepared by the general reactions which yield soluble salts: *viz.*, the reactions of the acid with the metals and their oxides, hydroxides, and salts of volatile acids. Sulfates and bisulfates may result from each of these reactions, depending on the relative proportions of the acid and basic substances. The insoluble sulfates, those of barium, strontium, and lead, are prepared by precipitation.

Reactions of the Sulfates. The sulfates of the active metals are stable toward hydrolysis, while the sulfates of the metals of low activity produce acidic solutions. The sulfates are not decomposed by the other common acids, because sulfuric acid is itself a strong acid of high boiling point. Sulfates react with sulfuric acid to form bisulfates, and are decomposed when heated

with silica. The sulfates are reduced to sulfides when they are heated with carbon.

Sodium Sulfate. Na_2SO_4. Some of the salt deposits in the southwestern part of the United States contain this substance in the form of the anhydrous salt; but the chief commercial source is the salt-cake, obtained in the preparation of hydrochloric acid by the reaction of sulfuric acid with salt. At temperatures below 32.4°, sodium sulfate crystallizes from solution as the decahydrate, $Na_2SO_4(H_2O)_{10}$. This substance is known as *Glauber's salt*, because the alchemist Glauber prepared it and used it for medicinal purposes in the seventeenth century. At temperatures above 32.4°, the anhydrous salt crystallizes from solution. The solubility of the anhydrous salt, unlike that of most salts, decreases with rise in temperature. Sodium sulfate is used in the manufacture of glass; but its principal use is in the production of wood pulp by the sulfate process. It is estimated that the annual requirements for this purpose in the United States are approximately 350,000 tons.

Potassium Sulfate. K_2SO_4. This substance is a constituent of the double salt, *schoenite*, $K_2SO_4MgSO_4(H_2O)_6$, and of the triple salt, *kainite*, $MgSO_4MgCl_2K_2SO_4(H_2O)_6$, found in the Stassfurt salt deposits. Potassium sulfate is prepared from schoenite by reaction with potassium chloride in the presence of a limited amount of water. Potassium sulfate is the least soluble of the salts involved and precipitates in the form of an anhydrous crystalline solid. This salt is used in the preparation of alums and as a fertilizer ingredient, especially for tobacco since its presence in the product does not give an ash of as low melting point as that caused by the use of potassium chloride.

Ammonium Sulfate. $(NH_4)_2SO_4$. Ammonia, produced by the destructive distillation of coal, is absorbed in sulfuric acid with the formation of ammonium sulfate, and thus separated from the other volatile products of the process. The amount of ammonium sulfate obtained from this source depends on the production of coke for the metal industries. A large proportion of the required amount of ammonium sulfate is produced from synthetic ammonia. The most extensive use of ammonium sulfate is in fertilizers for supplying combined nitrogen. It is also used to some extent in the production of other ammonium salts.

Cupric Sulfate. $CuSO_4$. The sulfate is the most familiar and important of the cupric salts. It may be prepared commercially by roasting the sulfide so as to form a mixture of the sulfate and oxide. These products are dissolved by dilute sulfuric acid, and cupric sulfate is crystallized from the solution. Cupric sulfate is also prepared by the displacement of silver from its sulfate solutions, and by the reaction of sulfuric acid with copper in the presence of air.

Cupric sulfate crystallizes from solution as the pentahydrate, $CuSO_4(H_2O)_5$, which is called "blue vitriol." The double sulfates of copper and the alkali metals may also be crystallized from solutions containing the ions of both metals. Copper sulfate is used in copper plating and in the electrorefining of copper, in batteries such as the gravity cell, and as a mordant in dyeing. A small proportion of copper sulfate may be added to water in swimming pools to prevent the growth of algae. In high concentrations, copper salts are poisonous to animals. Hydroxysulfates of copper, having varying composition, are precipitated by the addition of soluble metal hydroxides to solutions of copper sulfate. "Bordeaux mixture" containing the hydroxysulfate of copper mixed with calcium sulfate is prepared by the reaction of calcium hydroxide with copper sulfate. It is used as a fungicide, especially on fruit trees and vines.

Calcium Sulfate. $CaSO_4$. This salt occurs in nature in two forms, *anhydrite* and *gypsum*. The hydrated salt, gypsum, $CaSO_4(H_2O)_2$, is the solid phase in equilibrium with the saturated solution at temperatures below 63.5°; the anhydrous salt, at higher temperatures. The natural occurrence of anhydrite indicates its deposition from solution at relatively high temperatures. Both minerals have the same solubility at the transition temperature, approximately 0.2 g. per 100 ml. of water, and the solubility of the anhydrite decreases rapidly with rise in temperature, causing the deposition of boiler scale when water containing this salt is used in steam boilers.

Gypsum is partially dehydrated when it is heated at 125°.

$$2\ CaSO_4(H_2O)_2 \longrightarrow (CaSO_4)_2H_2O + 3\ H_2O.$$

The partially dehydrated product rapidly becomes hydrated again when it is moistened, and it sets to form a crystalline mass.

If gypsum is heated too strongly in the formation of plaster of Paris and all of the water of hydration is expelled, the "dead burnt" product absorbs water very slowly and does not set quickly. Plaster of Paris is used in making surgical bandages and different kinds of plaster casts. The most extensive use is in the making of plaster for the interior of buildings, size or glue being added to retard the rate of setting. Calcium sulfate is used in large quantities in the manufacture of stucco, wall-board, and in Portland cement.

One of the forms of anhydrous calcium sulfate absorbs water so readily that only a very low pressure of water vapor may remain in equilibrium with the solid. This substance, under the trade name "Drierite," is used as a drying agent for gases and liquids.

The Vitriols. The sulfates of magnesium, zinc, and ferrous iron crystallize from solution as heptahydrates. These sulfates are known as vitriols. They have similar crystalline structure and exhibit similar reactions, not only because they are sulfates, but also because the ferrous, zinc, and magnesium ions resemble each other in properties. These hydrated salts decompose when they are heated strongly; water and sulfur trioxide are driven out, and the oxide of the metal remains as a residue.

Magnesium sulfate is found in the water of mineral springs, such as that at Epsom in England, from which the name "Epsom salt" is derived. The hydrate, $MgSO_4(H_2O)_7$, occurs in salt deposits. In addition to its medicinal uses, this salt is used in weighting and sizing cotton and silk and in dyeing.

Zinc sulfate is used in large quantities in the production of lithopone, a mixture of the sulfide of zinc and the sulfate of barium.

$$BaS + ZnSO_4 \longrightarrow BaSO_4 + ZnS.$$

This material is used as a white body in paint, since it does not darken in air containing hydrogen sulfide as lead white does.

Ferrous sulfate, the most important of the ferrous salts, is produced as a by-product of the "pickling" of iron which is to be galvanized or otherwise metal-coated. The hydrate, $FeSO_4(H_2O)_7$, is known as *green vitriol* and also as *copperas*. Ferrous sulfate is used as a disinfectant, in dyeing, in water purification, and in the preparation of ink. The addition of ferrous sulfate to an extract of nut-galls yields ferrous tannate. Ferrous tannate is soluble and

colorless, but it is oxidized by air to form ferric tannate which is insoluble and black. A dye is added to the ferrous tannate solution to make writing visible from the first. Ink stains from this variety of ink can be washed out only by first reducing the iron compound. This may be accomplished by soaking the material containing the ink spot in an ammonium oxalate solution. Of course, this method cannot be used if the ammonium oxalate will damage the fabric or affect the color of dyes in the goods. Other inks are made from organic dyes, and printer's ink is a colloidal suspension of carbon black.

When a solution which contains equimolecular amounts of ferrous sulfate and ammonium sulfate is evaporated to the point of crystallization, a double salt, *Mohr's salt*, $(NH_4)_2SO_4FeSO_4(H_2O)_6$, is deposited in the form of pale green crystals. This salt is quite stable toward oxidation and is used as the common laboratory source of ferrous ions.

Aluminum Sulfate. $Al_2(SO_4)_3$. Aluminum sulfate is one of the most important of the aluminum salts. It is prepared by the reaction of the oxide with sulfuric acid.

$$Al_2O_3 + 6\ H_3O^+ + 3\ SO_4^{--} \longrightarrow 2\ Al^{+++} + 3\ SO_4^{--} + 9\ H_2O.$$

The hydrate, $Al_2(SO_4)_3(H_2O)_{18}$, may be crystallized from solutions of aluminum sulfate. This salt is soluble enough to melt in its own water of hydration when it is warmed. Its solutions are acidic on account of hydrolysis.

When solutions containing equimolecular amounts of aluminum sulfate and potassium sulfate are evaporated to the point of crystallization, octahedral crystals of the double salt, *potassium alum*, $KAl(SO_4)_2(H_2O)_{12}$, separate as the solution is allowed spontaneously to evaporate further. The ions of the other alkali metals except lithium, and the ammonium, silver, and thallous ions form isomorphous compounds of the same type. Other trivalent ions, such as the ferric, chromic, and titanic ions may replace the aluminum ions in these crystals, forming a class of products known as alums. The alums may be purified by crystallization, because they are much more soluble in hot water than in cold water. Alums are used in sizing paper and in fireproofing cloth; but the most important uses of aluminum sulfate and the aluminum alums depend on the hydrolysis of the aluminum ion to form

acidic solutions and on the precipitation of gelatinous aluminum hydroxide.

$$Al(H_2O)_6^{+++} + H_2O \rightleftharpoons Al(OH)(H_2O)_5^{++} + H_3O^+.$$
$$Al(H_2O)_6^{+++} + 3\ OH^- \rightleftharpoons Al(OH)_3(H_2O)_3\downarrow + 3\ H_2O.$$

The use of alum in baking powder depends on the formation of hydronium ions, which react with the bicarbonate ions to form carbon dioxide, when water is added. The same reaction is applied in some fire extinguishers, in which the acidic alum solution reacts with a bicarbonate solution containing organic substances which aid in the formation of a foam containing carbon dioxide. This blankets the fire, cutting off the oxygen necessary for combustion to continue. The reaction of sodium carbonate solution or of lime with an alum solution produces a precipitate of hydrated alumina, which adsorbs suspended matter in water and aids in the clarification of water as the precipitate settles. Certain dyes may also be adsorbed by the precipitate to produce pigment "lakes." The precipitate is filtered, dried, and ground in oil to prepare pigments for oil paints. Alums are used in mordanting cotton goods. The aluminum hydroxide which is formed and adsorbed by the fiber of the cloth adsorbs the dye.

Other Soluble Sulfates. The sulfates of most of the metals may be formed by one or more of the methods already mentioned. The reaction of hot, concentrated sulfuric acid with metals of low activity produces the ions of the metal in a compound from which other salts of the metal may be prepared. Thus, corrosive sublimate and calomel are commonly prepared from mercuric sulfate. The sulfates are common laboratory reagents to supply the metal ions.

Bisulfates and Pyrosulfates. Since sulfuric acid contains two replaceable protons in each molecule, it yields hydrogen sulfates, known as bisulfates, when an excess of sulfuric acid is used in any of the general acid reactions. The addition of sulfuric acid to the normal salt also produces the acid salt.

$$OH^- + H_3O^+ + HSO_4^- \longrightarrow 2\ H_2O + HSO_4^-.$$
$$SO_4^{--} + H_3O^+ + HSO_4^- \longrightarrow 2\ HSO_4^- + H_2O.$$

If potassium hydroxide and potassium sulfate are used in these reactions, potassium hydrogen sulfate, $KHSO_4$, may be crystal-

lized from the solution. Aqueous solutions of the bisulfates are acidic, because they contain the hydrogen sulfate ion which is an acid. $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{--}$.

Water is driven out, leaving a residue of the *pyrosulfate*, $K_2S_2O_7$, when solid potassium bisulfate is heated moderately.

$$2\ KHSO_4 \longrightarrow H_2O + K_2S_2O_7.$$

The pyrosulfate decomposes when it is strongly heated.

$$K_2S_2O_7 \longrightarrow K_2SO_4 + SO_3.$$

Pyrosulfates contain an excess of the non-metallic oxide; and on account of the presence of this substance, they react with the oxides of metals when the substances are heated together, forming a mixture of the sulfates.

$$3\ K_2S_2O_7 + Fe_2O_3 \longrightarrow 3\ K_2SO_4 + Fe_2(SO_4)_3.$$

Insoluble Sulfates. The sulfates of barium, strontium, and lead are so slightly soluble that they may easily be obtained as precipitates.

$$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4\downarrow.$$
$$[Ba^{++}] \times [SO_4^{--}] > S_{BaSO_4}.$$

The sulfates of barium and strontium are the chief natural sources of compounds of these metals. The soluble salts of barium and strontium are most readily obtained by first reducing the sulfate to the sulfide by heating it with carbon.

$$BaSO_4 + 4\ C \longrightarrow BaS + 4\ CO\uparrow.$$

The addition of hydrochloric acid to the sulfide causes the formation of the chloride; and of nitric acid, the nitrate. From these soluble salts, other compounds of barium are readily prepared.

$$BaS + 2\ H_3O^+ + 2\ Cl^- \longrightarrow Ba^{++} + 2\ Cl^- + H_2S\uparrow + 2\ H_2O.$$
$$3\ BaS + 8\ H_3O^+ + 8\ NO_3^- \longrightarrow$$
$$3\ Ba^{++} + 6\ NO_3^- + 3\ S\downarrow + 2\ NO\uparrow + 12\ H_2O.$$

Although lead sulfate is very slightly soluble as shown by its solubility product,

$$[Pb^{++}] \times [SO_4^{--}] = 6.2 \times 10^{-8},$$

it may be converted into the soluble salt, lead acetate, by boiling the sulfate with an ammonium acetate solution. In the presence

of a high concentration of acetate ions, the concentration of lead ions is reduced below that required to maintain the equilibrium with solid lead sulfate, due probably to the formation of a complex lead acetate ion, such as $Pb(C_2H_3O_2)_4^{--}$.

Test for the Sulfate Ion. The test for the presence of the sulfate ion in solution is based on the precipitation of barium sulfate. A number of anions yield precipitates with the barium ion in neutral and basic solutions, *e.g.*, the carbonate, phosphate, sulfite, and borate ions. These ions, however, are the anions of weak acids and the concentration of each of these simple ions in acidic solutions is very low.

$$PO_4^{---} + 2\,H_3O^+ \rightleftharpoons H_2PO_4^- + 2\,H_2O.$$

Consequently, barium phosphate does not precipitate when a barium salt is added to an acidic solution of a phosphate.

$$[Ba^{++}]^3 \times [PO_4^{---}]^2 < S_{Ba_3(PO_4)_2}.$$

A similar condition exists in acidic solutions of the carbonate, borate, and sulfite ions. Sulfuric acid is strong enough, so that the addition of another acid to a solution of the sulfate ion does not prevent the precipitation of barium sulfate. Consequently, the presence of sulfate ions may be determined by the formation of a white precipitate when a solution of barium ions is added to an acidic solution of the substance being tested.

Sulfites. The bisulfite is produced when a solution of sodium hydroxide is saturated with sulfur dioxide. The normal sulfite may be prepared by the reaction of the acid sulfite with an equimolar amount of sodium hydroxide.

$$OH^- + SO_2 \rightleftharpoons HSO_3^-.$$
$$OH^- + HSO_3^- \rightleftharpoons SO_3^{--} + H_2O.$$

The sulfites are the salts of the weak and unstable acid, sulfurous acid. They react with stronger acids with the evolution of sulfur dioxide. This reaction is used in the laboratory as a convenient method for the preparation of sulfur dioxide.

$$SO_3^{--} + 2\,H_3O^+ \rightleftharpoons 3\,H_2O + SO_2.$$

This reaction also serves as a test for the presence of sulfites. The gas evolved is identified by passing it into a dilute, acidic solution of potassium permanganate. The permanganate is de-

colorized because of the reduction of the permanganate ion to form the manganous ion, while the sulfur dioxide is oxidized to form the sulfate, which is identified by the usual sulfate test.

$$[MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O.] \times 2.$$
$$[SO_2 + 2\,H_2O \longrightarrow SO_4^{--} + 4\,H^+ + 2\,\epsilon.] \times 5.$$
$$2\,MnO_4^- + 5\,SO_2 + 2\,H_2O \longrightarrow 2\,Mn^{++} + 5\,SO_4^{--} + 4\,H^+.$$

The normal sulfites of barium and calcium are slightly soluble so that they may be prepared by precipitation. Calcium bisulfite, $Ca(HSO_3)_2$, is soluble and is extensively used in the manufacture of paper because it dissolves lignin from wood, leaving relatively pure cellulose.

Sodium Thiosulfate. $Na_2S_2O_3$. This salt is prepared by the reaction of the sulfite with an excess of sulfur in alkaline solution.

$$SO_3^{--} + S \longrightarrow S_2O_3^{--}.$$

Acidification of a solution of the thiosulfate yields a precipitate of free sulfur because the acid is unstable.

$$S_2O_3^{--} + 2\,H_3O^+ \longrightarrow 3\,H_2O + SO_2\uparrow + S\downarrow.$$

The thiosulfate is oxidized by iodine and other oxidizing agents with the formation of the tetrathionate.

$$2\,S_2O_3^{--} + I_2 \longrightarrow S_4O_6^{--} + 2\,I^-.$$

This reaction may be applied in quantitative analysis in the determination of iodine.

The pentahydrate, $Na_2S_2O_3(H_2O)_5$, is crystallized from solution. This salt is called "hypo" from the older name, hyposulfite. The salt is extensively used in photography to dissolve unchanged silver salts from developed films and prints.

$$AgBr + 2\,S_2O_3^{--} \rightleftharpoons Br^- + Ag(S_2O_3)_2^{---}.$$

Sodium thiosulfate is also used for the removal of the excess of chlorine employed for bleaching in the textile and paper industries.

THE PHOSPHATES

Calcium phosphate is the only naturally occurring phosphate of importance. This substance, *phosphorite*, $Ca_3(PO_4)_2$, is found in various parts of the earth. The chief supply has come from Florida, South Carolina, and Tennessee, but there are vast

deposits in Idaho, Wyoming, and Utah. The normal phosphates, with the exception of those of sodium, potassium, and ammonium, are insoluble. Insoluble phosphates are usually prepared by precipitation reactions; and the soluble phosphates, by the neutralization of phosphoric acid with the appropriate base.

Phosphates of Sodium. There are three orthophosphates of sodium, the dihydrogen phosphate, NaH_2PO_4, the monohydrogen phosphate, Na_2HPO_4, and the normal phosphate, Na_3PO_4. These salts are prepared by the reaction of phosphoric acid wit the calculated amount of sodium hydroxide. Sodium dihydrogen phosphate is slightly acidic; but the secondary phosphate, Na_2HPO_4, gives a slightly basic solution by hydrolysis. The tertiary stage of the ionization of phosphoric acid is so slight that the normal phosphate is almost completely hydrolyzed unless an excess of the base is present in the solution.

$$PO_4^{---} + H_2O \rightleftharpoons HPO_4^{--} + OH^-.$$

Sodium ammonium hydrogen phosphate, $NaNH_4HPO_4$, a soluble mixed salt known as *microcosmic salt*, is used as a laboratory reagent.

The acid phosphates of sodium are used in the preparation of some of the baking powders, and some of the phosphates have medicinal uses. Trisodium phosphate, the normal salt, is extensively used in water treatment for the removal of acidic substances and substances which yield insoluble phosphates. This salt is also an ingredient of many soap powders.

Phosphates of Calcium. Calcium phosphate is the most important of the phosphates. This substance is the naturally occurring mineral which serves as the source of the other phosphorus compounds. Approximately four million tons of this substance are mined annually in the United States, primarily for use in the preparation of fertilizers. Since the naturally occurring phosphate is insoluble, it is not suitable for direct use as a fertilizer. Calcium dihydrogen phosphate, however, is soluble and is suitable as a phosphorus-containing fertilizer. In order to convert the normal phosphate into the dihydrogen phosphate, the naturally occurring mineral is pulverized and treated with sulfuric acid. The chamber acid is suitable for this use because it is desirable to have enough water in the reacting mixture to hydrate the cal-

cium sulfate formed in the reaction, and thus prevent the subsequent caking of the product.

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\,CaSO_4.$$
$$CaSO_4 + 2\,H_2O \longrightarrow CaSO_4(H_2O)_2.$$

When the proper proportions of the reacting substances are used, a dry mixture of the two salts, known industrially as *superphosphate of lime*, is obtained. This material is used in the preparation of mixed fertilizers, nitrogen compounds, potassium salts, and inactive material being mixed with it.

A more concentrated phosphate fertilizer may be produced by the action of phosphoric acid on calcium phosphate.

$$Ca_3(PO_4)_2 + 4\,H_3PO_4 \longrightarrow 3\,Ca(H_2PO_4)_2.$$

By the absorption of ammonia in phosphoric acid, ammonium phosphate is produced. This product contains both nitrogen and phosphorus in a form available for plant assimilation. Due to the development of cheap electric furnace methods for the production of phosphoric acid, and the production of synthetic ammonia, this salt is now important in the fertilizer industry.

Effect of Heating Phosphates. The normal phosphates of the active metals are stable toward heat, but evolve phosphorus pentoxide when they are heated with silica. The hydrophosphates and those which contain the ammonium radical are decomposed when they are heated. When a dihydrogen phosphate is heated, one molecular proportion of water is evolved and a metaphosphate is formed. Microcosmic salt also yields a metaphosphate when heated.

$$NaH_2PO_4 \longrightarrow H_2O\uparrow + NaPO_3.$$
$$NaNH_4HPO_4 \longrightarrow H_2O\uparrow + NH_3\uparrow + NaPO_3.$$

When metaphosphates are heated with basic oxides, mixed orthophosphates are produced. Some of the products possess distinctive colors, so that they may be used as tests for metal radicals. Thus, cobaltous oxide produces a blue coloration. Fused metaphosphates exhibit an acidic reaction for the same reason as the pyrosulfates.

$$NaPO_3 + CoO \longrightarrow NaCoPO_4.$$

When a monohydrogen phosphate is heated, water is evolved and the pyrophosphate is formed. The metal ammonium phosphates also yield pyrophosphates.

$$2\ Na_2HPO_4 \longrightarrow H_2O + Na_4P_2O_7.$$
$$2\ MgNH_4PO_4 \longrightarrow H_2O + 2\ NH_3 + Mg_2P_2O_7.$$

Test for the Phosphate Ion. Ammonium molybdate produces a yellow precipitate with the phosphate ion in nitric acid solution. The approximate composition of the precipitate is represented by the formula, $(NH_4)_3PO_4(MoO_3)_{12}$, although the per cent of molybdic oxide may vary under differing conditions. The formation of this precipitate affords a means of separating the phosphate ion from metal ions which would produce insoluble phosphates in neutral or basic solution. Magnesium and ammonium ions produce a white crystalline precipitate of magnesium ammonium phosphate in weakly basic solution.

$$Mg^{++} + NH_4^+ + HPO_4^{--} + OH^- \longrightarrow MgNH_4PO_4\downarrow + H_2O.$$

Arsenates interfere, since they give similar precipitates with both the molybdate and the magnesium salt. The removal of arsenates, so as to eliminate this interference, may be accomplished by the precipitation of arsenic sulfide in acidic solution.

ARSENITES AND ARSENATES

The sodium and potassium salts are prepared by the reaction of the oxides of arsenic with the hydroxides of the metals. The salts of the other metals may be produced by precipitation, using the sodium or potassium salt as the source of the arsenite and arsenate ions. Sodium arsenite is used in the preparation of a poison bait for insects and as a weed killer. There are several arsenites of copper, *e.g.*, *Paris green*, $Cu_4(C_2H_3O_2)_2(AsO_3)_2$, and *Scheele's green*, $CuHAsO_3$. The arsenates of sodium are used in the preparation of the arsenates of lead and of calcium. Commercial lead arsenate is a mixture of the normal arsenate, $Pb_3(AsO_4)_2$, and the hydrogen arsenate, $PbHAsO_4$. It is used extensively as an insecticide, especially for spraying fruit trees. Calcium arsenate has been used extensively in the attempt to control infestations of the cotton boll weevil.

Compounds of arsenic in both of the common oxidation numbers, 3 + and 5 +, yield sulfide precipitates in acidic solution. Consequently, the compounds of this element are detected in the systematic analysis of the cations.

EXERCISES

1. Illustrate the preparation of sulfates by equations for the formation of sodium sulfate, silver sulfate, cupric sulfate, mercuric sulfate, and ferric sulfate.
2. Discuss in terms of the solubility product relationships the precipitation of lead sulfate and its solution by ammonium acetate.
3. What are the vitriols? Represent by equations the reactions which take place when ferrous sulfate is strongly heated.
4. What are the alums? Explain the use of potassium alum in the preparation of baking powder and the use of aluminum sulfate in the clarification of water.
5. Represent by equations the reactions which occur during the heating of the hydrogen sulfates and of the monohydrogen and dihydrogen phosphates.
6. How may soluble chlorides and nitrates be prepared from the insoluble sulfates of barium and strontium which occur in nature?
7. Discuss the use of phosphates in fertilizers. What three methods may be employed for the production of suitable fertilizer materials from the insoluble calcium phosphate?
8. Account for the fact that the fused pyrosulfates, metaphosphates, and pyrophosphates react with basic oxides. Illustrate by equations.
9. Explain the use of hydrochloric acid in the test for sulfates by precipitation of barium sulfate.
10. Why must the solution be basic in the test for the phosphate ion? What is the function of the ammonium chloride used in this test?

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CHAPTER XXX

SALTS IV. THE CARBONATES, SILICATES, AND BORATES

The carbonates and simple silicates are similar in composition and in many of their properties. They are salts of weak and unstable acids. Consequently, they react with most of the common acids. The soluble salts of these acids interact with water to form basic solutions. In addition to the simple silicates, there are a number of complex silicates which occur extensively in the outer part of the solid earth. The borates resemble the silicates, although boron is in a different periodic group from silicon.

THE CARBONATES

The most abundant of the carbonates is calcium carbonate, which occurs in *marble* and *limestone*. Magnesium carbonate occurs as *magnesite*, $MgCO_3$, and *dolomite*, $CaCO_3MgCO_3$. Sodium carbonate occurs in salt deposits and in lake waters, and the carbonates of barium and strontium occur to a limited extent. The carbonates of iron, lead, zinc, and copper are found in relatively small total amounts, but are important ores of these metals.

Reactions of the Carbonates. The carbonates react with hydronium ions to form the bicarbonate ion or carbon dioxide, depending on the concentrations of the ions. The equilibrium constant for the dissociation of the bicarbonate ion is,

$$\frac{[H_3O^+] \times [CO_3^{--}]}{[HCO_3^-]} = 4.7 \times 10^{-11};$$

and for carbon dioxide and water,

$$\frac{[H_3O^+] \times [HCO_3^-]}{[CO_2]} = 4.3 \times 10^{-7}.$$

Carbonates are converted into bicarbonates when the concentration of the hydrogen ion is maintained at a value which gives a ratio greater than that demanded by the dissociation constant

for the bicarbonate ion, but less than that required by the equilibrium constant for the bicarbonate ion with carbon dioxide. Water and carbon dioxide are formed if the ratio of the concentrations exceeds the equilibrium constant for the latter system.

FIG. 154. — Lake of Crystallized Soda in British East Africa. (Copyright by Publishers Photo Service.)

Water and carbon dioxide give a high enough concentration of hydrogen ions for the conversion of the carbonate into the bicarbonate, while the stronger acids cause the formation of carbon dioxide if they are added in excess.

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2.$$

$$CaCO_3 + 2\,H_3O^+ \longrightarrow Ca^{++} + 3\,H_2O + CO_2\uparrow.$$

The carbonates decompose to form the oxide of the metal and carbon dioxide when they are strongly heated, with the exception of those of sodium and potassium which are stable toward heat. The carbonates react with acidic oxides when the solids are heated together and carbon dioxide is formed.

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow.$$

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2\uparrow.$$

Sodium Carbonate. Na_2CO_3. Deposits of sodium carbonate are found in arid regions in various parts of the world. The two most important natural sources are at Owens Lake in California and at Lake Magadi in British East Africa, Figs. 154 and 155. Nevertheless, the major portion of the industrial supply is produced from common salt.

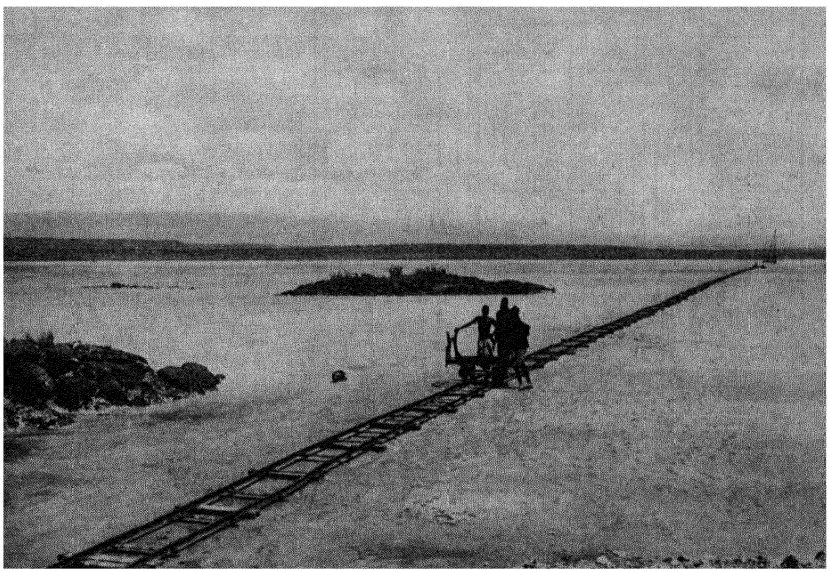
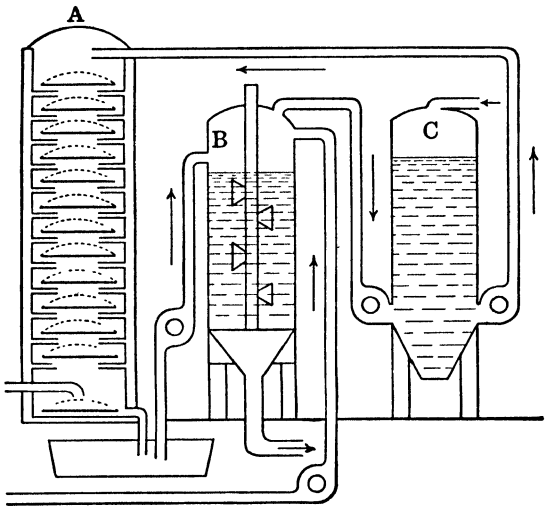


FIG. 155. — Track Across the Soda Lake. (Copyright by Publishers Photo Service.)

The Production of Sodium Carbonate. Before 1790, sodium carbonate was obtained exclusively from the natural deposits and from the ashes of sea plants. The first industrial process for the manufacture of sodium carbonate was developed by Le Blanc in 1790. In this process, sodium sulfate is first prepared from sodium chloride by reaction with sulfuric acid, hydrochloric acid being a by-product. When a solid mixture of sodium sulfate, calcium carbonate, and coal dust is heated at a temperature of 800°–900°, sodium carbonate, calcium sulfide, and carbon monoxide are formed. Sodium carbonate is leached from the residue and the solid is recovered by evaporation. This process was not able to withstand competition with the more efficient Solvay process

which was developed in 1866; and relatively little sodium carbonate is now manufactured by the Le Blanc process.

The preparation of sodium carbonate by the *Solvay process* depends on the precipitation of sodium hydrogen carbonate from solutions containing high concentrations of sodium and bicarbonate ions. The formation of the sodium bicarbonate takes place



A, Carbonating Tower.
B, Ammonia Recovery.
C, Preparation of Ammoniacal Brine.

FIG. 156. — Diagram of Solvay Process.

in the carbonating tower, Fig. 156, which is approximately fifty feet in height and eight feet in diameter. The towers are divided by a number of perforated partitions and filled with a concentrated sodium chloride solution saturated with ammonia. Carbon dioxide is forced in at the bottom of the tower and rises in small bubbles through the perforations in the partitions. Carbon dioxide is thus dissolved quickly in the solution and reacts with water and ammonia to form ammonium bicarbonate.

$$NH_3 + H_2O + CO_2 \rightleftharpoons NH_4^+ + HCO_3^-.$$

The reaction with sodium chloride occurs when the concentration of the bicarbonate ion becomes great enough to precipitate sodium bicarbonate, which is the least soluble of the salts in the solution.

$$Na^+ + HCO_3^- \rightleftharpoons NaHCO_3\downarrow.$$

The precipitated bicarbonate is separated from the solution and heated to convert it into the normal carbonate, "soda ash."

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2\uparrow.$$

The carbon dioxide used in the process is obtained by the thermal decomposition of limestone.

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow.$$

Ammonia, recovered from the ammonium salt solution by reaction with slaked lime, is absorbed in a saturated salt solution and the cycle is repeated.

$$CaO + H_2O \longrightarrow Ca(OH)_2.$$
$$2\,NH_4^+ + Ca(OH)_2 \longrightarrow 2\,NH_3 + 2\,H_2O + Ca^{++}.$$

The only raw materials consumed in the process are limestone and salt. Calcium chloride is a by-product. There is some loss of ammonia on account of its incomplete absorption and resulting escape from the solutions, and this must be supplied from some other source. The reactions take place at 35° so that the fuel costs are low. There is but little handling of solid materials, making small labor costs.

Properties and Reactions of Sodium Carbonate. The salt is a white crystalline solid which dissolves readily in water. It crystallizes from solution as the decahydrate, $Na_2CO_3(H_2O)_{10}$, at temperatures below 30°. This hydrate is known as washing soda. The heptahydrate, $Na_2CO_3(H_2O)_7$, is the stable form at temperatures of 30–35°; and the stable form in equilibrium with the saturated solution at higher temperatures is the monohydrate, $Na_2CO_3(H_2O)$. The anhydrous salt is called *soda ash.* The decahydrate effloresces to form the monohydrate.

Sodium carbonate exhibits the general reactions due to the carbonate ion. The hydrolysis of the carbonate produces solutions containing both the hydroxide and carbonate anions.

$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^-.$$

The reactions of such solutions with metal ions to precipitate carbonates, hydroxycarbonates, or hydroxides, depending on the relative solubilities of these products, are discussed in Chapter XIV.

Uses of Sodium Carbonate. Sodium carbonate is a very important substance. The estimated production of this salt in the United States in 1940 was approximately 3,157,000 tons. The production of the natural salt was about 107,000 tons. The

estimated distribution of sodium carbonate among the industries is shown in Table 40.

TABLE 40

ESTIMATED CONSUMPTION OF SODA ASH[1] IN THE UNITED STATES (TONS)

Industry	*1938*	*1939*	*1940*
Glass	660,000	820,000	904,000
Soap	187,000	190,000	182,000
Caustic and bicarbonate	665,000	810,000	780,000
Other chemicals	556,000	600,000	710,000
Cleaners and modified sodas	120,000	130,000	135,000
Pulp and paper	85,000	105,000	111,000
Water softeners	27,000	28,000	32,000
Petroleum refining	10,000	11,000	12,000
Textiles	30,000	43,000	45,000
Exports	51,000	80,000	61,000
Miscellaneous	149,000	144,000	185,000
Totals	2,530,000	2,961,000	3,157,000

Sodium Bicarbonate. $NaHCO_3$. This salt is the familiar *baking soda.* It is prepared by saturating a concentrated solution of the carbonate with carbon dioxide.

$$2\,Na^+ + CO_3^{--} + H_2O + CO_2 \longrightarrow 2\,NaHCO_3\downarrow.$$

This salt is used in making bread, in the preparation of baking powders, and in medicine. In order to leaven bread, minute bubbles of carbon dioxide are formed throughout the dough, causing it to rise. During the baking of the bread, the heat expands these minute gas bubbles, producing a light and porous product. In yeast breads, such as the bakers' loaf and rolls, carbon dioxide results from the fermentation caused by the yeast; but in breads made by the use of soda, an acid is added to react with the soda and form carbon dioxide.

$$H_3O^+ + HCO_3^- \rightleftharpoons 2\,H_2O + CO_2\uparrow.$$

Sour milk contains lactic acid, so that it may be used for this purpose; but prepared baking powders are more extensively employed in making cake, biscuit, and similar leavened breads.

A baking powder consists of a mixture of sodium bicarbonate with some solid acid substance, such as cream of tartar (potassium

[1] *Chem. Met. Eng.* **48**, Number 2, 93 (1941).

hydrogen tartrate, $KHC_4H_4O_6$), an acid phosphate, or an alum. Starch and other inactive materials are added to prevent the substances becoming wet because of the absorption of moisture from the air, and to make possible the securing of a uniform distribution of the active ingredients of the baking powder through the flour. The dry substances are inactive; but when water or milk is added, the acid solution reacts with the bicarbonate.

$$HC_4H_4O_6^- + HCO_3^- \longrightarrow C_4H_4O_6^{--} + H_2O + CO_2\uparrow.$$

The evolved carbon dioxide is emulsified and adsorbed by the glutinous material in the flour, so that it does not immediately escape into the air.

Potassium Carbonate. K_2CO_3. Potassium carbonate is present in wood ashes, from which it may be extracted with water. Due to the relatively high solubility of potassium hydrogen carbonate, this salt cannot be prepared by a process similar to the Solvay process for soda. Potassium carbonate is usually prepared by heating potassium chloride solution with a suspension of magnesium carbonate and carbon dioxide under pressure. These substances react to form the slightly soluble mixed salt, potassium magnesium acid carbonate.

$$2\,K^+ + 3\,MgCO_3 + CO_2 + H_2O \rightleftharpoons Mg^{++} + 2\,MgKH(CO_3)_2\downarrow.$$

When this acid salt is heated in the presence of water, it decomposes with the evolution of carbon dioxide, leaving a residue of insoluble magnesium carbonate and a solution of potassium carbonate.

$$2\,MgKH(CO_3)_2 \longrightarrow 2\,MgCO_3\downarrow + H_2O + CO_2 + 2\,K^+ + CO_3^{--}.$$

The solid is recovered from the solution by evaporation. Potassium carbonate, known as *pearl ash*, is used in the making of hard glass, soft soap, and many other substances.

Calcium Carbonate. $CaCO_3$. Calcium carbonate occurs in a relatively pure form in marble and in less pure forms in limestone and chalk. It also occurs in dolomite, the double carbonate with magnesium carbonate. Calcium carbonate is dimorphous, crystallizing from solution at temperatures below 30° in rhombohedral crystals of *calcite*, and at higher temperatures in rhombic crystals of *aragonite*. Although aragonite is unstable at temperatures below 30°, the rate of transition is slow.

Calcium carbonate exhibits the general carbonate reactions with acids and acidic oxides. It decomposes at temperatures of 700–1000° to form calcium oxide and carbon dioxide. Limestone is used extensively in the manufacture of glass, in the metallurgical industries to react with silica and the complex silicates to form a slag, and in the production of quicklime and cement. Large amounts of limestone and marble are used as building stone and in monuments.

Magnesium Carbonate. $MgCO_3$. The minerals, *magnesite* and *dolomite*, occur widely distributed in nature. The thermal decomposition of magnesium carbonate yields magnesium oxide, which is used in the manufacture of firebrick. Both magnesite and dolomite are used in lining furnaces in the steel industry, to aid in the removal of oxidized impurities of an acidic nature from pig iron. The addition of sodium carbonate to a solution of a magnesium salt yields a precipitate of magnesium basic carbonate, $Mg_4(OH)_2(CO_3)_3$. This substance has medicinal uses as "milk of magnesia," and is also used in the preparation of tooth paste and powder, and in silver polish. When basic magnesium carbonate is mixed with asbestos, the product is very porous. This material is extensively used as a heat insulator.

Bicarbonates. The formation of calcium bicarbonate by the reaction of water and carbon dioxide with calcium carbonate results in the gradual leaching out of limestone. If there is an upper stratum of resistant rock, caves are formed by this action. Mammoth Cave in Kentucky and numerous caves in Virginia and other limestone regions are examples of this. In other cases the rock is leached away and sink holes result. When carbon dioxide escapes from solutions of bicarbonates, the salt decomposes with the precipitation of the insoluble carbonate. This results in stalactites and stalagmites in caves. The bicarbonates of ferrous and magnesium ions are formed in a similar manner and they also occur in the natural waters in some regions. Bicarbonates may be converted into carbonates by reaction with basic substances and by thermal decomposition.

Hard Water. With the exception of rain water, natural waters usually contain dissolved salts in greater or smaller concentrations. Salts which are especially objectionable in water are the salts of calcium and magnesium. Water containing dissolved

bicarbonates is said to exhibit *temporary hardness*. The chlorides and sulfates of calcium and magnesium are also frequently present in natural waters. These compounds are not easily decomposed by heat and their presence constitutes *permanent hardness*.

The presence of calcium and magnesium salts in water renders it objectionable for use in the household and in the laundry, because these salts react with soap and form insoluble compounds. The formation of such precipitates increases the consumption of soap, because a solution of the soap is not obtained until all of the calcium or magnesium compound has been precipitated. These precipitates adhere to the fabric being washed and cause stains.

In the generation of steam, hard water causes the formation of a scale inside the tubes of the boiler. The deposits formed in this way are poor conductors of heat and their presence necessitates heating the tubes very hot to keep up steam. This involves a great waste of fuel and increases the corrosion of the tubes, by oxygen outside and by water inside the boiler. The presence of magnesium chloride is especially objectionable, because it reacts with water at the temperature of the boiler and forms hydrochloric acid, which corrodes the metal.

Water Softening. In order to remove the dissolved salts which cause the hardness of water, such water must be treated with the proper precipitating agents. The insoluble compounds thus formed are removed either by allowing them to settle out or by filtration. Bicarbonates, which cause temporary hardness, are easily removed by the addition of the correct amount of slaked lime to neutralize the free carbonic acid, and thus convert the acid carbonates into the normal carbonates which are insoluble.

$$Ca^{++} + 2\,HCO_3^- + Ca^{++} + 2\,OH^- \longrightarrow 2\,CaCO_3\downarrow + 2\,H_2O.$$

Magnesium chloride is removed through the precipitation of magnesium hydroxide by the addition of calcium hydroxide. This reaction, however, produces an equivalent amount of calcium chloride in the solution and this substance also is objectionable. Therefore, the calculated amount of soda ash is added to cause the precipitation of calcium carbonate, leaving only sodium salts in solution.

$$Mg^{++} + 2\,Cl^- + Ca^{++} + 2\,OH^- \longrightarrow Mg(OH)_2\downarrow + Ca^{++} + 2\,Cl^-.$$
$$Ca^{++} + 2\,Cl^- + 2\,Na^+ + CO_3^{--} \longrightarrow CaCO_3\downarrow + 2\,Na^+ + 2\,Cl^-.$$

Dissolved calcium salts, other than the bicarbonate, are removed by the addition of soda ash, as in the case of calcium chloride represented above. Sodium phosphate is also used in softening water. Its solution in water is basic, so that it neutralizes and precipitates the bicarbonates. The conversion of the other salts of calcium and magnesium into the insoluble phosphates causes their removal at the same time. Solutions of borax are basic and are used in the household for water softening.

In the *permutite* or *zeolite process* for softening water, the hard water is filtered through a zeolite filter, which is hydrated sodium aluminum silicate. Calcium, magnesium, and ferrous ions may replace sodium ions in this compound, forming insoluble products which remain in the filter. After about twelve hours of use, the filter is covered with a 10% solution of sodium chloride and allowed to stand. With the high concentration of sodium ions in this solution, the reaction is shifted in the other direction, and the calcium, magnesium, and ferrous ions are replaced by sodium ions. In this manner, the sodium compounds in the filter are regenerated, and it is ready for another period of use.

Basic Lead Carbonate. Paint. The basic carbonate of lead, $(PbCO_3)_2Pb(OH)_2$, is precipitated by the reaction of solutions of sodium carbonate and lead nitrate. This product is of the same composition as the white lead which is so extensively used in paint. In the "old Dutch process" for the manufacture of white lead, perforated disks of lead are placed over a small amount of acetic acid in earthenware pots. These pots are placed on layers of moist spent tanbark. A board floor is supported a few inches above the layer of pots and successive layers are similarly arranged until the room is full. The fermentation of the tanbark produces carbon dioxide, and heat is generated. Vapors from the acetic acid slowly react with the lead to form basic lead acetate, which reacts with carbon dioxide to form the basic lead carbonate. At the conclusion of the process, the basic lead carbonate is separated from any fragments of unchanged lead and ground with linseed oil.

Basic lead carbonate is also made by an electrolytic process. In this process the anodes are lead and the cathodes iron. A diaphragm about the cathode divides the cell so that the electrolytes around the two electrodes are separated except for ionic migration

through the diaphragm. Both solutions contain sodium acetate; but the anode liquid contains only a few tenths of one per cent of sodium carbonate, while the cathode liquid contains as much as five per cent. During the electrolysis, lead dissolves at the anode to form lead acetate which diffuses away from the anode and comes in contact with carbonate ions which are being electrolytically attracted toward the anode. The reaction of these two materials causes the precipitation of basic lead carbonate.

Paint consists of a quick-drying oil, a material to give good covering power, an inert filler, and a color pigment if a colored paint is desired. The drying oil, *the vehicle*, most extensively used is linseed oil. It "dries" due to oxidation and this results in the formation of a tough film which adheres to the wood and protects it. *Driers*, such as oxides of manganese, nickel, and cobalt, are sometimes added to catalyze the oxidation reaction and hasten the drying. Such substances are used particularly in paint for inside work where it is shielded from the action of sunlight. Covering power is secured by the use of substances which readily reflect light, *the body*. This renders the paint opaque and permits hiding the surface painted. For this purpose basic lead carbonate is most extensively used, because it gives the paint good covering power. Basic lead sulfate, lithopone, and zinc white are also used as the body in paints. Zinc white is used extensively in interior work and in other places where the paint is likely to be exposed to air containing hydrogen sulfide. Hydrogen sulfide slowly reacts with the basic ingredients of paint and causes lead white to darken, due to the formation of lead sulfide which is black. Zinc sulfide is white and the reaction of hydrogen sulfide with zinc white does not cause any darkening. The *filler* is added to the paint to prevent the body becoming spread too thin. Various oxides and other colored substances are used as pigments.

Test for the Carbonate Ion. The addition of an acid to a solution of a carbonate causes the evolution of carbon dioxide gas. The gas may be recognized by passing it into a solution of calcium hydroxide with which it reacts to form a white precipitate of calcium carbonate.

$$CO_3^{--} + 2\,H_3O^+ \longrightarrow CO_2\uparrow + 3\,H_2O.$$

$$Ca^{++} + 2\,OH^- + CO_2 \longrightarrow CaCO_3\downarrow + H_2O.$$

If a sulfite is present along with the carbonate, sulfur dioxide gas is also evolved. This oxide is more soluble and more strongly acidic than carbon dioxide. It is absorbed by calcium hydroxide to form the bisulfite, which is sufficiently acidic to reduce the carbonate ion concentration below the required value to precipitate calcium carbonate. Consequently, sulfites, if they are present, must be removed before this test for the carbonate is applied. This may be accomplished by oxidizing the sulfite to sulfate by the action of potassium permanganate in basic solution. Manganese dioxide is the reduction product under these conditions.

$$[MnO_4^- + 2\,H_2O + 3\,\epsilon \longrightarrow 4\,OH^- + MnO_2.] \quad \times 2.$$

$$[SO_3^{--} + 2\,OH^- \longrightarrow SO_4^{--} + H_2O + 2\,\epsilon.] \quad \times 3.$$

$$2\,MnO_4^- + H_2O + 3\,SO_3^{--} \longrightarrow 2\,MnO_2 + 3\,SO_4^{--} + 2\,OH^-.$$

SILICATES

The most abundant minerals in the outer part of the earth are the silicates. Rocks which have resulted from the solidification of the molten matter of the earth are igneous rocks. The most abundant of the igneous rocks is *granite*, which is a mixture of quartz, feldspar, and mica. The common *feldspar*, *orthoclase*, is a complex silicate of the composition $KAlSi_3O_8$. It is the most abundant of all of the minerals in the surface of the earth. The *micas* are acid salts of orthosilicic acid containing aluminum and the alkali metals, *e.g.*, *muscovite*, $KAl_3H_2(SiO_4)_3$. Some of the minerals of this class contain iron and magnesium in place of some of the aluminum. *Talc* is a magnesium salt of metasilicic acid of the composition, $Mg_3H_2(SiO_3)_4$. The name, *asbestos*, is applied to several of the magnesium silicates. Kaolin or clay is an impure material containing the mineral, *kaolinite*, $Al_2H_4Si_2O_9$, a salt of a condensed silicic acid. There are a large number of minerals which are polysilicates. Many of the natural silicates have important uses: *e.g.*, granite and sandstone for building materials; kaolin for the manufacture of brick and pottery; asbestos as a heat insulator; mica as an electrical insulator; talc in soap, talcum powder, roofing materials, and rubber; feldspar in pottery; and beryl as an ore of beryllium.

The continued breathing of air containing the dust of silicates results in a pulmonary disease known as *silicosis*. This condition

is frequently encountered among tunnel workers who have been drilling and blasting through silicate rock.

Decomposition of the Complex Silicates. Some of the natural silicates which are salts of orthosilicic acid and of metasilicic acid may be decomposed by the action of hydrochloric acid; but many of the complex silicates are not decomposed by the action of any of the common acids. Two methods are in common use for the decomposition of these complex materials. A mixture of simple silicates and metal oxides may be formed by fusing the complex silicate with sodium carbonate.

$$2\ KAlSi_3O_8 + 5\ Na_2CO_3 \longrightarrow K_2SiO_3 + 5\ Na_2SiO_3 + Al_2O_3 + 5\ CO_2.$$

This product may be decomposed by hydrochloric acid with the precipitation of hydrous silica and the formation of the chlorides of the metals. Hydrofluoric acid reacts with the silicates, forming gaseous silicon tetrafluoride and the fluorides of the metals.

$$KAlSi_3O_8 + 16\ HF \longrightarrow KF + AlF_3 + 3\ SiF_4 + 8\ H_2O.$$

A test for the presence of silicates may be based on this reaction. A drop of water held in a wire loop is placed in the fumes from a mixture of the material with hydrofluoric acid. If silicon fluoride is present in the fumes, the water becomes cloudy on account of the formation of silica by the hydrolysis of the fluoride.

$$3\ SiF_4 + 3\ H_2O \longrightarrow SiO_2(H_2O) + 2\ H_2SiF_6.$$

Soluble Silicates. The common water-soluble silicates are those of sodium and potassium. These salts may be prepared by the fusion of the metal hydroxide or carbonate with the proper proportions of silicon dioxide. The sodium salts are the more familiar. Both the metasilicate, Na_2SiO_3, and the orthosilicate, Na_4SiO_4, are prepared commercially for use in soap. These salts hydrolyze producing basic solutions which cause the removal of bicarbonate ions from hard water. They also furnish silicate ions which cause the precipitation of the insoluble silicates of the other metal ions which would interfere with the action of soap. A commercial product, known as *water glass*, is prepared by fusing powdered quartz with sodium carbonate and extracting the product with water. Water glass may also be prepared by boiling a suspension of silica in sodium hydroxide solution under a pres-

sure of approximately four atmospheres. The product is a syrupy liquid, containing the orthosilicate and metasilicate with an excess of silica in colloidal suspension. It is used as a fireproofing material, a sizing in paper, a glue for cardboard boxes, an egg preservative, a cement for tile, and in soap and washing powders.

Glass. Glass is a non-crystalline product formed by fusing sand and other non-metal oxides with various basic substances. The product is a supercooled liquid solution of the different components in each other at ordinary temperatures; and the composition may be varied depending on the uses for which the glass is intended. Glass has no fixed melting point but gradually softens when it is heated.

Various methods are employed for shaping the softened material into the objects made of glass. Some objects, such as bottles, are blown within a mold, much of the work now being done by automatically operated machinery. Other objects are made by pouring the fluid material into a mold and allowing it to cool and harden. Window glass in the United States is made by mechanically drawing a flat sheet of glass. The details of the processes used by different manufacturers differ. In the Fourcault process, the sheet forms in the slot of a fireclay block on the surface of the melted glass and is drawn vertically upward through this slot. In the Colburn process, a sheet of glass is drawn continuously through and over rollers from a hearth supplied with the molten material. The sheet of glass cools and hardens as it passes over a flattening table and is annealed by passage through a chamber where it cools slowly. Plate glass may be made by pouring the molten material on a large cast iron table and rolling it with a hot roller.

The properties of glass differ depending on its composition. Common *soda glass* contains silicates and silica in proportions equivalent to approximately 75% of silica, 15% of sodium oxide, and 10% of calcium oxide, although aluminum compounds may also be present and these proportions may be varied. This glass is used in making bottles, window glass, glass tubing, and many other products. It is called *soft glass* because it softens enough to be shaped and worked at moderately low temperatures, such as those given by the flame of the Bunsen burner. *Potassium glass* contains potassium instead of sodium in the silicate. It softens at

higher temperatures and is called *hard glass*. The potassium-lead glass, known as *flint glass*, has high density and reflects light to a high degree. It is used in making cut-glass objects and optical instruments. A glass composed of borates and silicates is made by the addition of boric oxide to the charge. "Pyrex" glass contains large percentages of acidic oxides, about 80% of silicon dioxide and 12% of boric oxide. It has a low coefficient of expansion so that it is suitable for the manufacture of laboratory apparatus and ovenware.

A new process for the manufacture of a glass of high silica content has been developed recently. By the selection of suitable raw materials, a mixture of two products is obtained, the one high in silica, the other soluble in acids and containing almost no silica. This product is shaped into the desired objects in the usual manner; and the soluble material is leached out. The object is now porous so that it must be heated to form a clear solid. During this stage the volume of the material decreases an amount equal to the volume of the substances leached out. Consequently, the objects are made oversize to allow for this shrinkage. This material has been designated "96% Silica Glass" and is marketed under the trade name "Pyrex Vycor."

Different substances may be added to the charge in order to produce colored glass. Ferrous compounds, present in cheap glass, give an unattractive green color; oxides of copper and of chromium give a deep green color; cobalt, blue; and manganese, violet. Organic matter, such as carbonized straw, gives a brown color; and selenium compounds, a deep-red color. Through the addition of stannic oxide or calcium fluoride, "milk glass" is obtained.

Glass which is cooled quickly is very brittle on account of stresses within the mass, caused by the more rapid cooling of the outer part of the glass than the interior, and the contraction which accompanies the cooling of glass. Consequently, it is annealed by passing it slowly through a furnace which is hot at one end and much cooler at the other. In this way the glass cools slowly and uniformly and internal stresses are not developed, or are relieved. In thick glass objects the process of annealing may take a long time. The annealing of the 200-inch reflector for the great telescope at Mt. Palomar, California, required about one year.

The greatest demand for plate glass is now in the automobile industry. The danger of serious injury resulting from broken windows and flying glass has led to the development of "shatter-proof" glass. Two layers of plate glass are cemented together with an intermediate layer of cellulose acetate. When this glass is broken, the fragments are held together by the center layer. Bullet-proof windows are made in the same manner through the use of five or more layers.

Glass bricks and tile are now being used as construction materials in buildings. Finely divided glass fiber is extensively used in the heat insulation of buildings, and it has possible use as a textile fiber.

Portland Cement. The extensive use of Portland cement has developed since about 1900 and has completely revolutionized the methods employed in building operations. It is prepared by heating a mixture of finely ground limestone and clay of the proper composition. The mixed materials are "burned" in a rotary kiln,

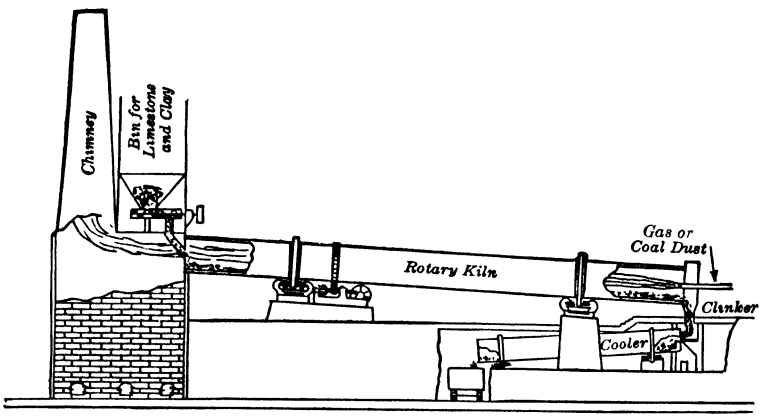


FIG. 157. — Diagram of a Cement Kiln.

Fig. 157, in which they gradually work down to the hot end, where the temperature is 1400–1600°. At this temperature, the substances partially fuse and form lumps, known as clinker. After cooling, the product is ground with 2–3% of gypsum. The product consists for the most part of three compounds, dicalcium silicate, Ca_2SiO_4, tricalcium silicate, Ca_3SiO_5, and calcium aluminate, $Ca_3(AlO_3)_2$. The setting of the cement is due to the hydration of these compounds and the rate of setting is regulated by the

gypsum. Gelatinous products are formed and these gradually harden and cement the crystals together. The changes which occur during hardening of cement are very complex and they continue for a long time, though the first stages are complete in 28–30 hours. Approximately 125 million barrels of cement were produced in the United States in 1939. It is used primarily in the form of a mixture with rock and sand to make concrete. The fact that it will set beneath the surface of water permits its use in building dams, piers for bridges, canal locks, and many other structures.

Ceramic Products. The ceramic products include brick, tile, pottery, porcelain, and different varieties of earthenware. Mixtures of quartz, clay, and feldspar are used in different proportions and baked at different temperatures in the production of a great variety of ceramic products. Bricks, tiles, and most of the varieties of pottery are made from naturally occurring, sandy clays which contain feldspar; and they are usually red, yellow, or brown in color, due to iron oxide in the clay. The clay of suitable composition is mixed with water to the proper consistency and then cut or molded into shape. The articles are baked in kilns, and changes in the chemical composition of the kaolin take place. The feldspar melts at about 1200° and binds the clay and quartz together. Surface glaze may be obtained by throwing salt into the kilns toward the end of the firing. Articles of china and porcelain are made from a white porcelain clay which contains no iron, a small per cent of feldspar being added unless enough is present in the natural material. A high per cent of calcium phosphate may be used to produce a soft porcelain; but in general there is only a small difference in the composition of the products, the differences in the finished product being due, for the most part, to the methods of manufacture. After the first baking, the product is porous; and a glaze is produced by spreading a paste of feldspar and silica on the surface of the articles and firing them a second time.

BORATES

The borates are the salts of the weak and slightly soluble boric acids. In addition to the simple borates, there are a number of polyborates, such as *borax*, $Na_2B_4O_7(H_2O)_{10}$, and *colemanite*, $Ca_2B_6O_{11}(H_2O)_5$.

Borax. $Na_2B_4O_7(H_2O)_{10}$. This salt of tetraboric acid is the most important of the borates. It is produced in large quantities from the mother liquor after the crystallization of potassium chloride from the brines of Searles Lake in California. The decahydrate crystallizes from solution at temperatures below 60°, while the pentahydrate is obtained at higher temperatures. A metastable tetrahydrate, called *kernite*, $Na_2B_4O_7(H_2O)_4$, also occurs. The reaction of boric acid with basic hydroxides produces the tetraborates.

$$4\,H_3BO_3 + 2\,OH^- \rightleftharpoons B_4O_7^{--} + 7\,H_2O.$$

Borax exhibits three important reactions. With strong acids it yields boric acid.

$$B_4O_7^{--} + 2\,H_3O^+ + 3\,H_2O \longrightarrow 4\,H_3BO_3\downarrow.$$

It hydrolyzes to give a basic solution.

$$B_4O_7^{--} + 7\,H_2O \rightleftharpoons 4\,H_3BO_3 + 2\,OH^-.$$

Because of this property it is used in the household as a water softener and cleansing agent. Borax fuses to form a clear, glasslike melt, which has acidic properties on account of the presence of an excess of boric oxide. Consequently, the fused material reacts with metal oxides to form a mixture of metaborates.

$$Na_2B_4O_7 + CuO \longrightarrow 2\,NaBO_2 + Cu(BO_2)_2.$$

The identification of some of the metal ions may be based on the color of the metaborate. The test, known as the *borax bead test*, is carried out by fusing borax to a clear, glasslike bead in a small loop of platinum wire. A minute amount of the solid to be tested is caught up by bringing the bead into contact with the substance, and it is again melted. The color of the bead differs for some of the metal ions depending on whether it has been heated in the outer, oxidizing flame or the inner, reducing flame. Some of the characteristic borax bead colors are shown in Table 41.

The use of borax as a flux in soldering and welding depends on the acidic reaction of the fused material. Enamels are made by melting borax with glass, forming a glasslike product of low melting point. The addition of calcium phosphate, stannic oxide, or calcium fluoride produces a white enamel.

TABLE 41

BORAX BEAD COLORS

Element	*Reducing Flame*	*Oxidizing Flame*
Cobalt	Blue	Blue
Chromium	Green	Green
Copper	Red	Blue
Iron	Green	Yellow
Manganese	Colorless	Violet

Peroxyborates. The most important of these salts is sodium peroxyborate, $NaBO_3(H_2O)_4$. It may be prepared by the reaction of hydrogen peroxide with borax and by the electrolytic oxidation of borates.

$$B_4O_7^{--} + 2\ OH^- + 4\ H_2O_2 \rightleftharpoons 4\ BO_3^- + 5\ H_2O.$$

The salt liberates hydrogen peroxide in aqueous solution and has bleaching properties. It is used as an antiseptic material in certain tooth powders. Because of its close relation to the peroxides, the graphic formulas are written in the following manner.

H—O—O—B=O
Peroxyboric acid

Na—O—O—B=O
Sodium peroxyborate

EXERCISES

1. Account for the basic properties of the simple carbonates, silicates, and borates.
2. Account for the fact that calcium bicarbonate exhibits both basic and acidic properties.
3. Account for the acidic properties of fused polysilicates and polyborates.
4. Describe the production of sodium carbonate and write equations for all of the reactions which are involved.
5. Write equations to represent one reaction for the conversion of a carbonate into a bicarbonate and two for the reverse change.
6. In terms of the solubility product principle and the ionic equilibria, account for the solution of calcium carbonate in water containing carbon dioxide.
7. What is hard water? Give three reasons why it may be unsuited to industrial use. Illustrate by equations.
8. Discuss the softening of hard water, showing by equations how the use of lime, sodium carbonate, sodium phosphate, sodium silicate, and sodium tetraborate aid in the removal of objectionable impurities.
9. Describe a test for carbonates in the presence of sulfites.
10. Discuss the production of glass, showing how the properties are altered through changes in the composition of the charge used in glass making.

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CHAPTER XXXI

COMPOUNDS OF CHROMIUM AND MANGANESE

The transition elements are composed of atoms containing two incomplete shells of electrons. As the number of electrons in the outer shell of the kernel of the atom increases, the similarities of the elements of consecutive atomic numbers become more apparent, as is shown by the relationships of iron, cobalt, and nickel. The elements of Groups VI–B and VII–B resemble each other in the formation of two series of compounds. The compounds in the lower oxidation states are similar to those of the other metals; and the compounds in the higher oxidation states are similar to those of the other non-metals.

The formation of compounds in which these elements are in their lower oxidation states is associated with the electrons in the valence shell and, in some of their reactions, with one or two of the electrons in the incomplete outer shell of the kernel of the atom also. The elements produce similar electrovalent ions, because their atoms contain the same number of electrons in the valence shell. The formation of compounds in the high oxidation states involves changes affecting not only the electrons in the valence shell but also those in excess of eight in the next shell. Since these numbers differ for atoms in the different periodic groups, the compounds of the elements in their highest oxidation states in one of the groups differ from those in another group. The transition in properties from metallic to non-metallic, as the oxidation number rises, gives a relationship between the compounds of a single element which is analogous to that previously observed for an entire group of elements. The chemistry of a particular element in the transition series is, therefore, complicated not only by the number of its oxidation states and the dissimilarities in the compounds which it forms in the different states, but also by the oxidation-reduction reactions into which these compounds enter. Because of the dual nature of these elements, the concentrations

of hydronium and hydroxide ions in the solutions play an important rôle in determining both the nature of the oxidation-reduction products and also the activity of the reactants.

The compounds of chromium and manganese are discussed to illustrate a relationship which has not been observed so prominently among the compounds of the simpler elements. This relationship is general among the elements in the transition series, particularly those in the vanadium, chromium, and manganese groups.

COMPOUNDS OF CHROMIUM

Chromium yields compounds in three oxidation states. These states and the formulas of representative compounds in each are listed in Table 42.

TABLE 42

CHROMIUM COMPOUNDS

Oxidation State	*Oxide*	*Hydroxide*	*Reaction*	*Ions*
2+	CrO	$Cr(OH)_2$	Basic	Cr^{++}
3+	Cr_2O_3	$Cr_2O_3(H_2O)_x$	Amphoteric	Cr^{+++} $Cr(OH)_4^-$
6+	CrO_3	H_2CrO_4 $H_2Cr_2O_7$	Acidic Acidic	CrO_4^{--} $Cr_2O_7^{--}$

The compounds in the 3+ and 6+ states are the most stable and important compounds of the element.

Chromous Compounds. Chromous salts may be prepared by the reduction of chromic salts by zinc in acidic solution. The chloride and sulfate are soluble salts which may be used as sources of the chromous ion. Solutions containing this ion are blue in color. The hydroxide is slightly soluble and is basic in properties. Chromous compounds are similar to ferrous compounds, except that the chromous ion is less stable than the ferrous ion.

Chromic Compounds and Chromites. *Chromic Oxide,* Cr_2O_3, is the most stable of the oxides of chromium. It is formed when the metal and other oxides of the metal are heated strongly in air. It is a finely divided green powder which is important as a green pigment in paint. The *hydrous oxide,* containing variable and indefinite proportions of water, $Cr_2O_3(H_2O)_x$, frequently

called chromic hydroxide, may be precipitated from solutions of chromic salts and from metachromites.

The chromic ion exists in solution in two different degrees of hydration, $Cr(H_2O)_6^{+++}$, and $Cr(H_2O)_4^{+++}$. Solutions containing the $Cr(H_2O)_6^{+++}$ ion are formed by dissolving chromic salts in cold water and have a violet color. A complex ion with the negative ion, such as the chloride complex $Cr(H_2O)_4Cl_2^+$, formed in concentrated and hot solutions, is green. The common chromic salts are the sulfate, $Cr_2(SO_4)_3(HO_2)_{18}$, the chloride, $CrCl_3(H_2O)_6$, and chrome alum, $KCr(SO_4)_2(H_2O)_{12}$. The chromic salts are usually prepared by the reduction of the dichromates in acidic solution. The chromic ion hydrolyzes to form an acidic solution.

$$Cr(H_2O)_6^{+++} + H_2O \rightleftharpoons Cr(OH)(H_2O)_5^{++} + H_3O^+.$$

The essential changes involving the reactions of the chromic ion may be shown by the use of simple formulas in which the water of hydration of the ions is not represented. The addition of a weak base to a solution containing the chromic ion leads to the precipitation of the hydrous oxide, to which the formula, $Cr_2O_3(H_2O)_3$, will be assigned although the actual proportions of water are indefinite.

$$2\,Cr^{+++} + 6\,OH^- \rightleftharpoons Cr_2O_3(H_2O)_3\downarrow.$$
$$2\,Cr^{+++} + 6\,C_2H_3O_2^- + 6\,H_2O \rightleftharpoons Cr_2O_3(H_2O)_3\downarrow + 6\,HC_2H_3O_2.$$

The hydrous oxide reacts with strong acids to form chromic ions, and with alkalies to form the metachromite complex ion.

$$Cr_2O_3(H_2O)_3 + 6\,H_3O^+ \rightleftharpoons 2\,Cr^{+++} + 12\,H_2O.$$
$$Cr_2O_3(H_2O)_3 + 2\,OH^- \rightleftharpoons 2\,Cr(OH)_4^-.$$

The metachromite is decomposed, with the reprecipitation of the oxide, by boiling the solution and by the action of weak acids.

$$2\,Cr(OH)_4^- + 2\,H_3O^+ \longrightarrow Cr_2O_3(H_2O)_3\downarrow + 4\,H_2O.$$

Chromates and Dichromates. In the high state of oxidation, chromium is non-metallic in nature. *Chromic anhydride*, CrO_3, reacts with water to form chromic acid, H_2CrO_4, and dichromic acid, $H_2Cr_2O_7$. The oxide is usually prepared as a red, crystalline product by the reaction of concentrated sulfuric acid with a cold concentrated solution of potassium dichromate.

The *chromates* of *sodium* and *potassium* are prepared by heating the naturally occurring mineral *chromite*, $Fe(CrO_2)_2$, with the alkali carbonate in a current of air.

$$4\ Fe(CrO_2)_2 + 8\ K_2CO_3 + 7\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ K_2CrO_4 + 8\ CO_2.$$

The product is crushed and leached with water, and the chromate is crystallized from the solution. Slightly soluble chromates, such as those of barium and lead, are prepared by mixing solutions of their ions.

$$Ba^{++} + CrO_4^{--} \rightleftharpoons BaCrO_4\downarrow.$$
$$Pb^{++} + CrO_4^{--} \rightleftharpoons PbCrO_4\downarrow.$$

Several of the chromates are important pigments in paint: *e.g.*, chrome yellow, $PbCrO_4$; chrome red, Pb_2OCrO_4; and zinc chromate, $ZnCrO_4$.

Soluble chromates hydrolyze in solution to form an equilibrium mixture of the chromate and dichromate.

$$2\ CrO_4^{--} + H_2O \rightleftharpoons Cr_2O_7^{--} + 2\ OH^-.$$

The addition of an acid disturbs this equilibrium producing the dichromate, so that the dichromates of sodium and potassium may be prepared from the chromates by the addition of an acid followed by the crystallization of the salt from the solution. An excess of a strong base converts the dichromate to the chromate.

$$Cr_2O_7^{--} + 2\ OH^- \longrightarrow 2\ CrO_4^{--} + H_2O.$$

Sodium dichromate is used in tanning leather. The hide is soaked in a solution of sodium dichromate; and when this material is subsequently reduced, chromic oxide is deposited in the pores of the hide. The dichromates are active oxidizing agents and potassium dichromate is used in analytical chemistry because of this property. A solution of chromic acid, prepared by the reaction of concentrated sulfuric acid with sodium chromate, is used as a "cleaning solution" for laboratory glassware.

The Oxidation of Chromic Compounds. Since chromium in its high oxidation state is non-metallic in nature, the oxidation of chromic compounds occurs most readily in the presence of a base, as discussed in Chapter XVII. The oxidation of chromic compounds may be carried out in aqueous solution or through the use of fused materials. Starting with a solution of a chromic salt, the reaction proceeds in two stages: *viz.*, the conversion of the

chromic ion to the metachromite; and the oxidation of the metachromite to the chromate. There are several oxidizing agents which are active enough in basic solution to oxidize the metachromites; for example, sodium hypochlorite, sodium peroxide, and hydrogen peroxide.

$$[ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-.] \times 3.$$
$$[Cr(OH)_4^- + 4\,OH^- \longrightarrow CrO_4^{--} + 4\,H_2O + 3\,\epsilon.] \times 2.$$
$$3\,ClO^- + 2\,Cr(OH)_4^- + 2\,OH^- \longrightarrow 3\,Cl^- + 2\,CrO_4^{--} + 5\,H_2O.$$

Clearly, the basic medium is a favorable condition for this reaction, since hydroxide ions are consumed.

Anhydrous chromic oxide does not dissolve readily in basic solutions, so that the oxidation of the oxide is best carried out in the presence of the fused alkali hydroxide or carbonate. Suitable oxidizing agents under these conditions are the alkali nitrates and chlorates. The equations for these reactions are most easily balanced by noting the changes in oxidation numbers.

$$\begin{array}{c} Cl^{5+} \text{———————} (-6) \text{———————} Cl^- \\ Cr_2O_3 + KClO_3 + 4\,KOH \longrightarrow 2\,K_2CrO_4 + KCl + 2\,H_2O. \\ 2\,Cr^{3+} \text{———————} (+6) \text{———} 2\,Cr^{6+} \end{array}$$

The Reduction of Dichromates. The reduction of chromium compounds from the high oxidation state takes place most actively in acidic solution because hydronium ions enter into this reaction, and the concentration of hydronium ions is greater in acidic solution than in neutral and basic solutions. Under these conditions, the reaction involves the reduction of the dichromate ion to the chromic ion. The customary oxidation products of the various classes of reducing agents with acidic oxidizing agents are obtained in these reactions. The ferrous ion, for example, is oxidized to form the ferric ion.

$$Cr_2O_7^{--} + 14\,H^+ + 6\,\epsilon \longrightarrow 2\,Cr^{+++} + 7\,H_2O.$$
$$[Fe^{++} \longrightarrow Fe^{+++} + 1\,\epsilon.] \times 6.$$
$$Cr_2O_7^{--} + 14\,H^+ + 6\,Fe^{++} \longrightarrow 2\,Cr^{+++} + 6\,Fe^{+++} + 7\,H_2O.$$

Chromates may also react as oxidizing agents. The reduction occurs in basic solution and the metachromite is the product in such solutions. The oxidizing activity of the chromates is not so great as that of the dichromates, and the substance is much less important as an oxidizing agent. Sulfites may be oxidized to

form sulfates by the action of a basic solution of potassium chromate.

$$[CrO_4^{--} + 4\,H_2O + 3\,\epsilon \longrightarrow Cr(OH)_4^- + 4\,OH^-.] \times 2.$$
$$[SO_3^{--} + 2\,OH^- \longrightarrow SO_4^{--} + H_2O + 2\,\epsilon.] \times 3.$$
$$2\,CrO_4^{--} + 3\,SO_3^{--} + 5\,H_2O \longrightarrow 2\,Cr(OH)_4^- + 3\,SO_4^{--} + 2\,OH^-.$$

Test for the Chromic Ion. The chromic ion reacts with a solution of ammonia containing an excess of ammonium ions to precipitate the hydrous oxide, as a member of the iron group of cations. When the precipitate is digested with sodium hydroxide and sodium peroxide or hydrogen peroxide, the chromate is formed.

$$[Na_2O_2 + 2\,H_2O + 2\,\epsilon \longrightarrow 2\,Na^+ + 4\,OH^-.] \times 3.$$
$$Cr_2O_3 + 10\,OH^- \longrightarrow 2\,CrO_4^{--} + 5\,H_2O + 6\,\epsilon.$$
$$3\,Na_2O_2 + Cr_2O_3 + H_2O \longrightarrow 6\,Na^+ + 2\,CrO_4^{--} + 2\,OH^-.$$

The filtrate may now be made weakly acidic with acetic acid and a yellow precipitate of lead chromate may be precipitated by reaction with lead ions.

$$CrO_4^{--} + Pb^{++} \rightleftharpoons PbCrO_4\downarrow.$$

Hydrogen peroxide reacts with acidic solutions of the dichromate to produce a deep-blue solution of the peroxychromate of uncertain composition. The color of the solution fades after a short time. The acid may be extracted from the aqueous solution with ether, producing a blue ether extract, as a delicate test for the chromate.

COMPOUNDS OF MANGANESE

Manganese may form compounds in five oxidation states. These states and the formulas of typical compounds are shown in Table 43.

TABLE 43

MANGANESE COMPOUNDS

Oxidation State	*Oxide*	*Hydroxide*	*Reaction*	*Ions*
2	MnO	$Mn(OH)_2$	Basic	Mn^{++}
3	Mn_2O_3	$Mn(OH)_3$	Basic	Mn^{+++}
4	MnO_2	$Mn(OH)_4$	Amphoteric	MnO_3^{--}
6	MnO_3	H_2MnO_4	Acidic	MnO_4^{--}
7	Mn_2O_7	$HMnO_4$	Acidic	MnO_4^-

Compounds containing the manganic ion, Mn^{+++}, are unstable and produce the manganous ion and manganese dioxide.

$$2\ Mn^{+++} + 6\ H_2O \longrightarrow Mn^{++} + MnO_2 + 4\ H_3O^+.$$

This oxidation state of manganese is unimportant and will be omitted from further discussion.

Manganous Compounds. Manganese exhibits the behavior of a metallic element in the divalent state and yields compounds which are similar to those of magnesium and ferrous iron. The common manganous salts are the chloride and the sulfate. These may be formed by the reduction of manganese dioxide in acidic solution. The insoluble manganous compounds, such as the carbonate, the sulfide, the phosphate, and the hydroxide, are prepared by precipitation. Manganous ion yields a white crystalline precipitate of manganous ammonium phosphate in the presence of a soluble phosphate and ammonia.

$$Mn^{++} + HPO_4^{--} + NH_3 \rightleftharpoons MnNH_4PO_4\downarrow.$$

The presence of ammonium ions in an ammoniacal solution reduces the concentration of the hydroxide ions so greatly that manganous hydroxide does not precipitate. The addition of sodium hydroxide to a solution of a manganous salt does cause the precipitation of manganous hydroxide.

$$Mn^{++} + 2\ OH^- \rightleftharpoons Mn(OH)_2\downarrow.$$

When the ammoniacal solution of a manganous salt is allowed to stand exposed to air, atmospheric oxidation causes the formation of a brown precipitate of manganous manganite, $MnMnO_3$. A similar darkening of suspended manganous hydroxide occurs in contact with air.

$$4\ Mn(OH)_2 + O_2 \longrightarrow 2\ MnMnO_3 + 4\ H_2O.$$

Manganese Dioxide. Manganites. The most important compound of tetravalent manganese is the dioxide, MnO_2, which occurs as the natural mineral, *pyrolusite*. This oxide is both basic and acidic, but is not active in either respect. With cold, concentrated hydrochloric acid it yields a green solution of the tetrachloride; but with hot hydrochloric acid, the manganese is reduced to the manganous condition by the chloride ions.

$$MnO_2 + 4\ H_3O^+ + 4\ Cl^- \longrightarrow MnCl_4 + 6\ H_2O.$$
$$MnO_2 + 4\ H_3O^+ + 4\ Cl^- \longrightarrow Mn^{++} + 2\ Cl^- + Cl_2 + 6\ H_2O.$$

The dioxide does not react readily with solutions of the alkalies; but manganites may be formed by fusing the dioxide with some of the metal oxides and hydroxides. If manganese dioxide is precipitated from a solution containing manganous and zinc ions, the manganites of these ions are formed also.

Manganese dioxide is used in the production of paint and varnish as an agent to catalyze the oxidation of the oil. It is often employed in the glass industry to oxidize ferrous compounds to ferric compounds. Since the colors of manganous and ferric silicates are complementary, a colorless glass may be obtained if both of these silicates are present in the correct proportions, whereas ferrous silicate alone imparts a green color to glass. The most extensive direct use of manganese dioxide is in dry cells.

Manganates. The manganates are salts in which manganese has an oxidation number of 6 + and is actively non-metallic in its chemical behavior. These salts are green in color, a color attributed to the divalent manganate ion. The manganates are formed as intermediate products in the preparation of the permanganates. Potassium manganate is formed by fusing manganese dioxide with potassium hydroxide in the presence of a free supply of air.

$$2\ MnO_2 + 4\ KOH + O_2 \longrightarrow 2\ K_2MnO_4 + 2\ H_2O.$$

The manganates are stable in basic solution, but the addition of an acid causes the spontaneous decomposition of the manganate ion to yield manganese dioxide and an equivalent amount of the permanganate, showing that the element yields more stable compounds in its lower and higher valence states than in the manganate.

$$4\ H_3O^+ + 3\ MnO_4^{--} \longrightarrow 2\ MnO_4^- + MnO_2\downarrow + 6\ H_2O.$$

This is an oxidation-reduction reaction of the same nature as that which occurs when a solution of a hypochlorite is warmed.

Permanganates. The permanganates and permanganic acid are fairly stable in dilute solution in the absence of reducing substances. These solutions are characterized by a purple color due to the permanganate ion. In the commercial preparation of the permanganate, the manganate is first formed and is then oxidized to the permanganate by the action of chlorine in basic solution.

$$2\ MnO_4^{--} + ClO^- + H_2O \longrightarrow 2\ MnO_4^- + Cl^- + 2\ OH^-.$$

The oxidation of the manganate to the permanganate is also accomplished electrolytically at the anode by the passage of a direct current of electricity through a solution of the manganate. Solutions of the permanganates are active oxidizing agents which have a number of important uses. They are also used as germicidal solutions. The reaction of cold, concentrated sulfuric acid with solid potassium permanganate yields the oxide Mn_2O_7.

$$2\,KMnO_4 + 2\,H_2SO_4 \longrightarrow 2\,KHSO_4 + Mn_2O_7 + H_2O.$$

This substance is an unstable brown liquid.

The Oxidation of Manganous Compounds. The oxidation of the manganous compounds takes place readily in the presence of a basic substance, because the stability of the product in the high oxidation numbers of manganese is increased in basic solution. Manganese dioxide is the usual product of the oxidation of manganous compounds in aqueous basic solutions, because this product is very slightly soluble.

$$Mn(OH)_2 + BrO^- \longrightarrow MnO_2 + Br^- + H_2O.$$

Strong oxidizing agents in concentrated solution may convert a portion of the manganous salt directly to the manganate stage of oxidation; but the oxidation to form manganates is much more rapidly and completely accomplished through the use of a fused base than in aqueous solution.

$$\begin{array}{c} N^{5+}\text{——————}(-2)\text{——}N^{3+} \\ 2\,KNO_3 + MnO + K_2CO_3 \longrightarrow 2\,KNO_2 + K_2MnO_4 + CO_2. \\ Mn^{2+}\text{————}(+4)\text{————}Mn^{6+} \end{array}$$

The Oxidation of Manganese Dioxide. The oxidation of manganese dioxide to the manganate is best accomplished by the action of oxidizing agents in the presence of a melted base. Suitable oxidizing agents are oxygen and the alkali metal peroxides, nitrates, and chlorates.

$$KNO_3 + MnO_2 + K_2CO_3 \longrightarrow KNO_2 + K_2MnO_4 + CO_2.$$

The Reduction of Permanganates. Permanganates may be reduced in either basic or acidic solution; and the nature of the reduction product which they yield is determined both by the basicity or acidity of the solution and by the strength of the reducing agent.

The Reduction of Permanganates in Basic Solution. The compounds of manganese in its lower non-metallic stage of oxidation are produced by reduction under these conditions. By mild reduction, the manganate may be formed; but the usual product of the basic reduction of permanganates is manganese dioxide. This reduction may be brought about by the action of sulfites, which are themselves converted into sulfates. This reaction has been discussed previously for the elimination of the interference caused by sulfites in the carbonate test. Manganous compounds may be oxidized to manganese dioxide by the action of potassium permanganate in basic solution.

$$[MnO_4^- + 2\,H_2O + 3\,\epsilon \longrightarrow MnO_2 + 4\,OH^-.] \quad \times 2.$$
$$[Mn(OH)_2 + 2\,OH^- \longrightarrow MnO_2 + 2\,H_2O + 2\,\epsilon.] \quad \times 3.$$
$$2\,MnO_4^- + 3\,Mn(OH)_2 \longrightarrow 5\,MnO_2 + 2\,OH^- + 2\,H_2O.$$

The Reduction of Permanganates in Acid Solution. Manganous salts result from the acidic reduction of permanganates. There are a number of reducing agents which may cause this reaction; and the customary products of acidic oxidation are produced, as discussed in Chapter XVII. The chloride ion, for example, is oxidized to form free chlorine.

$$[MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O.] \quad \times 2.$$
$$[2\,Cl^- \longrightarrow Cl_2 + 2\,\epsilon.] \quad \times 5.$$
$$2\,MnO_4^- + 16\,H^+ + 10\,Cl^- \longrightarrow 2\,Mn^{++} + 5\,Cl_2 + 8\,H_2O.$$

The oxalate ion is oxidized to form carbon dioxide.

$$[MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O.] \quad \times 2.$$
$$[C_2O_4^{--} \longrightarrow 2\,CO_2 + 2\,\epsilon.] \quad \times 5.$$
$$2\,MnO_4^- + 16\,H^+ + 5\,C_2O_4^{--} \longrightarrow 2\,Mn^{++} + 10\,CO_2 + 8\,H_2O.$$

Solutions of potassium permanganate of known concentration are used in analytical chemistry as standard solutions for the determination of the amount of some reducing agent, by measuring the volume of the standard permanganate required to oxidize the reducing substance from one state of oxidation to another.

Test for the Manganous Ion. Manganese is analytically a member of the nickel group. Its sulfide, like that of zinc, is dissolved by dilute hydrochloric acid, leaving a residue of the sulfides of nickel and cobalt. Manganous hydroxide is precipitated from

the solution containing manganous and zinc ions by the addition of an excess of sodium hydroxide, zinc remaining in solution as the zincate ion. The final distinctive test for manganese may be made by fusing the hydroxide with sodium carbonate and potassium nitrate in a loop in platinum wire, with the formation of the green manganate.

EXERCISES

1. Discuss the oxidation states of chromium and manganese and show how these oxidation states are correlated with the positions of the elements in the periodic table.
2. Discuss and illustrate by equations the chemical behavior of chromium and of manganese in the important states of oxidation.
3. State the conditions which are favorable for each of the changes indicated below and tell why these conditions are favorable:
   (*a*) Chromic compounds to chromates.
   (*b*) Manganous compounds to manganese dioxide.
   (*c*) Manganous compounds to manganates.
   (*d*) Manganates to permanganates.
   (*e*) Dichromates to chromic salts.
   (*f*) Permanganates to manganese dioxide.
   (*g*) Manganese dioxide to manganous compounds.
   (*h*) Permanganates to manganous compounds.
4. Select oxidizing and reducing agents which may be used to bring about the changes indicated in question 3; and represent the reactions by equations balanced by the electronic method.
5. Classify the common reducing agents according to their chemical nature. State the conditions which you consider most favorable for the oxidation of the members of each class and tell why you think so. What is the nature of the product formed in each class of reducing agents under the conditions you have selected?
6. Choose a specific reducing agent from each of the groups into which you have classified these substances. Select a different oxidizing agent for the oxidation of each of these reducing agents under the conditions which you have stated to be most favorable. Write equations, balanced by the electronic method, for the reactions involved.

SUPPLEMENTARY READINGS

Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*, Chapters XVII and XVIII.

Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Volumes XI (1931) and XII (1932).

Jette, *Oxidation-Reduction Reactions* (The Century Company).

Hammett, *Solutions of Electrolytes*, Chapter VI.

CHAPTER XXXII

ELECTRIC CELLS

Oxidation-reduction reactions involving ionic materials are accompanied by a transfer of electrons. When the reacting substances are in contact with each other, the electron transfer takes place directly between the atoms and the ions, and the energy change is observed in the form of heat energy. In order to secure an electric current from such reactions it is necessary to arrange the materials in a cell, as discussed in Chapter XVII, so that electrons are transported over an outside metallic conductor. The difference in potential must be great enough to overcome the resistance of the conductor. The unit of potential difference is the *volt*, the difference in potential necessary to cause a current to flow at the rate of one ampere when the resistance is one ohm. The current strength is one *ampere* when it flows at the rate of one coulomb per second. The *coulomb* is by definition the amount of electricity required to deposit 0.0011180 g. of silver from a solution of a silver salt. The *ohm*, the unit of resistance, is, by definition also, equal to the resistance offered at 0° by a column of mercury which is 106.300 centimeters in length and of such cross section that it weighs 14.4521 g. These units are so related that the arbitrary definition of two of them fixes the third, because the current strength is directly proportional to the voltage and inversely proportional to the resistance.

$$I \text{ (amperes)} = \frac{E \text{ (volts)}}{R \text{ (ohms)}}.$$

The unit of electrical energy, one *joule*, is equal to the product of the quantity and intensity factors.

$$\text{Joules} = \text{Coulombs} \times \text{Volts}.$$

The amount of electrical power, measured in *watts*, depends on the intensity and the rate at which electricity is supplied.

$$\text{Watts} = \text{Amperes} \times \text{Volts}.$$

One horse power is equivalent to 746 watts and one kilowatt is 1000 watts.

Electrical Energy from Chemical Reactions. All reactions in which the complete transfer of electrons occurs lead to changes in the electrical condition of the reactants. In some of these reactions, electrical energy is converted into chemical energy by the changes which take place at the electrodes; and the products contain a greater amount of chemical energy than the reacting substances. Changes of this nature occur during *electrolysis*. In certain other reactions, the oxidizing and reducing agents are active enough to react exothermically and spontaneously with each other when they are brought together in solution. Such reactions may be carried out in a *cell* so as to produce an electric current. The arrangement of the materials for this purpose is shown diagrammatically in Fig. 158. The oxidizing agent and the reducing agent are placed in separate compartments in the cell. The oxidizing action at the one electrode results in the liberation of electrons and the reducing action at the other electrode in the consumption of electrons. A porous partition permits the migration of ions from one part of the cell to the other so as to maintain equivalent concentrations of positive and negative ions in the two compartments and complete the circuit internally. Electrodes and connecting conductors are required to complete the external circuit.

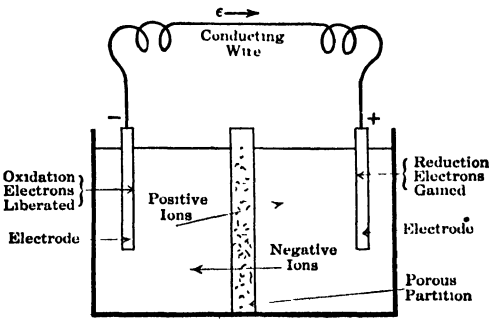

FIG. 158

Electrode Potential. The difference in potential between two electrodes in a cell depends on the electrical condition of each of them. The difference in potential is, therefore, the result of the reactions which occur at the surfaces of the electrodes.

Active metals readily form positive ions by the loss of electrons, so that relatively large quantities of energy are evolved. When an active metal is placed in a solution of one of its salts, the formation of the positive ions of the metal occurs and electrons

accumulate on the surface of the metal, unless its activity is so great that it displaces hydrogen from the solution. In consequence of the accumulation of electrons on the metal, a charge is developed which prevents the uniform dispersal of ions throughout the solution. The resulting condition may be represented graphically as an electrical double layer, with an excess of electrons at the surface of the metal and an excess of positive ions in the solution which is immediately adjacent, Fig. 159. Equilibrium is established when the charge on the metal and the concentration of the ions in the solution have become adjusted so that ions are formed and discharged at the same rate.

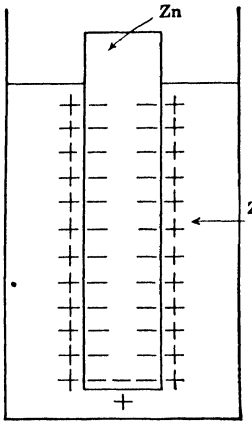

FIG. 159

$$Zn \rightleftharpoons Zn^{++} + 2\epsilon.$$

The equilibrium conditions depend on the activity of the metal, the concentration of its ions in the solution, and the temperature. Therefore, the electrode potential, which is a measure of the reducing activity of a specific metal, varies as the temperature and concentration of active ions in the solution change. If the concentration of the ions of the active metal is increased, the electrode potential required for the equilibrium is algebraically greater than in a more dilute solution; *i.e.*, the excess of electrons on the metal is less.

Inactive metals show little tendency to form ions in aqueous solution; and their ions are readily discharged by the gain of electrons. If a metal of low activity, such as copper, is placed in a solution of one of its salts, electrons are taken away from the metal more rapidly than they are supplied to it; and a deficiency of electrons is developed at the surface of the metal. Consequently, other positive ions in the solution are repelled, leaving an excess of negative ions in the immediate vicinity of the metal. This condition may also be represented by an electrical double layer, Fig. 160. A state of equilibrium exists when the deficiency of electrons at the surface of the metal has become adjusted to

the low concentration of positive ions of the metal in the adjacent solution.

$$Cu \rightleftharpoons Cu^{++} + 2\epsilon.$$

This equilibrium is affected by changes in the concentration of ions in the opposite direction to that for the active metal. The higher the concentration of the ions of a metal of low activity in the solution in contact with the metal, the greater the charge necessary for equilibrium.

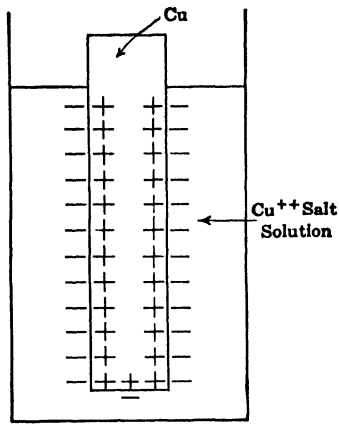

FIG. 160

There is no direct method of measuring the potential of any single electrode, because its electrical condition is disturbed as soon as connections are made in the attempt to do so. The difference in potential of the two electrodes in a cell may be measured by connecting a galvanometer in the external circuit, and balancing this potential difference against a known potential applied in the opposite direction from an external source. In order to bring the electrode potentials of different oxidizing and reducing agents into a related system, *a reference electrode* is adopted. The difference in potential between other electrodes and this reference electrode may be measured experimentally. An electrode, made of platinum, coated with platinum black, and saturated with hydrogen gas at a pressure of one atmosphere, in a solution of hydronium ions of unit activity (*i.e.*, an effective concentration of the hydronium ion equal to one gram ion in 1000 g. of water) is known as the *hydrogen electrode*. The reaction at this electrode is,

$$2\,H_3O^+ + 2\,\epsilon \rightleftharpoons H_2 + 2\,H_2O.$$

This electrode is the primary, reproducible, standard reference electrode. Since there is no method by which the potential of this single electrode may be measured, it is arbitrarily assigned a zero potential; and the entire difference in potential between some other electrode and the hydrogen electrode in a cell is attributed to the other electrode. The electrode potentials change with changes in concentration, so that it is necessary also to define a

standard of concentration. *The standard electrode potential* of a metal is the difference in potential which it develops toward the standard hydrogen electrode in a solution of its ions at unit activity.

Metals which are more active than hydrogen give up electrons more readily and become negative toward the hydrogen electrode. Metals less active than hydrogen become positive. The potentials are often expressed with the opposite sign to conform with the practice used in the description of cells in which electrolysis occurs. In line with these definitions, the electrode to which the electrons flow in the external circuit is the cathode and positive ions are discharged at this electrode. Either designation of the sign of an electrode potential may be justified with a considerable amount of logic. Nevertheless, when oxidation-reduction takes place spontaneously in a cell so as to produce a current, the flow of electrons in the external circuit is maintained by the reactions which occur in the cell rather than by some external source. Consequently, the relation of the electronic changes to the principles of oxidation-reduction is more apparent if the electrode at which electrons are liberated is called the *negative electrode;* and the electrode at which electrons are taken up by ions is called the *positive electrode.* In this manner, the sign of the electrode is attributed to the result of the cell reaction rather than the reverse. This practice is followed in the discussion of specific cells, and the direction of the current is considered to be the direction in which electrons flow in the external circuit.

The standard electrode potentials of a number of the metals are shown in the *Electromotive Series of the Metals* in Table VI in the Appendix. Each metal in this list tends to displace the ions of those which follow, unless they are so active that they displace hydrogen from water. This means, of course, that the ions of the less active metals oxidize the more active metals. The voltage of a cell based on the reaction of an oxidizing agent with a reducing agent, in solutions of unit activity, at 25° is equal to the algebraic difference between the two standard electrode potentials. Thus, the electrode potential of zinc is -0.762 volts and of copper $+0.345$ volts. The voltage of a cell based on the displacement of cupric ions by zinc in solutions which are one molal with respect to the significant ions is:

$$E = 0.345 - (-0.762) = 1.107 \text{ volts.}$$

The electrode potential for silver is + 0.799 volts; and the voltage of the cell based on the displacement of silver ions by copper is:

$$E = 0.799 - (+0.345) = 0.654 \text{ volts.}$$

The Effect of Changes in Concentration. As has already been mentioned, an increase in the concentration of the reacting ions in the solution about the electrodes causes an algebraic increase in the electrode potential required for equilibrium. If an active metal is placed in a concentrated solution of its ions, a smaller additional number of ions is required to meet the conditions of equilibrium than in solutions which are more dilute. The electrode potential of the active metal is negative, so the effect of the increased concentration of its ions is to make the electrode less negative, thus decreasing the numerical value of the electrode potential. For inactive metals, the effect is of the opposite nature. In the more concentrated solution, a greater number of ions must be discharged to establish equilibrium, thus taking up a greater number of electrons than in the dilute solution. The electrode potential of such metals is positive and the numerical value is increased with increasing concentrations of its ions. The effect is shown approximately by the formula,

$$\Delta E = \frac{0.59}{n} \log \frac{C_1}{C_2},$$

in which ΔE represents the change in potential, n the charge of the ions, and C_1 and C_2 the two ion concentrations. A cell may be constructed by placing a solution of zinc chloride in one compartment and a more dilute solution of the same salt in the other compartment. Zinc electrodes placed in these solutions are found to exhibit a difference in potential toward each other, with the electrode in the more dilute solution negative toward the other, Fig. 161.

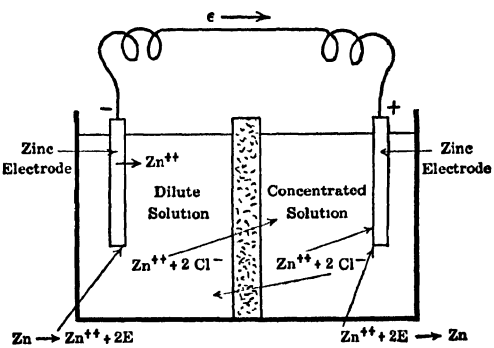

FIG. 161

If the solution about the one electrode is 0.1 molal in effective ion concentration and the other 0.01 molal,

$$\Delta E = \frac{0.059}{2} \log \frac{0.1}{0.01} = 0.0295.$$

Simple Voltaic Cells. Polarization. When zinc and copper electrodes are placed in dilute sulfuric acid and are connected by an external conductor, Fig. 162, a current flows through the circuit. Zinc ions are formed at the surface of the zinc and the electrons pass along the conductor to the copper electrode. Hydronium ions gain electrons at the copper electrode and gaseous hydrogen is discharged at this electrode. Positive ions are being formed so rapidly and in such great numbers at the zinc electrode that a great excess of positive ions is present in the solution in immediate contact with the metal, so that hydrogen ions are discharged more readily at the copper electrode than directly at the zinc electrode. In the solution as a whole, the equivalent numbers of positive ions are present at all times and the solution is electrically neutral.

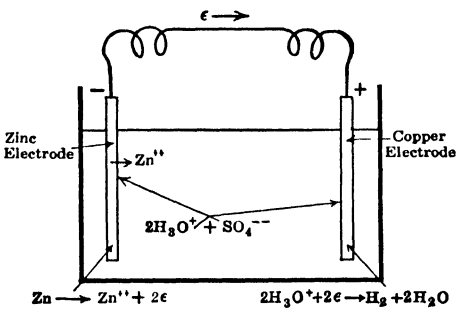

FIG. 162

A voltmeter in the circuit shows that there is a rapid drop in the voltage of this cell. This is due to the formation of molecular hydrogen which is adsorbed at the surface of the copper electrode. The presence of this gas not only increases the internal resistance of the cell, but also changes the chemical nature of the surface molecules of the electrode. This causes a reverse potential due to the formation of hydrogen ions with the liberation of electrons. The voltage of the cell is reduced to the extent caused by this reverse potential. The production of a counter electrical potential by the operation of a cell is called *polarization.*

Electric Couples. Corrosion. When pure zinc is placed in dilute sulfuric acid, little change can be observed. The displacement of hydrogen occurs uniformly at all points on the surface of the metal so that a thin layer of the gas soon coats the metal

and prevents contact between it and the acidic solution. If the zinc is impure and contains even small proportions of less active metals, such as copper, the action proceeds rapidly. The two metals of different activity in contact with each other and with the acid constitute a minute voltaic cell. Hydrogen is now discharged on the inactive impurity and does not coat the zinc so as to prevent the action of the acid.

Pure iron is corroded only slowly by water containing dissolved electrolytes; but all of the commercial varieties of iron are impure and contain carbon or other metals of low activity. Impure iron corrodes rapidly in contact with electrolytes in solution, the carbon or inactive metal serving as a member of the couple. *Tinned iron, tinplate*, is an electric couple, tin being less active than iron. When tinplate is damaged so that there are perforations through the tin coating, the iron rusts rapidly in contact with water containing electrolytes. In *galvanized iron*, zinc is the more active member of the couple. If the coating of zinc over the iron is damaged, it is the zinc which is attacked in contact with electrolytic solutions. If exposed to water containing carbon dioxide, a basic carbonate is formed. This compound is insoluble and coats and protects the metal. The aluminum alloy, *duralumin*, contains metals which are less active than aluminum, so that it is subject to corrosion. "*Alclad sheet*" consists of duralumin which is coated with a layer of pure aluminum. This material is not subject to rapid corrosion, because the aluminum of the outer layer becomes coated with an adherent protective film of aluminum oxide.

The Daniell Cell. A Nonpolarizing Cell. This cell employs the displacement of cupric ions by zinc as the source of electrical energy. Zinc ions are formed by the loss of electrons at the zinc electrode and copper ions are discharged at the surface of the copper electrode. A difference in potential between the two metals is thus developed and electrons pass along the conductor which connects them. Since there is no change in the composition of either electrode during the operation of the cell, the cell is a nonpolarizing cell. The electromotive force of this cell is about 1.1 volts and there is very little change in its voltage when the cell is in operation.

The same reaction may be carried out in the *gravity cell*,

Fig. 163. The copper electrode is placed at the bottom of the battery jar containing a dilute solution of zinc sulfate, or some other electrolyte. The zinc electrode is supported at the top of the jar so that it is suspended in the upper part of the solution. A dense saturated solution of cupric sulfate is now introduced carefully so as to form a separate layer at the bottom of the jar and an excess of solid copper sulfate crystals is added in order that the concentration of the cupric ion may be maintained at an approximately constant value. The difference in density aids in preventing the mixing of the cell solutions. During the operation of the cell, cupric ions travel toward the copper electrode at the bottom of the jar. Thus, diffusion of cupric ions up into the zinc salt solution takes place only very slowly. A covered copper wire leads up through the zinc sulfate solution to permit the connections for the completion of the external circuit.

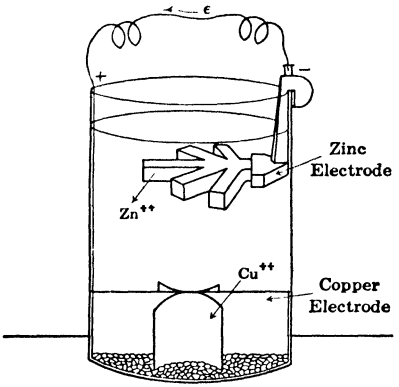

FIG. 163

The Bunsen Cell. This cell is a device for securing electrical energy from the oxidation of zinc by nitric acid. The cell may be constructed by placing the zinc electrode in a salt solution in a battery jar. A carbon rod to serve as the inert electrode is placed in a nitric acid solution in a porous cup in the jar, Fig. 164. When the external circuit is completed, electrons travel from the zinc to the carbon electrode. The electrode reactions are:

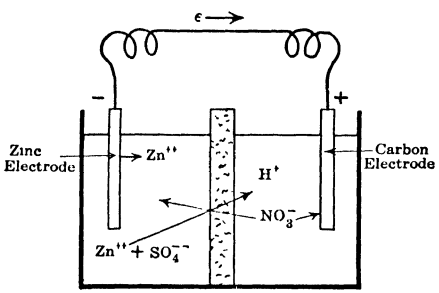

FIG. 164

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon.$$

$$NO_3^- + 4\,H^+ + 3\,\epsilon \longrightarrow 2\,H_2O + 2\,NO.$$

The cell develops an electromotive force of about 1.7 volts, the exact value depending on the concentration. During the operation

of the cell, some of the nitrate ions pass through the wall of the porous cup and maintain the two solutions at the same potential. The nitric acid, consequently, serves the double function of oxidizing the metal and furnishing nitrate ions, as in the direct oxidation of the metal placed in nitric acid solution.

The Dichromate Cell. Acidic solutions of potassium dichromate are very active oxidizing agents and a cell may be constructed on the basis of the oxidation of zinc by this substance. As in the Bunsen cell, an inactive conductor such as a graphite rod is placed in the acidic solution of the dichromate in the porous cup in the cell, and the zinc electrode is in a dilute solution of sulfuric acid in the battery jar. Electrons are liberated by the formation of zinc ions and these flow along the wire to the carbon electrode, from which they are removed by the reduction of the dichromate ions to form chromic ions. The electrode reactions are:

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon.$$

$$Cr_2O_7^{--} + 14\,H^+ + 6\,\epsilon \longrightarrow 2\,Cr^{+++} + 7\,H_2O.$$

The voltage of the cell is about two volts.

The Dry Cell. A Depolarizing Cell. The cells discussed in the preceding paragraphs illustrate the types of reactions which may be used in the production of an electric current by chemical reactions, and the arrangement of the materials required for this purpose. Some of these types of cells are still in use, particularly the gravity cell; but they are no longer important.

The most familiar of the electric cells in general use is the dry cell, Fig. 165. This cell is based on the displacement of ammonium ions by zinc.

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon.$$

$$2\,NH_4^+ + 2\,\epsilon + 2\,H_2O \longrightarrow 2\,NH_3 + H_2.$$

The ammonia is absorbed in the water in the cell and reacts with zinc ions to form the zinc ammonia complex ion. The hydrogen produced in the reaction causes polarization and manganese dioxide is packed about the carbon electrode to oxidize the hydrogen to water and depolarize the cell during periods of rest.

$$2\,MnO_2 + H_2 \longrightarrow Mn_2O_3 + H_2O.$$

Graphite is mixed with the manganese dioxide to decrease the resistance. The outer container is made of zinc and is itself the

active electrode. A layer of thick absorbent paper serves as a liner to separate the graphite and manganese dioxide mixture from the metallic zinc. A narrow space between the liner and the zinc can is filled with a flour paste containing some of the electrolytic substances. In some of the cells, especially those made for flashlights, the liner is eliminated and the paste itself separates the graphite mixture from the zinc. The cell is sealed with pitch to prevent the evaporation of the water which is absorbed in the porous contents of the cell. The voltage of the cell is about 1.4 volts.

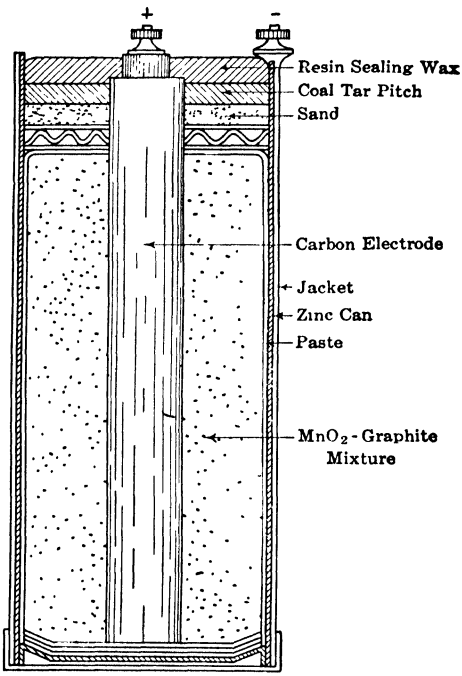

FIG. 165. — Dry Cell.

The Alkaline Cells. A type of cell, known as the Lalande cell, is based on the reaction of zinc with a solution of sodium hydroxide. In this cell the active metal, zinc, is one of the electrodes as in all of the commercially important primary cells. The other electrode is composed of cupric oxide compressed into a cake and coated at the surface with metallic copper to make it a conductor. The electrolyte is a 20–25% solution of sodium hydroxide. Zinc ions are formed with the liberation of electrons.

$$Zn \longrightarrow Zn^{++} + 2\,\epsilon.$$

In the alkaline solution the zinc ions are converted into the complex zincate ion. Hydronium ions are discharged at the copper oxide electrode and the elementary hydrogen is oxidized almost as fast as formed by the action of copper oxide.

$$2\,H_3O^+ + 2\,\epsilon \longrightarrow H_2 + 2\,H_2O.$$
$$H_2 + CuO \longrightarrow Cu + H_2O.$$

The cell is a depolarizing cell which operates at about 0.65 volt.

The Eveready air cell is also an alkaline cell based on this same reaction. The inactive electrode is made of porous carbon and the upper end is exposed to air so that oxygen is adsorbed in the carbon. Hydrogen is liberated at this electrode but combines with the adsorbed oxygen and the cell is depolarized by this reaction. This cell gives an operating voltage of approximately 1.2 volts.

The Voltage and Amperage of Cells. All of the cells described thus far are *primary cells.* In primary cells the substances required for the reaction are placed directly in the cell. When any one of these substances is consumed, the activity of the cell is ended until the substance which has been completely consumed is replaced.

The electromotive force developed by a cell is dependent on the nature of the substances of which the cell is constructed and is affected also by the concentration of the reacting substances and by the temperature. Higher potentials may be obtained by connecting a number of cells in series, thus multiplying the effect. The capacity of the cell depends on the total amount of the reacting substances which are capable of undergoing oxidation-reduction. Large cells, containing large amounts of the reacting substances, furnish a greater amount of electricity, but do not develop a higher voltage, than small cells containing the same materials. A cell delivers 96,500 coulombs of electricity for each gram equivalent weight of the substance oxidized at one electrode and reduced at the other. The amperage of the current depends on the rate at which the reactions occur, while the voltage depends on the activity of the reactants.

Storage Cells. The reactions which take place in a primary cell result in the formation of the reduction products at one electrode and the oxidation products at the other. In some cases it is possible to reverse the reactions which occur at the electrodes by the passage of a direct current of electricity through the cell, thus restoring the active materials in the cell by electrolysis. A cell may be constructed so that it will serve alternately to store energy and to supply energy. During electrolysis, electrical energy is converted into chemical energy by the reactions which are caused at the electrodes. While the electric current is being drawn from the cell, chemical energy is converted into electrical

energy by the reactions which occur spontaneously at the electrodes.

The Lead Storage Cell. The ordinary storage cell, *the lead accumulator* used in the batteries for automobiles, is constructed of materials with which it is possible to carry out the reverse changes repeatedly. The poles are gratings of lead, containing 5–12% of antimony. The antimony gives a better casting and

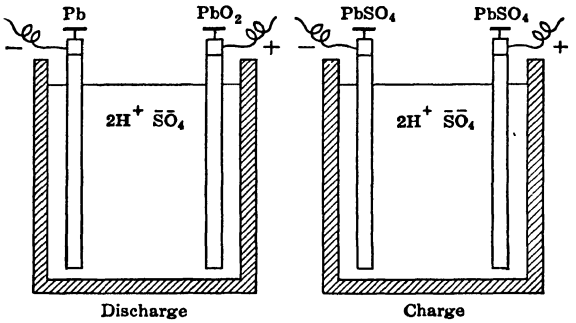

FIG. 166

adds mechanical strength, but increases the internal resistance. One plate is coated with finely divided, spongy lead and the other with lead dioxide. The cell is filled with sulfuric acid diluted to a specific gravity of about 1.2.

During the discharge of the cell, Fig. 166, electrical energy is produced, as in other primary cells, by the reactions which occur. The oxidation of lead in the presence of sulfate ions yields lead sulfate, and the electrode becomes negatively charged on account of the liberation of electrons. At the other electrode, the reduction of the lead dioxide in the presence of hydronium and sulfate ions also yields lead sulfate, and the electrode becomes positively charged. These reactions are represented by the following equations, each of which summarizes several probable intermediate steps.

$$Pb + SO_4^{--} \longrightarrow PbSO_4 + 2\,\epsilon.$$

$$2\,\epsilon + PbO_2 + 4\,H^+ + 2\,SO_4^{--} \longrightarrow PbSO_4 + 2\,H_2O + SO_4^{--}.$$

The complete change in the cell may be represented by the equation:

$$Pb + PbO_2 + 4\,H^+ + 2\,SO_4^{--} \longrightarrow PbSO_4 + PbSO_4 + 2\,H_2O.$$

The lead sulfate is insoluble and adheres to the plates. Sulfuric acid enters into the reaction at each electrode and the density of the solution decreases. During the discharge of the cell, the two electrodes approach the same composition and the voltage falls.

During the charging of the cell, a direct current of electricity, flowing in the opposite direction to that of the discharge, is passed through the cell. The electrodes, therefore, retain the same sign toward each other as during discharge; but electrons now enter the cell at the negative electrode from which they leave the cell during its discharge. The changes which occur involve the electrolysis of sulfuric acid, between electrodes which are coated with lead sulfate. Since these electrodes are active, hydrogen and oxygen, which are obtained when inactive electrodes are used, are not the main products of this electrolysis, although they are formed to some extent and their formation decreases the efficiency of the process. At the cathode, lead sulfate is reduced to metallic lead.

$$PbSO_4 + 2\,\epsilon \longrightarrow Pb + SO_4^{--}.$$

$$PbSO_4 + 2\,H_2O + SO_4^{--} \longrightarrow PbO_2 + 4\,H^+ + 2\,SO_4^{--} + 2\,\epsilon.$$

The density of the solution increases during the charging of the cell and the condition of the cell may be determined by measuring the specific gravity of the cell liquid. The charged cell has a voltage of about 2.2 volts; and when the voltage has dropped to 1.9 volts, specific gravity of the acid 1.05, the cell should be recharged. Hydrogen and oxygen are evolved to some extent during the charging of the cell and it is necessary from time to time to add distilled water to the cell. The efficiency of the cell is about 75%. By the connection of a number of cells in series, a battery may be constructed so as to deliver electrical energy at higher electromotive force.

The Edison Storage Cell. In the charged cell, the one electrode is coated with finely divided iron and the other with nickel dioxide. The electrolyte is a 21% solution of potassium hydroxide. During the discharge of the cell, iron is oxidized to ferrous hydroxide and the iron electrode becomes negatively charged. Nickel dioxide is reduced to nickel hydroxide, so that this electrode becomes positively charged. Different equations have been proposed to represent the reactions which occur in this cell; but the

essential changes may be shown by the following electrode reactions.

$$Fe + 2\,HOH \longrightarrow Fe(OH)_2 + 2\,H^+ + 2\,\epsilon.$$
$$2\,\epsilon + NiO_2 + 2\,HOH \longrightarrow Ni(OH)_2 + 2\,OH^-.$$

These products adhere to the electrodes and the reactions of opposite effect occur during the charging of the cell. The operating voltage of the charged cell averages approximately 1.2 volts at 25°.

EXERCISES

1. What types of reactions are suitable for use in the production of electrical energy?
2. What arrangement of the materials is necessary to secure an electric current from a chemical reaction?
3. What is meant by the electrode potential? How is a negative electrode potential developed? A positive potential?
4. What is the source of electrons in all of the common primary cells?
5. Draw a diagram showing the arrangement of the materials necessary to obtain an electric current from each of the following oxidation-reduction reactions and write the ion-electron equations for the reaction at each electrode in each cell.
   (*a*) Zinc with silver sulfate.
   (*b*) Copper with nitric acid.
   (*c*) Zinc with an acidic solution of potassium permanganate.
   (*d*) Ferrous sulfate with an acidic solution of potassium dichromate.
   (*e*) Lead with lead dioxide.
6. What is meant by polarization? What kind of materials are necessary for the construction of a nonpolarizing cell? a depolarizing cell?
7. Explain why a low-carbon steel corrodes more rapidly than a high-grade wrought iron.
8. What factors determine the voltage of a cell? the amperage? For what purposes are cells connected in series? in parallel?
9. What is a storage cell? Would it be possible to base a storage cell on the zinc-copper salt system? on the hydrogen-oxygen system?
10. Describe the operation of the lead accumulator and of the Edison accumulator.

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CHAPTER XXXIII

THE NUCLEUS OF THE ATOM

The hypothesis of the complex atom is now accepted as being fully established. Accordingly, the atom is assumed to consist of a positively charged nucleus containing most of the mass of the atom, with a number of electrons outside of the nucleus equal to its charge. It has been shown by numerous examples that the chemical reactions of the elements may be correlated with the number of electrons in the atoms, particularly those in the valence shell. Since the positive charge of the nucleus determines both the number of electrons and their distribution, the chemical reactions of the elements depend on the atomic numbers; but the composition of the nucleus is not altered during such changes. The loss of an electron from the valence shell of an atom produces a positive ion, and the gain of an electron a negative ion. The energy changes in such reactions are small relative to those which accompany nuclear changes; and these electronic changes are readily reversible.

The Composition of the Nucleus. The nucleus of the atom contains neutrons and protons, except that the nucleus of the principal isotope of hydrogen contains only a single proton. The charge of the nucleus is determined by the number of protons, and the mass by the sum of the numbers of neutrons and protons. These particles are very close together in atomic nuclei, so that the radius of the nucleus ranges from about 2×10^{-13} cm. for helium to about 8×10^{-13} cm. for uranium. The mass of the complex nucleus is less than the sum of the masses of all of its neutrons and protons as separate particles. This decrease in mass represents the binding energy of the particles in the nucleus, the "packing effect" mentioned in Chapter VI.

The numbers of protons and neutrons in the nuclei of the atoms of the lower atomic numbers are nearly equal; but the relative number of neutrons becomes increasingly great for the elements

of higher atomic numbers, as shown in Fig. 167. In the uranium atom, the number of neutrons is approximately one and a half times the number of protons.

For each variety of element, the number of protons in the nucleus of the atom is definite; but the number of neutrons may vary within certain fixed limits, as observed in the different isotopes of a particular element. From a consideration of the number of isotopes of the different elements, shown in Table 9, Chapter VI, and in the other tables dealing with the properties of the groups of elements, it is apparent that the range in the ratio between the numbers of neutrons and protons is greater for the elements of even atomic numbers than for the elements of odd atomic numbers.

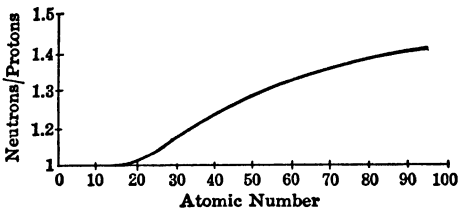

FIG. 167

Nuclear Transformations. The nuclei of some of the naturally occurring elements are unstable; and others may be made unstable by bombarding them with different high energy particles, such as protons, neutrons, deuterons, and alpha particles. If the ratio between the numbers of neutrons and protons is either less or greater than the range of stable ratios for any individual atom, the energy content of the nucleus is so great that it undergoes a change in structure, a nuclear reaction, with the emission of different types of radiation. The evaporation of these simple particles from the highly energetic nuclei causes the system to cool down to a stable nucleus.

In some atomic nuclei, *the number of neutrons is too great, i.e.*, the ratio between the numbers of neutrons and protons is greater than the stable limit. There are two changes which such unstable nuclei may undergo in order to reduce the excess of neutrons over protons and bring the energy relationships within stable limits. If the nucleus contains a very large amount of energy, *neutrons may be emitted.* Changes of this nature accompany a number of atomic disintegrations, such as that resulting when beryllium is bombarded with alpha rays. In the change in which neutrons are emitted, the atomic number of the atom is not altered, but the

atomic weight is decreased. If, however, the nucleus is less highly excited, *the neutrons may become transformed into protons through the emission of electrons.* Among the natural radioactive elements, the emission of electrons, beta rays, is the change commonly observed by which the excess of neutrons in the nucleus is reduced. The loss of a beta particle causes no perceptible change in the mass of the atom, but it increases the atomic number by one unit. The product of this disintegration is the nucleus of an element in the next higher group in the periodic system.

In the other type of unstable atomic nucleus, *the number of neutrons is too small; i.e.*, the ratio between the numbers of neutrons and protons is below the stable limit. This means that the charge of the nucleus is too high relative to its mass. Such atoms undergo nuclear changes by which this excessive charge is reduced. There are several changes which produce this result. The change effecting this result which is most commonly observed among the elements of high atomic weight is *the emission of alpha rays.* Alpha rays are the nuclei of helium atoms containing two neutrons and two protons. Hence, the loss of an alpha particle reduces the charge of the atom two units and the weight four units. The element produced in a change of this type is in the periodic group two numbers below the disintegrating atom.

The emission of protons by the atomic nucleus also reduces its charge and increases the ratio between the numbers of neutrons and protons. This type of nuclear change has not been detected among the naturally occurring radioactive elements; but it occurs frequently during the decomposition of a number of the lighter atomic nuclei when they are bombarded with alpha particles or with deuterons. The loss of a proton produces the nucleus of an atom of an element in the next lower group of the periodic system. The transmutation of nitrogen first observed by Lord Rutherford in 1919 is a change of this variety. It is assumed that the nucleus of the nitrogen atom combines with an alpha particle during this change with the production of an unstable nucleus having mass 18 and charge 9. This nucleus then decomposes with the emission of a proton, leaving a stable isotope of oxygen having mass 17 and charge 8.

The emission of alpha particles and of protons causes reduction in both the mass and the charge of the nucleus. The reduction

of the charge, however, bears a greater ratio to the total charge than the reduction in mass bears to the total mass. Consequently, the stability of the atomic nucleus is increased by the change.

A third type of change shown by nuclei which have too great charge relative to the mass is the *emission of positrons*, particles having the mass of the electron and unit positive charge. In this change the mass is not appreciably altered, but the charge of the nucleus is reduced one unit for each positron emitted, forming an atom in the next lower periodic group. The positron, like the electron emitted during nuclear reactions, is assumed to be a product of the energy changes which take place inside of the nucleus, not a particle actually residing in the nucleus. The emission of the positron is commonly observed during the disintegration of radioactive elements produced by the bombardment of atomic nuclei of the lower atomic weights by particles containing high energy. This radiation has not been observed from the naturally occurring radioactive substances. The positron does not persist for an appreciable length of time in matter surrounding atomic nuclei because there are too many negative electrons with which it exerts mutual attraction. Positrons and electrons coming together are both annihilated by conversion to gamma radiation.

The positive charge of the nucleus may also be reduced by the *capture of electrons* from the innermost electron shell of the atom. It is assumed that the electrons which are absorbed by the nuclei do not exist as separate particles in the nucleus, because the size and energy relationships do not permit the assumption of the presence of the electron in the nucleus. It is assumed that a proton in the nucleus and the captured electron combine to form a neutron as a distinct particle, not simply a proton and an electron physically attached to each other. This change is opposite in nature to that which occurs during beta ray emission. An electron from some outer shell in the atom immediately drops into the inner shell to replace the absorbed electron, and X-rays are emitted in consequence of this change in energy level. It is believed that this change occurs frequently in the atoms of the elements of the higher atomic numbers; but the only experimental evidence which can be detected is the emission of X-rays.

The emission of particles from atomic nuclei is frequently

accompanied by *gamma radiation.* Gamma rays are of the same nature as X-rays, but have much higher frequencies. The formation of gamma rays by the mutual annihilation of positrons and electrons has been mentioned. The excess of energy in some nuclear reactions is emitted directly in the form of gamma radiation. Gamma radiation is commonly observed both among the natural radioactive substances and those which are made radioactive by bombardment with high energy particles.

The Natural Radioactive Elements. The discovery of radioactivity by Becquerel in 1896 and the nature of the radiations which are emitted have been discussed in Chapter VI, to which reference should be made for review. It has also been pointed out that, according to the disintegration theory of Rutherford and Soddy, the atoms of the radioactive substances spontaneously disintegrate to form other atoms which are somewhat less complex, and that alpha particles, beta particles, and gamma radiation are emitted during such transmutations of the elements. If a radioactive element is purified so as to remove all of its disintegration products, it is found after a time that these products are again present, having been formed by the spontaneous disintegration of the atoms.

Radium is present in all uranium ores and the ratio of the two elements in the unaltered ores is constant, about one part of radium to three million parts of uranium. The principal sources of radium are in the deposits of uranium minerals in the Belgian Congo and in northern Canada. Large quantities of the ore must be worked to secure small quantities of radium. Radium is produced in the form of its salts, usually the chloride and the bromide. Radium is used in the treatment of cancer because its radiations are effective in stopping the uncontrolled growth of the cancerous tissue.

Only a certain definite proportion of the atoms in any radioactive substance reaches, in a given period of time, the state of instability which causes decomposition. Only one out of every one hundred million atoms of radium decomposes per second, so that an infinite time would be necessary for the complete decomposition of a sample. No changes to which the substances may be subjected, either chemical or physical, have been found to affect in any manner the rate of the change or the nature of the products

which are formed. From the rate at which the disintegration proceeds, it is possible to calculate the time required for the decomposition of one half of a sample to occur. This time is known as the "*period*" of the element. The periods of radioactive elements vary from a few seconds to billions of years. Nuclear transformations are attended by the evolution of enormous amounts of energy relative to the changes in chemical processes. Radium evolves energy at a rate equivalent to 137 calories per gram during each hour and continues at this rate throughout its entire life.

There are a number of radioactive elements in the *uranium series*. The spontaneous disintegration of the nuclei of the atoms leads successively to the formation of each element from its predecessor. Alpha particles are emitted during some of these changes and beta particles during others. The relations of these elements are shown in Table 44.

TABLE 44

DISINTEGRATION PRODUCTS OF URANIUM

Substance	*Atomic Number*	*Atomic Weight*	*Particle Ejected*	*Period*
Uranium I	92	238	Alpha	4.5×10^9 years
Uranium X_1	90	234	Beta	24.5 days
Uranium X_2	91	234	Beta	1.14 minutes
Uranium II	92	234	Alpha	2×10^6 years
Ionium	90	230	Alpha	7.6×10^4 years
Radium	88	226	Alpha	1590 years
Radon	86	222	Alpha	3.8 days
Radium A	84	218	Alpha	3.0 minutes
Radium B	82	214	Beta	26.8 minutes
Radium C	83	214	Beta	19.5 minutes
Radium C′	84	214	Alpha	1×10^{-4} seconds
Radium D	82	210	Beta	25 years
Radium E	83	210	Beta	4.85 days
Polonium	84	210	Alpha	136 days
Lead	82	206		Stable

In a preceding paragraph it was observed that the emission of an alpha particle causes a decrease of 2 in the atomic number and the loss of a beta particle causes an increase of 1. The positions in the periodic table occupied by the disintegration products of uranium are shown in Fig. 168. In order to show the effect of the

emission of alpha and beta particles in a continuous line, the table is rearranged by shifting the columns for Groups I, II, III–B, IV–B, V–B, and VI–B to the right, so that Group VIII, the inert gases, is at the center. Certain other groups have been omitted

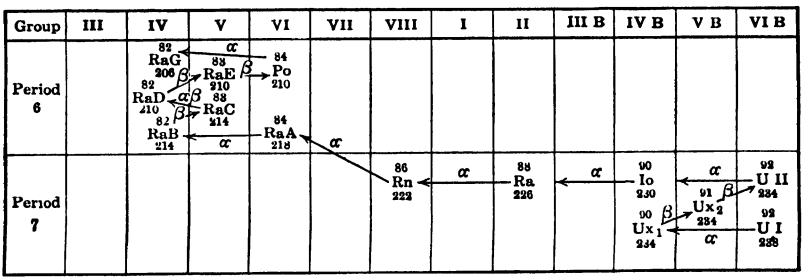

FIG. 168

as of no significance in this connection. The numbers above the symbols are the atomic numbers and those below, the atomic weights.

An interesting application of the results obtained in the investigations of radioactivity is the calculation of the age of certain rocks in the outer layer of the earth, a method first suggested by Boltwood. Uranium minerals always contain lead. By determining the relative amounts of uranium and lead in the mineral it is possible to calculate the length of time which has been necessary for the formation of the proportion of lead actually found. Calculated on this basis, Kovarik obtained 1852 million years as the minimum age of a uraninite specimen from Sinyaya Pala, Karelia, U. S. S. R., the oldest mineral known.

There are two other series of natural radioactive elements, *the thorium series* and *the actinium series*. In each series, the successive elements are produced by the spontaneous disintegration of the more unstable atomic nuclei with the emission of alpha or beta particles, as in the uranium series. Since actinium is always present in constant proportions in uranium ores, it is assumed that the actinium series is produced also from uranium, probably from the isotope, U 235. A number of isotopes are present in the disintegration products in these series of elements. In each series there is a chemically inert gas, radon, thoron, and actinon, respectively, having atomic number 86; and each series terminates with

a stable isotope of lead. Among the natural elements, radioactivity is not common for atomic numbers below 83.

Some of the radioactive elements are used in the preparation of a luminous paint for watch and clock dials and other similar uses. A compound of the radioactive element is mixed with a crystalline variety of zinc sulfide. The radiations cause the zinc sulfide to fluoresce. Radium salts are used to some extent for this purpose; but mesothorium I, which disintegrates much more rapidly, is largely used for the preparation of luminous paint.

Transmutation of the Elements. A number of the elements which are composed of stable atoms yield unstable products when they are bombarded by particles possessing high energy. The bombarding particles most commonly used are alpha particles, deuterons, protons, and neutrons. The first three of these particles bear positive charges and are repelled by the highly charged atomic nuclei, so that they must possess high kinetic energy in order to overcome this force of repulsion and enter the atomic nucleus. Since the alpha particle has a charge of two units, the potential barrier which it must overcome is greater than that for the deuteron and proton. The alpha particle, however, is discharged from the nuclei of the naturally radioactive elements with high enough velocity to cause a number of atomic decompositions. Nuclear changes may be represented by equations in which the symbol represents the atomic nucleus together with its atomic number, and a superscript is written following the symbol to denote the atomic weight of the particular isotope involved. A number of the lighter atomic nuclei undergo transmutation by capturing alpha particles, with the formation of unstable nuclei which immediately decompose to give out protons: *e.g.*, B^{10}; N^{14}; F^{19}; Ne^{23}; Mg^{24}; Al^{27}; etc. The transmutation of nitrogen first observed by Rutherford may be represented by the following equation,

$$N^{14} + He^4 \longrightarrow F^{18} \longrightarrow O^{17} + H^1.$$

The loss of a proton reduces the charge of the nucleus and improves the neutron-proton ratio so as to give stability to the product. In other instances, the unstable atomic nucleus resulting from the capture of the alpha particle has too high a neutron-proton ratio for stability. Such nuclei decompose with the emis-

sion of a neutron. This may be observed with such atoms as Li^6, Li^7, Be^9, Be^{10}, Na^{23}, Mg^{24}, etc.

$$Be^9 + He^4 \longrightarrow C^{13} \longrightarrow C^{12} + n^1.$$
$$Li^7 + He^4 \longrightarrow B^{11} \longrightarrow B^{10} + n^1.$$

Experimental techniques have been developed by which charged particles, such as protons and deuterons, may be given high velocity, so that they possess great kinetic energy. The *cyclotron*, Fig. 169, invented by Lawrence, is a device by which such particles may

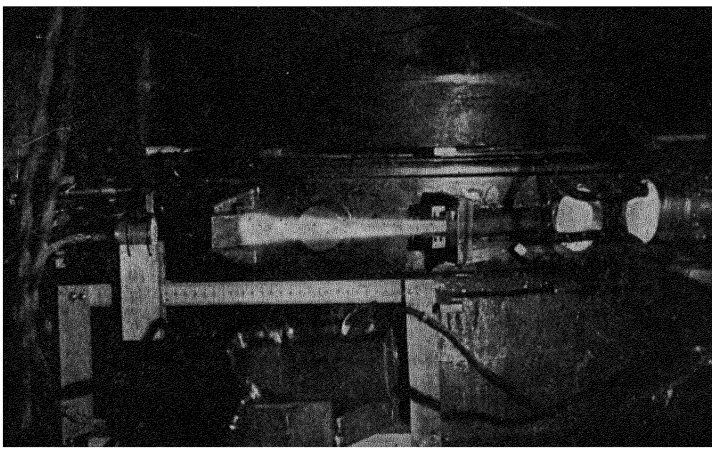

FIG. 169. — The Cyclotron.

A beam of deuterons with an energy of nearly six million electron-volts passes through twelve inches of air before coming to rest. (Dr. Donald Cooksey, University of California.)

be accelerated in multiple stages. A narrow beam of the charged particles is bent by the use of a powerful electromagnet so that it follows a circular path. A high frequency alternating potential is applied to the magnet at the proper frequency to give an added impulse to the particles each time they pass through a given region, Fig. 170. As the energy of the particles increases, they follow a spiral path and may be allowed to pass out of the accelerating chamber and strike the substance under investigation. Such particles have acquired enough energy to overcome the repulsion of the atomic nuclei caused by their electric charges. The kinetic energy of the fast-moving particles is conveniently expressed

in electron volts. *The electron volt* is so defined that an electron travelling through a vacuum between two points which differ in potential by one million volts acquires an energy of one million electron volts. Protons and deuterons may be accelerated in the chamber so as to acquire energies in excess of 6 million electron volts.

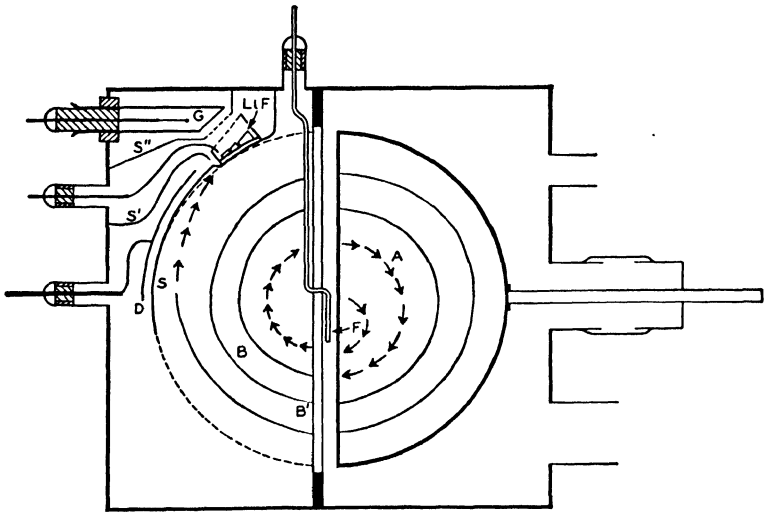

FIG. 170. — (From Darrow, *The Renaissance of Physics.*)

A number of transmutations are caused by the fast-moving *protons and deuterons.* Practically all of the nuclear varieties have been caused to undergo some kind of transmutation. The actual quantities of material produced by this procedure are small, because only a relatively small proportion of the high velocity particles actually strike an atomic nucleus so as to cause transmutation. The lithium nucleus of atomic weight 7 and the boron nucleus of atomic weight 11 yield alpha particles when they are bombarded with protons.

$$Li^7 + H^1 \longrightarrow 2\,He^4.$$
$$B^{11} + H^1 \longrightarrow 3\,He^4.$$

The nitrogen nucleus decomposes to form an isotope of carbon, and beryllium yields an isotope of the same atomic number with a deuteron.

$$N^{14} + H^1 \longrightarrow C^{11} + He^4.$$
$$Be^9 + H^1 \longrightarrow Be^8 + H^2.$$

There are several isotopes which undergo transmutation with the emission of neutrons when they are bombarded with deuterons.

$$H^2 + H^2 \longrightarrow He^3 + n^1.$$
$$Li^7 + H^2 \longrightarrow 2\,He^4 + n^1.$$
$$Li^6 + H^2 \longrightarrow Li^7 + H^1.$$
$$Na^{23} + H^2 \longrightarrow Ne^{21} + He^4.$$

The neutron cannot be accelerated in an electromagnetic field since it has no charge. However, the neutrons produced by the bombardment of beryllium with alpha particles and by the action of deuterons on deuterium have large kinetic energies and readily penetrate atomic nuclei. The energy of the nucleus is greatly increased by the absorption of a neutron because a portion of the mass of the neutron is converted into energy. This produces a great heating effect on the nucleus and causes the evaporation of small particles in order to release some of the surplus energy.

$$Na^{23} + n^1 \longrightarrow Na^{24}.$$
$$Al^{27} + n^1 \longrightarrow Na^{24} + He^4.$$
$$Al^{27} + n^1 \longrightarrow Mg^{27} + H^1.$$

Since the nuclei formed in these reactions are unstable, they decompose so as to reduce the ratio of the number of neutrons to the number of protons by the emission of electrons and thus show beta ray activity.

$$Na^{24} \longrightarrow Mg^{24} + \epsilon.$$
$$Mg^{27} \longrightarrow Al^{27} + \epsilon.$$

A number of applications of the radioactive isotopes are being developed. Since these substances emit radiations their presence can be easily detected. Consequently, the presence of a small proportion of a radioactive isotope with a large quantity of the ordinary variety of the element makes it possible to trace the atoms in various chemical reactions and biological processes. Since many of these substances have short half-life periods, they may be used much more freely for medicinal treatment of tumors than the long-lived natural radioactive elements. Among the possible developments is the injection of a salt into the flesh surrounding the growth to be irradiated and then causing the development of radioactivity by neutron bombardment. Since it will be possible to produce the radioactive isotopes of many of the elements at much lower cost than that of the extraction of radium

from its minerals, such isotopes are potentially useful for all of the purposes for which the natural radioactive elements are applied.

The energy change in the radioactive processes leads to the desire to make available a portion of the large store of energy in the atom through the use of radioactive transmutations. The energy evolution from the chemical reaction in which hydrogen and oxygen combine to form water is between two and three electron volts per molecule of water formed. Alpha rays from the various radioactive substances possess energies of 8–10 million electron volts; and gamma rays have energies of 4–8 million electron volts. Many of the fast particles produced in nuclear reactions have energies measured in the millions of electron volts. Nevertheless, the frequency of the transmutations when the bombarding particles are directed against a target is so low that they do not at present furnish a practicable source of energy. The total useful energy which might be made available from such rays is but a small fraction of the total energy which must be expended in the production of the rays.

Nuclear Fission. In the transmutations considered in the preceding paragraphs, the division of the unstable nucleus results in the formation of particles of very unequal mass and charge. Another type of transmutation has been observed recently in atoms of thorium, protactinium, and uranium. This transmutation is one in which the nucleus becomes split into two particles of nearly equal mass and charge. This change is called *nuclear fission.* It is caused by the entry of slow neutrons into the atomic nuclei and is accompanied by the release of enormous amounts of energy and the formation of a large number of radioactive elements. The energy emitted in the nuclear fission amounts to approximately 200 million electron volts.

Slow neutrons result from the passage of neutrons, initially having high velocities, through layers of paraffin or water, so that they lose a great deal of their energy. These neutrons may be absorbed by the nuclei of the atoms of thorium, ${}_{90}Th^{232}$, protactinium, ${}_{91}Pa^{231}$, and uranium ${}_{92}U^{234}$, ${}_{92}U^{235}$, ${}_{92}U^{238}$. These atoms in their natural states have an instability which causes them spontaneously to disintegrate. The absorption of a neutron so greatly decreases the stability of the atomic nuclei, that they suffer fission with the formation of a large number of radioactive prod-

ucts, some of which have been observed from no other source. Among the "fission products" two groups of radioactive atoms, varying somewhat in mass and charge, have been recognized. One group includes isotopes of familiar elements ranging in consecutive atomic numbers from $_{34}$Se to $_{42}$Mo; and the other group includes isotopes of the elements from $_{52}$Te to $_{57}$La. Several different isotopes may be distinguished for some of these atomic numbers: three of barium; three of strontium; four of iodine; and seven of tellurium. The amounts of energy evolved in the fission are far beyond any quantities that have been observed in any other changes.

The fission of the uranium atom has been investigated more extensively than that of the other two atoms mentioned above. The barium isotope, $_{56}Ba^{139}$, has been identified as one of the products. Let us assume that the uranium isotope, $_{92}U^{235}$, absorbs a slow neutron forming the unstable nucleus, $_{92}U^{236}$, which splits to form the barium isotope, $_{56}Ba^{139}$. If we assume also that all that remains of the uranium nucleus is in one particle, its charge must be 36, and mass 97, *i.e.*, an isotope of krypton, $_{36}Kr^{97}$. This change represents the principal source of the large energy evolution during the fission reaction. Since, however, the heaviest stable isotope of krypton is $_{36}Kr^{86}$, it is apparent that the number of neutrons is too great compared to the number of protons, for a stable nucleus. This condition may remedy itself, as considered in preceding paragraphs, by neutron emission in successive steps, so as to reduce the mass to 86, or by electron emission so as to increase the charge of the nucleus to form a stable particle of mass 97, such as Mo^{97}, having an atomic number of 42. It is obvious that both of these changes may occur, with the formation of a series of unstable intermediate products.

A greater number of neutrons is given out in consequence of the fission of the atom than required to cause fission. Some of these neutrons may be absorbed by other atoms of uranium, thus causing the change continually to accelerate itself. Such changes might be expected to build up the velocity of the reaction to explosive violence. Since it does not do so it is evident that there are natural causes which break the sequence of these nuclear events. In the impure uranium mineral, the nuclei of other elements may absorb neutrons to form stable products, thus pre-

venting their absorption by uranium nuclei. Furthermore, the neutrons given out by the disintegrating atoms are fast neutrons which may escape capture, since it appears to be the absorption of slow neutrons by the atoms of $_{92}U^{235}$ which causes fission. The more abundant isotope of uranium, $_{92}U^{238}$, does not appear to undergo fission on capturing neutrons. If this be true, the separation of the isotopes of uranium so as to secure the one free from the other might lead to a self-sustaining nuclear fission, with the evolution of enormous amounts of energy. Whether this energy could be harnessed to serve useful ends or would lead to a catastrophic explosion cannot now be predicted. On the basis of such knowledge as is now available, the separation of the isotopes so as to secure a sufficient supply of U^{235} to cause a self-sustaining reaction which might serve as the source of energy for industrial processes, seems improbable.

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CHAPTER XXXIV

LIQUID AND GASEOUS FUELS. THE HYDROCARBONS

The substances which are burned as the sources of energy are known as fuels. Some of the important industrial fuels are solids, some are liquids, and others are gases. Many of the fuels, such as coal, wood, and natural gas, are used directly in essentially the same composition as they are found in nature. Many of the other fuels, particularly the liquid and gaseous fuels, are modified in various industrial processes to improve their qualities for the uses to which they are applied.

LIQUID FUELS

The most important liquid fuels are compounds of carbon with hydrogen, known as hydrocarbons. These compounds are obtained largely from petroleum, which is essentially a solution of various hydrocarbons in each other. There are also a large number of hydrocarbons which are produced in industrial processes. Benzene is a product of the destructive distillation of coal, and liquid fuels result from the hydrogenation of coal. Grain alcohol, a product of the fermentation of sugar and starch, and methanol, a product of the distillation of wood, may eventually be used in large quantities as liquid fuels.

Petroleum. This dark-colored, viscous liquid is found in many parts of the world; and the demand for petroleum is so great that millions of barrels are produced annually from the oil wells. The control of an adequate supply of petroleum is essential to national existence. The production of petroleum in the United States in 1939 was more than a billion and a quarter barrels, which was approximately two thirds of the world's supply. The first oil well was drilled by Drake near Titusville, Pennsylvania, in 1859.

Petroleum is a complex liquid containing many substances in solution in each other. These substances have different boiling

points, so that the more volatile fractions may be separated from those which are less volatile by *fractional distillation*, Fig. 171. The commercial products which are collected separately are not single substances. Consequently, the temperature limits for the collection of the various fractions may be varied at will, so as to secure the maximum yield of the products for which the demand is greatest. At one time, the chief demand was for kerosene, and

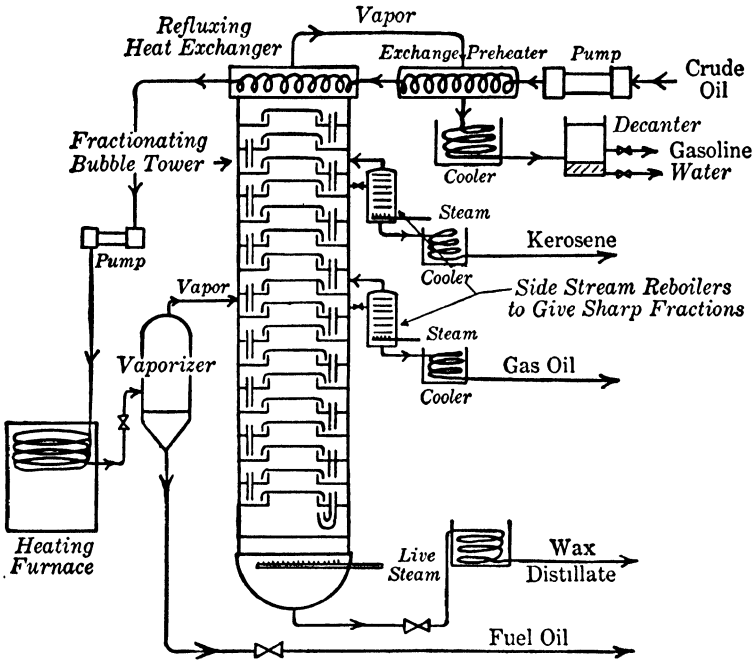


FIG. 171. — Diagram of a Modern Crude Oil Distillation Unit. (From Conant, *The Chemistry of Organic Compounds.*)

the fraction boiling at temperatures from 150° to 300° was collected and marketed for use as an illuminant and as a fuel. The more volatile fractions were collected separately, chiefly because of the danger of explosions during the use of kerosene which included them. At that time, these volatile fractions had little value. With the development of the internal combustion engines, the volatile components of petroleum have become the most valuable products.

Fuel oils, lubricating oils, vaseline, and paraffin may be separated from the higher boiling fractions of petroleum. The tar

residue in the retort is used as an artificial asphalt. A great variety of products may be separated from petroleum; and still others may be produced by synthetic processes using these substances as crudes. The greatest demand, however, is for motor fuel, lubricating oils, and fuel oils. The percentages of the refined products from the distillation of petroleum, as an approximate average distribution, are shown in Table 45.

TABLE 45

PERCENTAGE YIELD OF REFINED PRODUCTS

Motor fuel	11.2
Kerosene	5.8
Distillate fuel oil	10.1
Residual fuel oil	26.1
Lubricants	2.9
Wax	0.2
Coke	0.8
Asphalt	1.8
Road oil	0.7
Still gas	5.2
Other finished products	0.2
Shortage	1.3

The proportions of these products may be varied within certain limits according to the demand.

A large amount of gasoline is produced from the natural gas which occurs in many of the petroleum fields. This gas contains the vapors of many compounds which may be liquefied at ordinary temperatures when they are separated from the gas. These substances may be condensed from the gas under high pressure and may be adsorbed on the surface of charcoal. This product separated from natural gas, known as *casinghead gasoline*, is a volatile liquid which may be mixed with higher boiling fractions obtained during the straight distillation of petroleum to produce a blended gasoline.

A cracking process, by which hydrocarbons having a boiling point low enough to fit them for use in gasoline may be produced from the higher boiling fractions of petroleum, was discovered by Burton in 1913. A number of cracking processes have come into use since that time. In all of these processes the oil is heated to a fairly high temperature, and the molecules of the less volatile

hydrocarbons are decomposed to form molecules of lower molecular weight, which have boiling points within the gasoline range. Large amounts of hydrocarbons which do not condense at room temperature are also formed during these processes. In some of the processes, the cracking takes place in the liquid phase, at pressures from a few hundred pounds to a thousand pounds per square inch, and temperatures of 400–500°. In other processes, the cracking occurs in the gas phase at ordinary pressures, and temperatures up to approximately 600°. In many of these processes catalysts are used, as, for example, in the McAfee process in which anhydrous aluminum chloride is used. Free carbon is formed during the cracking processes, but the yield of gasoline is greatly increased. Further improvements have been made by developing processes which involve *hydrogenation* at the same time as cracking, and thus avoid the great loss due to the formation of uncombined carbon. These processes are carried out by heating the petroleum to be cracked, with hydrogen at high pressure, in the presence of a catalyst. The process is subject to operating control so as to increase greatly the yield of the product for which the industrial demand is the greatest.

Oil shales are found in extensive deposits in Utah, Colorado, Montana, and other states. This shale does not actually contain petroleum; but there are complex organic compounds in the shale, and these compounds decompose when they are heated in a retort to give a product similar to petroleum. As the natural supply of petroleum becomes depleted, these shales will become increasingly important in supplying the demand for liquid fuels.

Reactions have recently come into use for the production of liquid hydrocarbons by causing gaseous molecules of certain hydrocarbons of low molecular weight to combine with one another, *polymerize*, to build up products of higher molecular weight, which are liquids at ordinary temperatures. This change is opposite in effect to that which occurs during the processes for the cracking of the oils of high boiling point. Gaseous hydrocarbons of the type known as olefines are produced in large volumes in the petroleum cracking processes. *The polymerization* of such hydrocarbons is accomplished at temperatures of 500–600° and pressures of 1000–3000 pounds per square inch. Catalytic processes which operate at lower temperatures and pressures are

also used. Hydrocarbons of the paraffin type, which are present in natural gas and also in the gases from the cracking processes, may themselves be converted into the olefinic hydrocarbons for use in the polymerization processes. Hydrogenation of the polymerized products may be carried out if required to produce a gasoline of specific composition. By the use of these processes, both the gaseous hydrocarbons produced in the refining and cracking of petroleum oils and the hydrocarbons in natural gas may be converted into liquid fuels of the gasoline type. It has been calculated on the basis of the production data for 1936 that approximately one billion gallons of gasoline are potentially available annually from the refinery gases, three billion gallons from cracked gas, and five billion gallons from natural gas.

In addition to the production of liquid hydrocarbons and their separation into the commercial fractions used for fuels, lubricants, etc., the refining of petroleum requires the removal from the various fractions of the substances which impart objectionable characteristics. Agitation with sulfuric acid is used to aid in the removal of tars and organic sulfur compounds. After separation from the acid, the oil is then agitated with sodium hydroxide solution to remove the last of the acid. Many different methods are used for deriving the product best fitted to the desired uses. In the refining of lubricating oils, the methods of treatment have been greatly improved through the use of solvents, such as propane under pressure, to remove waxes, tars, and other substances which are undesirable.

The large production and consumption of petroleum in the preparation of motor fuels and the different types of fuel oils and lubricants has led to repeated predictions of the early depletion of the supply. This date has been moved forward as the result of several factors. New sources of supply have been discovered by extended explorations and by drilling deeper wells, some of them now being 12,000 feet or more in depth; and methods of removing the petroleum more nearly completely from the sands have been developed. The cracking and hydrogenation of the oils and the polymerization of gaseous hydrocarbons have greatly increased the proportions of motor fuel which may be obtained from petroleum. The improvement of internal combustion engines to develop the high compression engines, and of gasolines so as to

fit them for use in such engines, has increased the efficiency of the process for the conversion of the chemical energy of the fuel into useful work.

Gasoline from different sources varies greatly in its properties. Many of the gasolines produced by the procedures indicated above "knock" badly in high compression engines due to the explosion of the mixture before the passage of the spark. The rating of the gasoline in its antiknock properties is determined by the use of a sample in a special engine of such high compression that it knocks badly except with the very best fuels. The knocking is recorded electrically by means of a bouncing pin, which rises to make an electrical contact each time the engine knocks. The antiknock properties of the gasoline are expressed in terms of the "octane number," which is defined as the per cent of one of the octanes in a synthetic mixture with heptane which gives the same antiknock properties as the gasoline under consideration. In order to improve the properties of the gasoline with respect to knocking, lead tetraethyl is added in appropriate proportions.

The Destructive Distillation of Coal. A number of volatile products are evolved during the distillation of coal. These products, known as *by-products of coke*, are so important that most of the coke used in the United States is now produced in by-product coke ovens, Fig. 172. When these products are cooled, coal tar condenses; but small percentages of volatile hydrocarbons are carried along in the coal gas. These substances may be separated from the gas if industrial demand justifies it.

Coal tar contains a number of hydrocarbons and other substances which are important in the synthesis of dyes, drugs, explosives, plastics, and other products. The distillation of coal tar results in its separation into several fractions, from which the substances listed below may be produced by further refining: *a light oil* yielding benzene, toluene, and the xylenes; *a middle oil*, phenol, the cresols, and naphthalene; *a heavy oil*, cresols and phenol; *a green oil*, anthracene; and *a complex pitch*, which still contains the bulk of the materials in the coal tar. By the destructive distillation of coal at temperatures of 500° to 600°, *the low temperature carbonization of the coal*, instead of at 1000°, a tar is produced from which it is possible to prepare liquid fuels and lubricating oils similar to those obtained from petroleum.

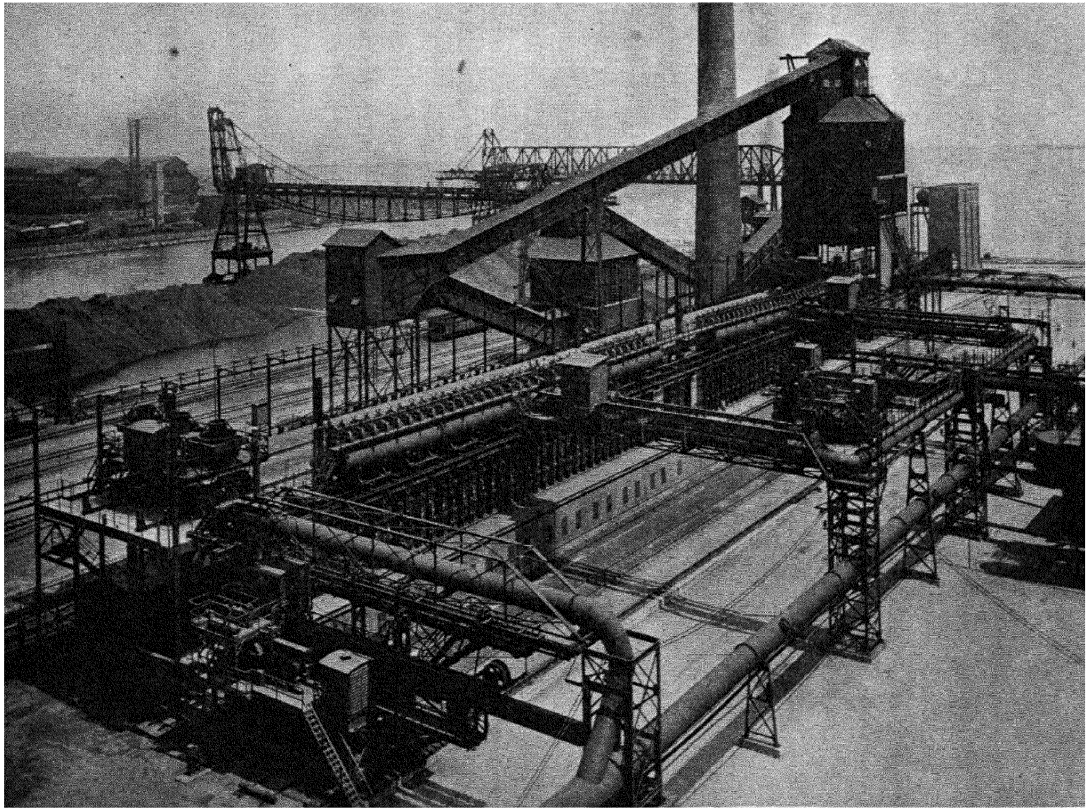


FIG. 172. — Koppers By-Product Coke Oven. (Courtesy of the Koppers Construction Company.)

Processes for the hydrogenation of coal to produce liquid fuels have been developed in Germany by Bergius. The crushed coal is suspended in a suitable vehicle and heated at a temperature of 400° to 500° with hydrogen under a pressure of approximately 250 atmospheres. Liquid hydrocarbons are obtained which can be fractionated, cracked, and further hydrogenated in the preparation of products suitable for use as gasoline, fuel oils, and lubricating oils, as in the treatment of petroleum. This process is in industrial use in Germany and in England; and large quantities of liquid fuels are now produced annually by the hydrogenation process.

GASEOUS FUELS

A number of the combustible gases may be used as fuels. Gas fuels are convenient in supply and use, and it is possible to construct burners, furnaces, and engines using gaseous fuels which are more efficient than those which employ solid fuels. Consequently, some of the gaseous fuels are produced from coal, coke, and their products. Among the gases which are used as fuels are hydrocarbons of low molecular weight, hydrogen, and carbon monoxide. Most of the gaseous fuels, especially the manufactured ones, are mixtures containing a number of components.

Natural Gas. Natural gas occurs in a number of different places in this country, notably in West Virginia, Pennsylvania, Ohio, Oklahoma, Texas, and California. During the formation of coal or oil under natural conditions, certain volatile substances are evolved. In many localities these gaseous products have accumulated in the earth under great pressure, entrapped beneath impervious layers of overlying materials. Natural gas consists chiefly of compounds of carbon and hydrogen, 80–95% being methane, CH_4. The heat of combustion of methane is large.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 213{,}500 \text{ cal.}$$

Consequently, this gas has great value as a fuel, and is now secured in large amounts from these natural accumulations, and is distributed to industrial centers by means of extensive systems of pipe lines.

Coal Gas. This gas is produced by the destructive distillation of coal. The gas is passed through condensers and scrubbers

where the water, coal tar, and ammonia are removed. It then passes into purifiers where it is led over trays containing iron oxide which serves to remove hydrogen sulfide. Coal gas contains approximately 50% of hydrogen, 30–35% of methane, 8% of carbon monoxide, 2% of other hydrocarbons, the remainder being chiefly nitrogen.

Producer Gas. This fuel gas is manufactured by the incomplete combustion of coal. In a suitable furnace, coal or coke is piled in a thick bed, about five or six feet deep, so that it burns at the base when a current of air is forced through the mass. In this part of the furnace carbon dioxide is formed. As the carbon dioxide passes up through the hot coal, it is reduced to carbon monoxide. No air is admitted above the coal so that the carbon monoxide escapes combustion and may be conducted away for use as a fuel in gas burners and gas engines. Producer gas contains about 40% of combustible substances, largely carbon monoxide. The remaining 60% of the gas is chiefly nitrogen from the air which was blown through the hot coal. The heating value of the gas is relatively low because of the large amount of inert material which it contains.

Water Gas. The reaction of steam with coke at a temperature of 1000° or higher produces a mixture of carbon monoxide and hydrogen.

$$C + H_2O \longrightarrow CO + H_2 - 23{,}300 \text{ cal.}$$

This reaction has been discussed in a previous chapter as one of the important industrial sources of hydrogen. In the production of this fuel gas, coke or anthracite coal burns fiercely under a forced draft, Fig. 173, until it is white hot, the carbon dioxide being a waste product. The air draft is then shut off and steam is forced through the hot coke. The reaction is endothermic and the temperature falls so that after about ten minutes it is too low for further effective reaction. The steam is then cut off and the air again admitted. The production of the water gas is continued in this manner as an intermittent process. Water gas contains approximately 50% of hydrogen and 40% of carbon monoxide and has high heating value.

Both carbon monoxide and hydrogen burn with a non-luminous flame; but the flame may be made luminous by the addition of

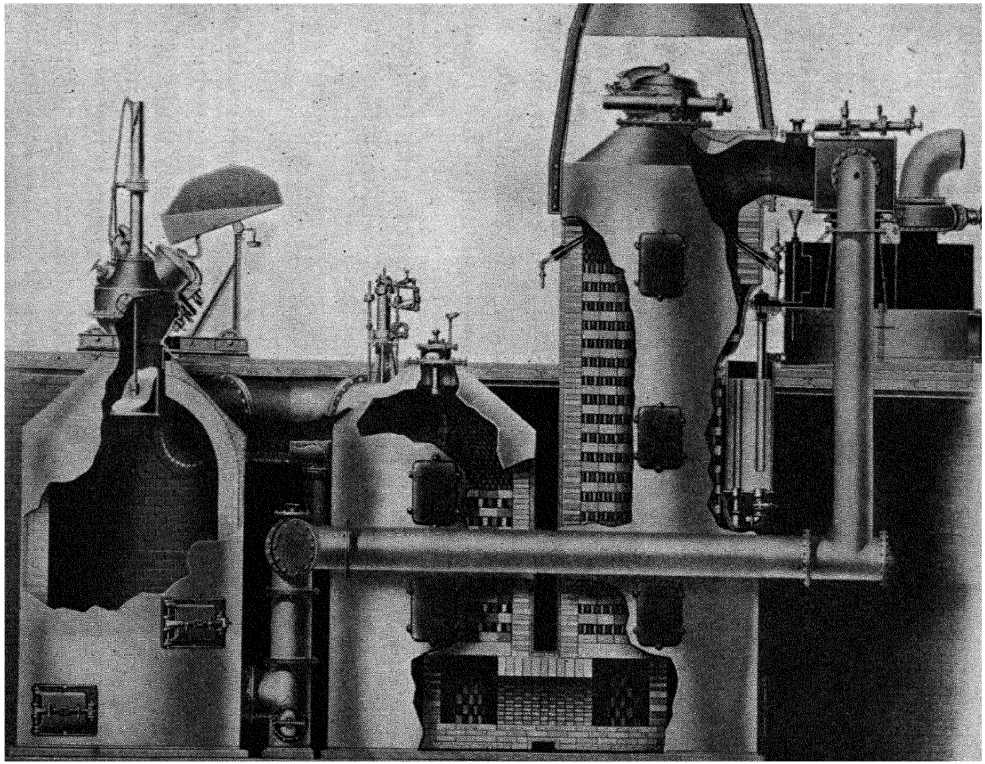


FIG. 173.— Semet-Solvay Water Gas Machine. (Courtesy of Semet-Solvay Engineering Corporation.)

hydrocarbons containing a high percentage of carbon. In order to introduce these compounds, water gas is passed through a tower containing a checker work of heated brick over which oil is sprayed. The hot gas enriched with oil vapor passes into another tower of similar construction, known as the superheater, where it is heated to a temperature high enough to decompose the complex hydrocarbons in the oil and form simpler hydrocarbons which are gaseous at ordinary temperature and burn with a luminous flame. The gas mixture is next cooled, washed to remove soluble compounds, and stored in gas holders for delivery into the gas mains. This product, known as carbureted water gas, contains up to 15% of illuminants in addition to hydrogen and carbon monoxide.

Flames. Mixtures of combustible gases and oxygen or air are explosive mixtures if the proportions are within certain limits, determined by the specific nature of the combustible gas. If a spark is introduced into such mixtures, the combustion occurs so rapidly that large volumes of material react almost instantaneously and a large amount of heat is evolved. This causes the gaseous products to expand and exert great force. Many disastrous explosions in coal mines have resulted from this cause; and the explosion which destroyed the school building at New London, Texas, in 1937 resulted from the ignition of an explosive gas-air mixture.

When, however, a combustible gas is delivered into air by means of a suitable burner, its combustion proceeds at a controlled rate. The rapid union of gaseous substances is accompanied by a flame. In a simple flame in which only one reaction occurs, as in the union of hydrogen with oxygen, two zones are observed. The inner zone contains the unburned gas, and outside of it there is the reaction zone. Some of the gases burn with nearly colorless flames, *e.g.*, hydrogen and carbon monoxide. In such flames, nearly all of the energy of the reaction is evolved as heat. Solids suspended in such flames may become heated to incandescence and emit light. For gas illumination, the Welsbach mantle may be used.

The flame produced by a burning candle or by carbureted water gas is more complex than the simple flame mentioned above. At least three zones may be observed, Fig. 174. The inner or fuel

zone is similar to that of the simple flame. The upper part of this zone is known as the *reducing flame* because it contains an excess of the unburned fuel. In the next zone hydrocarbons, such as ethylene, are broken down into hydrogen and carbon. The burning hydrogen produces a sufficiently high temperature to cause the finely divided particles of carbon to become incandescent, and this area of the flame is luminous. If this cone of the flame is allowed to impinge on a cold object, a deposit of soot is formed. The *hottest part* of the flame is at the tip of this middle cone. Outside of the luminous area there is a region of complete combustion, where enough air has become admixed to burn all of the combustible substances. There is an excess of oxygen in this area of the flame so that it is the *oxidizing flame*. This region of the flame is nearly colorless.

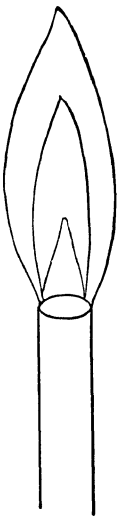


FIG. 174

Luminosity is not always due to the presence of solid particles, but some reactions, such as the combustion of ammonia, are accompanied by the direct emission of light. Various conditions for which a complete explanation cannot be given affect the luminosity of flames. Frankland conducted a number of experiments about 1868, as a result of which he came to the conclusion that the luminosity of a given flame is greater when the gases are more dense than when they are more rarefied. The luminosity of the flame may be increased by preheating the gases which enter into the reaction, and may be decreased by the admixture of some cold gas such as air or nitrogen.

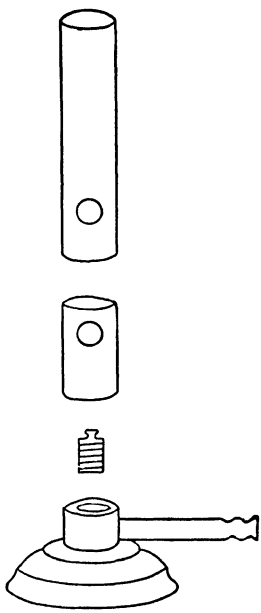


FIG. 175. — Parts of Bunsen Burner.

Gas Burners. Most of the gas burners are constructed so that the combustible gas becomes mixed with air before reaching the end of the burner where the combustion takes place. This gives a smaller, hotter flame, in which combustion is more nearly complete than in the cases where the fuel gas is delivered to the tip

of the burner without the admixture of air. The Bunsen burner, Fig. 175, is the common type for laboratory use. The mixture in the barrel of the burner contains both combustible gas and air, and must be delivered fast enough to maintain the combustion area at the top of the barrel. The burners on gas ranges and other household appliances are based on this principle. When a relatively large proportion of air is admitted at the base of the burner, a leaner mixture is formed and the rate of combustion is increased so that a smaller flame results. If too much air is admitted, the flame "strikes back" and combustion takes place at the base of the burner.

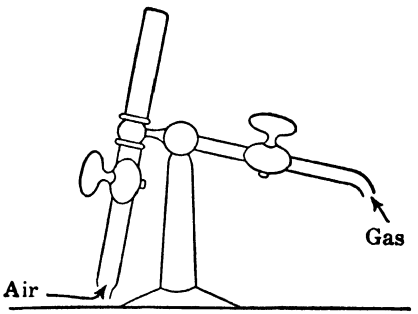


FIG. 176

In the blast lamp, Fig. 176, compressed air, forced in through an inner tube in the burner, is delivered along with the gas at the tip of the burner. By this means a lean mixture is formed and the combustion takes place very rapidly so that a hotter flame may be obtained than in the Bunsen burner. The Fisher and Méker burners, Fig. 177, are similar to the Bunsen burner. The barrel of this burner is, however, much larger than in the Bunsen burner and the holes for the admission of air are much larger. A metal grid is placed over the top of the burner. This permits the use of more efficient gas-air mixtures and the combustion occurs in a smaller area, thus giving a hotter flame than in the Bunsen burner. The presence of the grid prevents the striking back of the flame.

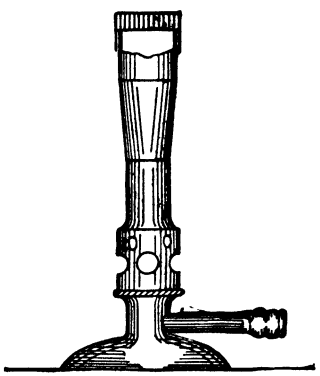


FIG. 177. — Méker Burner.

The Safety Lamp. When a wire gauze is held a few inches above a Bunsen burner, it is possible to burn the gas above the gauze without igniting that below it. The gauze conducts away the heat so rapidly that the gas below the gauze does not become

heated to its kindling temperature. Sir Humphry Davy applied this principle in constructing the miner's safety lamp, Fig. 178, by the substitution of a wire gauze for the glass chimney of a lantern. In an atmosphere which contains methane, "fire damp," the gases burn inside of this gauze chimney, but the gauze prevents the ignition of the explosive mixture outside.

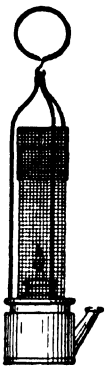


FIG. 178

THE HYDROCARBONS

Carbon is unique among the elements in the extent to which it exhibits the property of linking atom to atom to build up complex molecules. The linking of the atoms of carbon to each other, due to covalent bonds, makes possible the existence of a large number of compounds containing only a few elements. There are many compounds composed of two elements, carbon and hydrogen. These compounds are called hydrocarbons. The hydrocarbons occur in natural gas, petroleum, and coal. Many of these substances are separated from these natural materials for industrial use, and many others are produced by the decomposition of naturally occurring materials, with the formation of simpler products. There are also a large number of hydrocarbons which are not separated from natural products but are prepared by synthetic procedures from simpler materials.

The hydrocarbons may be grouped into a number of series depending on the relative amounts of carbon and hydrogen which they contain, and on the properties which they exhibit. In each of these series, there is a constant difference in composition between each member and the one which immediately precedes or follows it. Such a series of compounds is an *homologous series*, and the members of the series are *homologues* of each other. A few of the members of four series of hydrocarbons will be discussed briefly to illustrate the use of structural formulas in the correlation of the properties and reactions of these different substances. There are many additional members of each series, and also other series of hydrocarbons which are not included in this brief account.

Isomers. There are a number of instances in which two or more substances possess the same composition and molecular weight. In 1828, Wöhler discovered that the organic substance,

FRIEDRICH WÖHLER (1800–1882).

In 1827 Wöhler isolated the metal aluminum. Due to illness, he barely missed the discovery of vanadium. His fame, however, is not dimmed by this, for in 1828 he discovered the conversion of ammonium cyanate into urea, showing that it is possible for organic compounds to be produced from inorganic substances and that two or more compounds may possess the same composition. Coming as it did at a time when it was generally believed that the compounds formed by animal and plant organisms could not be synthesized in the laboratory, this discovery marks the beginning of modern organic chemistry.

urea, may be produced by heating ammonium cyanate, through a rearrangement of the atoms in the molecules. Each of these substances has the same composition and molecular weight as the other; and different formulas are used to represent them. The conversion of ammonium cyanate to urea is represented by the equation,

$$NH_4CNO \longrightarrow (NH_2)_2CO.$$

Previous to this time it had been believed that a specific composition could be shown by only one substance. Berzelius suggested the name, "isomerism," for this phenomenon of the existence of more than one substance having the same composition and molecular weight. This phenomenon is very common among the hydrocarbons and their derivatives, and accounts for the existence of so many compounds containing the same few elements. There are nine isomeric hydrocarbons known as heptanes, having the composition represented by the empirical formula C_7H_{16}; and the number of isomers increases rapidly with the number of atoms of carbon in the molecule. It is calculated that 336,319 isomers are theoretically possible for the composition $C_{20}H_{42}$.

The composition of the compounds is important in the study of the relation of the organic compounds to each other, but a knowledge of the constitution of the substances is of even greater importance. The determination of the constitution of complex organic compounds is a difficult task. It is first necessary to secure the pure compound. The compound is then decomposed by the use of reactions of known effect and the decomposition products are identified. Finally it is necessary to reconstruct the complex compound from its fragments through the use of reactions whose exact nature is known in order clearly to establish the molecular constitution of the substance.

Structural Formulas. The theory upon which the constitution of organic molecules is represented so as to afford an interpretation of the experimental results, was advanced in 1858, independently by Kekulé and by Couper. The theory assumes that the carbon atom has a covalence of four in all of the organic compounds and that carbon atoms may be attached to other carbon atoms by the sharing of electrons. On the basis of these two assumptions it has been found possible to construct *graphic or structural formulas* representing the compounds. In these formu-

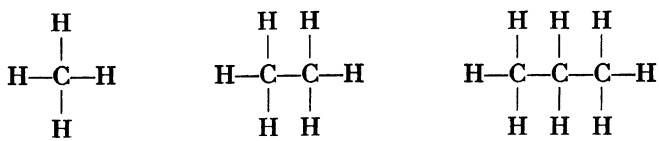
las, *the covalence bond* is represented by a line connecting the symbols of the atoms. Since carbon is assumed to possess a covalence of four in all of these compounds, each carbon atom has four bonds.

The symbols for other atoms in the molecules may be represented at the free ends of these bonds.

The use of structural formulas in representing the constitution and chemical nature of a few different classes of organic compounds will be illustrated by means of typical examples in this and the next chapter. The entire fabric of the science of organic chemistry has developed with its foundations based on the interpretation of molecular structures in graphic formulas.

The Methane Series of Hydrocarbons. The simplest of the hydrocarbons is methane, also known as marsh gas because it is formed by the anaerobic fermentation of vegetable matter beneath the surface of water in marshes. The series of hydrocarbons of which methane is the simplest member is known as the methane series. These substances have little chemical activity and are also known as *paraffin hydrocarbons*. The methane series is an homologous series in which the constant difference between successive members is CH_2; and the entire series may be represented by the type formula, C_nH_{2n+2}, in which n is the number of atoms of carbon in a molecule. A few of the lower members of the series are: methane, CH_4; ethane, C_2H_6; propane, C_3H_8; butane, C_4H_{10}. After the first four members of the series, the names are derived from the Greek numerals for the numbers of carbon atoms in one molecule of each compound. Thus, decane has the formula $C_{10}H_{22}$.

The graphic formulas of the first members of this series are:



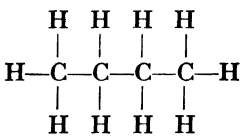
Methane Ethane Propane

It is now clear that the constant difference, CH_2, between the formulas representing two successive members of the series is due to the substitution of one $—CH_3$ group for an atom of hydrogen. These formulas may be written more compactly in the form:

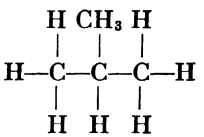
CH_4, $CH_3—CH_3$, $CH_3—CH_2—CH_3$, $CH_3—CH_2—CH_2—CH_3$.

To the chemist the latter formulas have the complete significance of graphic formulas.

No carbon atom is linked to more than two other atoms of carbon in the graphic formulas written above. In the case of any one of the first three members of the series, it is not possible for one to write graphic formulas showing linkages different from those represented above; and only one compound represented by each composition is known. There are, however, two different substances which have the composition shown by the formula C_4H_{10}. Obviously, the two compounds have different internal structures. Attempts to arrange the elements in different graphic formulas correctly representing the covalence bonds show two, and only two, possibilities:



Butane



Isobutane

The name butane is assigned to the substance which exhibits the normal properties of the group; and it is represented by the regular straight chain formula. The other substance, an isomer of butane is called isobutane; and it is represented by the structure with the branching chain. There are three isomers which have the composition represented by the formula, C_5H_{12}.

Properties of the Hydrocarbons of the Methane Series. The boiling points of a few of the lower members of this series are shown in Table 46. The members are arranged in the order of increasing complexity and consequently increasing molecular weight.

The first four members of this series are gases at ordinary temperatures and pressures, those containing from five to fifteen atoms of carbon per molecule are liquids, and those containing more than sixteen atoms of carbon per molecule are usually solids. Refer-

TABLE 46

BOILING POINT OF METHANE HYDROCARBONS

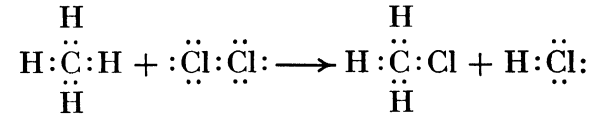
Methane	CH_4	− 161°
Ethane	C_2H_6	− 88°
Propane	C_3H_8	− 45°
Butane	C_4H_{10}	1°
Pentane	C_5H_{12}	36°
Hexane	C_6H_{14}	69°
Hexadecane	$C_{16}H_{34}$	287°, m.p. 18°

ence to the table shows that there is a fairly uniform increase in boiling point from the members of low molecular weight to those of high molecular weight. There is also a regular increase in a number of other physical properties. The boiling points of the iso-compounds are usually lower than those of the normal substances. The boiling point of butane is 1° and that of isobutane − 11°.

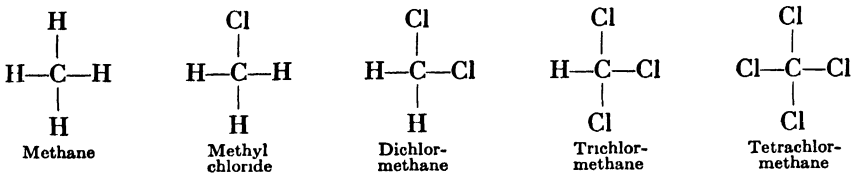
Reactions of the Methane Hydrocarbons. These substances burn, when they are heated in air and in oxygen, with the formation of water and carbon dioxide. The higher members of the series are less active than the lower members. In direct sunlight, the lower members of the series react with chlorine and with bromine to form a number of products containing atoms of the halogen in place of atoms of hydrogen.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl.$$

This reaction may be represented by the following electronic equation:



The reaction is known as a *substitution reaction;* and the hydrocarbons which may react only by substitution of other atoms for their hydrogen atoms are *saturated hydrocarbons.* Substitution occurs in several stages and a mixture of products is obtained. The relation of the substitution products to each other and to the hydrocarbon is shown by the following graphic formulas for the chlorine products formed from methane.



The monosubstitution product, CH_3Cl, is called *methyl chloride*, and the $—CH_3$ group is called the *methyl radical.* The corresponding radical obtained from ethane is the *ethyl radical;* and the radicals formed by the substitution of one hydrogen atom per molecule in the various hydrocarbons of this series are known as *alkyl radicals.* Some of these halogen substitution products have direct uses which are important. *Methyl chloride is used as a refrigerant. Carbon tetrachloride, CCl_4,* is extensively used as a solvent and in some types of fire extinguishers. *Chloroform, $CHCl_3$,* is also used as a solvent and to a limited extent as an anaesthetic. These substances are not usually prepared by direct substitution. Carbon tetrachloride is produced by the reaction of carbon disulfide with chlorine; and chloroform, by reducing carbon tetrachloride with iron and water.

Preparation of the Methane Hydrocarbons. Industrial products containing mixtures of these hydrocarbons are obtained by the fractionation of petroleum and by the destructive distillation of coal. The pure hydrocarbon may be prepared by the action of water on the *Grignard reagent* produced by the reaction of magnesium with the halogen derivative of the hydrocarbon. In dry ether, ethyl bromide, for example, reacts with magnesium to form ethyl magnesium bromide, which may be decomposed by water to produce pure ethane.

$$C_2H_5Br + Mg \longrightarrow C_2H_5MgBr.$$
$$C_2H_5MgBr + H_2O \longrightarrow C_2H_6 + Mg(OH)Br.$$

Higher members of the series may be prepared by the reaction of metallic sodium with the halogen derivatives which contain the desired alkyl groups to produce the hydrocarbon. The reaction is known as the Wurtz reaction. Propane may be prepared in this manner from a mixture of methyl and ethyl iodides.

$$CH_3I + C_2H_5I + 2\,Na \longrightarrow CH_3CH_2CH_3 + 2\,NaI.$$

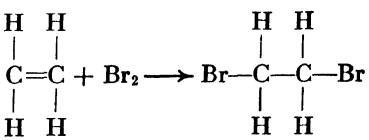
A mixture of products is usually obtained in this reaction so that the separation of these substances is necessary; and this separation may offer difficulties if the boiling points of the products are close together.

Ethylene. C_2H_4. Unsaturated Hydrocarbons. The substance ethylene is the first member of a series of hydrocarbons which contain smaller percentages of hydrogen than the corresponding members of the methane series. The series is represented by the type formula, C_nH_{2n}. Ethylene may be prepared by the dehydration of ethyl alcohol by the action of sulfuric acid at 180°.

$$C_2H_5OH \longrightarrow H_2O + C_2H_4.$$

Ethylene is prepared commercially by either the catalytic dehydration of ethyl alcohol over heated kaolin, or by the cracking of petroleum oils and natural gas. Large quantities of this substance are produced in a complex gas mixture as a by-product of the cracking of petroleum.

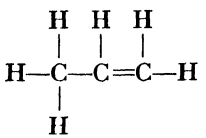
The members of this series are capable of reacting through the *addition* of other atoms. The color of bromine disappears when ethylene is passed into bromine water, and the compound $C_2H_4Br_2$ is formed. Compounds capable of reaction in this manner are known as *unsaturated* compounds. The property of undergoing addition reactions is represented in the formula of the hydrocarbon by the use of a *double bond.* The product of the addition reaction is a saturated compound, so that the double bond is said to be broken during the reaction. The following equation represents the reaction of ethylene with bromine:

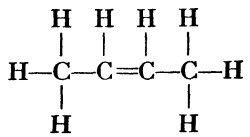


Ethylene is used as an anaesthetic in surgery and there seems to be less discomfort following its use than the use of ether. Citrus fruits develop a uniform yellow or orange color when exposed to ethylene, thus giving the fruit a more pleasing appearance; and the compressed gas is used for this purpose. Ethylene is also suitable for use in blowpipes to develop a high temperature gas flame. The most extensive use of ethylene is as a starting point

in the production of a number of organic compounds. It reacts with sulfur monochloride to form the compound known as "mustard gas" which is used as a military gas. With chlorine in the presence of antimony trichloride as a catalyst, ethylene yields ethylene dichloride which is itself used in the preparation of glycol and other synthetic products.

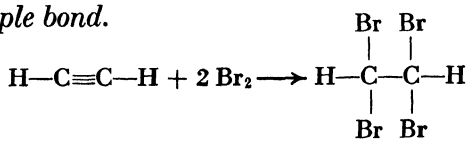
A series of hydrocarbons which are homologues of ethylene may be formed. In this series, there is the same relation between successive members as in the methane series. The next two higher homologues of ethylene are shown by the following formulas:





The unsaturated hydrocarbons of this series are known as *olefins*. A second class of hydrocarbons, closely related to the ethylene series, contains two double bonds. These substances are *diolefins*. The simplest member of the series is allene, $CH_2{=}C{=}CH_2$. An important member of this series is butadiene, $CH_2{=}CH{-}CH{=}CH_2$. The diolefins readily polymerize, that is, the molecules combine to produce more complex products of the same percentage composition but of molecular weights which are multiples of that of the simple member. Artificial rubber has been produced by the polymerization of butadiene.

Acetylene. C_2H_2. This substance is the first member of a series of hydrocarbons containing still smaller percentages of hydrogen than the corresponding member of the ethylene series. This series is represented by the type formula, C_nH_{2n-2}. Acetylene is capable of undergoing addition reactions with bromine and of adding twice as many atoms per molecule as in the case of ethylene. This higher degree of unsaturation is represented by the use of a *triple bond*.



Acetylene is an endothermic compound which has a high heat of combustion. Its familiar use in the oxyacetylene blowpipe is due to this fact.

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 624{,}000 \text{ cal.}$$

In the presence of sulfuric acid, acetylene undergoes an addition reaction with water to form acetaldehyde, from which acetic acid and a number of other important products may be obtained by synthetic processes. "Neoprene," an artificial rubber, may be prepared through the use of acetylene as an initial substance. In the presence of an aqueous solution of a copper salt as a catalyst, acetylene yields a product known as vinylacetylene.

$$2\,CH{\equiv}CH \longrightarrow CH{\equiv}C{-}CH{=}CH_2.$$

This substance reacts with hydrogen chloride gas to form chloroprene.

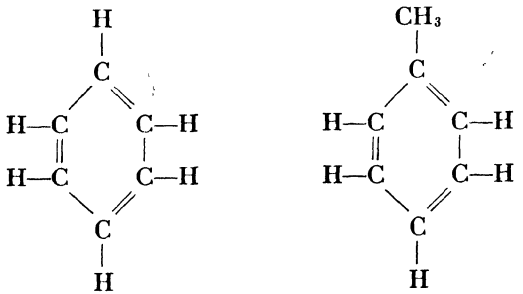
$$CH{\equiv}C{-}CH{=}CH_2 + HCl \longrightarrow CH_2{=}CCl{-}CH{=}CH_2.$$

The molecules of this substance undergo polymerization to form a complex product which has many of the properties of natural rubber. This reaction affords a method which may be used for the production of rubber from mineral substances. The great expansion in the production of rubber latex from plantations of rubber trees has been able to meet the demands for this material in the past; but the synthetic material bids fair to become increasingly important in the future.

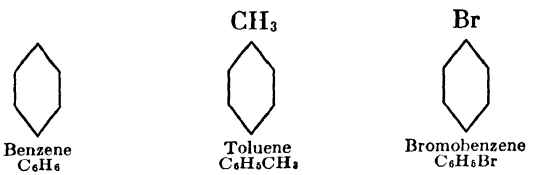
The Benzene Series. A number of hydrocarbons of this series are produced in the destructive distillation of coal. They are separated from coal tar by distillation and by chemical treatment. These hydrocarbons are known as *aromatic hydrocarbons*. The type formula for the series is C_nH_{2n-6}. The small percentage of hydrogen in these compounds and their ability to undergo certain addition reactions show that they are unsaturated compounds. Nevertheless, they do not readily add most of the reagents which usually add to the unsaturated compounds of the types already considered; and their most important reactions are those in which atoms of hydrogen are replaced by other atoms or groups, such as the halogens or the nitro group.

***Benzene,* C_6H_6,** is the first member of this series. The behavior of benzene and its homologues indicates that the molecules of these compounds contain a nucleus of six carbon atoms, held together by such strong forces that this group is not broken down in a great variety of chemical reactions. Much difficulty was

experienced in constructing a formula which would be in accord with these facts and at the same time represent the valences of all of the atoms involved in a satisfactory manner. Kekulé suggested the formula which represents the observed relations in a satisfactory manner. The carbon atoms are arranged in the form of a hexagon, forming a closed ring structure, known as the *benzene ring*. One atom of hydrogen is attached to each of the carbon atoms, and alternate double bonds are used. The formulas for benzene and toluene, the next higher homologue of benzene, are written:

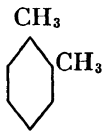


For practical purposes an outline formula is commonly used and benzene is represented by a simple hexagon without writing in the symbols of any of the atoms which the molecule contains. It is assumed that the group CH is represented at each corner. In the homologues and derivatives of benzene, the atoms and groups of atoms which have replaced atoms of hydrogen are represented at the appropriate corners of the hexagon. This is shown by the following outline formulas.



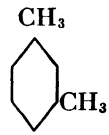
There are three isomers having the composition represented by the condensed formula $C_6H_4(CH_3)_2$. These substances are the xylenes. A consideration of their structure indicates the significance attached to different relative positions in the benzene ring. Having introduced one methyl group, $—CH_3$, into the benzene ring in place of one of the hydrogen atoms, there are three posi-

tions relative to this in which the second group may be placed. These positions are known as the ortho, meta, and para positions.



o-Xylene

p-Xylene



m-Xylene

EXERCISES

1. What is petroleum? What process is used for the separation of petroleum into different commercial products?
2. What are some of the other methods which may be used for the production of liquid fuels?
3. What is meant by destructive distillation? What are some of the products of the destructive distillation of coal?
4. Discuss the fuel gases, taking into account advantages gained by the use of gaseous fuels and the methods of preparing these materials.
5. What are the important zones in the flame of a burner? What is meant by the reducing flame? the oxidizing flame?
6. How is it possible to account for the existence of so great a number of compounds containing only a few elements, as one finds in the study of the compounds of carbon?
7. What is meant by isomerism? polymerization?
8. What is the significance of structural formulas?
9. What differences characterize the hydrocarbons in the four series discussed in this chapter?
10. What two methods are available for the production of hydrocarbons of the methane series?

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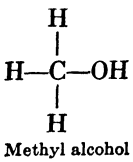
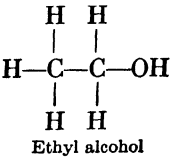
CHAPTER XXXV

DERIVATIVES OF THE HYDROCARBONS

There are a large number of substances which are classified as derivatives of the hydrocarbons. The structural relationships of these substances are represented by replacing one or more atoms of hydrogen in the hydrocarbon by some other atom or group of atoms. Nevertheless, direct substitution is not the usual method for the preparation of such compounds. The derivatives may be classified further into groups of compounds which are similar in constitution and behavior. For each of these derivatives, there is a reactive group of atoms which characterizes all of the members of the class. A few members of several classes of derivatives will be discussed to indicate the relation of the properties of the compounds to these specific *functional groups*. The derivatives in the methane series and in the benzene series will receive primary consideration.

The Alcohols. The alcohols are a class of compounds which contain the hydroxide group in the place of an atom of hydrogen in the molecule of the hydrocarbon. These substances make up an homologous series of compounds with the same constant difference between successive members as in the hydrocarbons themselves. The alcohols of the methane hydrocarbons are represented by a type formula, *ROH*, in which *R* signifies an organic radical, such as the methyl radical. These substances are structurally analogous to the hydroxides of the metals, although they yield no appreciable concentration of hydroxide ions and are not true bases. Only one hydroxide derivative of methane is known, and only two of ethane. From this, and other considerations, it is concluded that no more than one hydroxide group can normally be held in combination by the same atom of carbon in the molecule. The alcohols containing one hydroxide group are *monohydric* alcohols.


Methyl alcohol


Ethyl alcohol

If the hydrocarbon contains more than two atoms of carbon, two different monohydric alcohols are possible. The one in which the hydroxide group is attached to a terminal carbon in a straight chain compound is the *normal* or *primary* alcohol. The other, in which the hydroxide group is attached to a carbon atom which is itself linked to two other atoms of carbon, is the *iso* or *secondary* alcohol; and it exhibits different properties from those of the primary alcohol. In alcohols containing four or more atoms of carbon, a third configuration is possible. In this type, the hydroxide group is combined with an atom of carbon which is linked to three other atoms of carbon. Such alcohols are *tertiary* alcohols.

Methyl alcohol, methanol, CH_3OH, also called wood alcohol, is a product of the destructive distillation of wood. Acetic acid, water, acetone, and other substances are produced during this process, so that it is necessary to separate the wood alcohol from these other condensed products. Formerly, this was the only industrial source of methyl alcohol; but synthetic processes which yield a large portion of the world's supply have been developed since 1920. The synthetic product is usually marketed under the name *methanol.* The synthesis of methanol is the result of the union of carbon monoxide and hydrogen at a pressure of about 200 atmospheres and a temperature of 300° to 400°, in the presence of a catalyst, such as a mixture of the oxides of zinc and chromium.

$$CO + 2\,H_2 \rightleftharpoons CH_3OH.$$

The gas mixture is obtained from water gas by introducing the correct additional proportion of hydrogen. The combination reaction is exothermic and is reversible, and the conditions which are used are favorable for the same reasons as in the synthesis of ammonia.

Methanol is a colorless liquid with a boiling point of 67.4°. It burns with a pale blue flame giving out a large amount of heat. Methyl alcohol is highly poisonous. Small amounts taken internally often cause blindness, and larger amounts, death. Methanol

is used extensively for the preparation of formaldehyde for industrial consumption in the production of synthetic resins, such as "Bakelite," and as a solvent for varnishes. It has been used as a denaturant to make grain alcohol unsuitable for beverage use, so that it may be sold free from tax for industrial use. The boiling point of wood alcohol is near enough to that of grain alcohol so that simple distillation does not give a satisfactory separation.

Ethyl alcohol, ethanol, C_2H_5OH, is commonly produced by the fermentation of sugar and starch under the influence of certain enzymes. These enzymes are substances which are produced in the growth of microörganisms such as yeast. The reactions which occur during fermentation are catalyzed by the enzymes. Yeast produces the two enzymes required for the fermentation of cane sugar. In the presence of *invertase*, cane sugar is converted into a mixture of the two isomeric sugars, glucose and fructose, by an addition reaction with water.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

In the presence of *zymase*, these substances decompose to form ethyl alcohol and carbon dioxide.

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2.$$

The fermentation of starch requires the action of the enzyme, *diastase*, which is formed when barley begins to sprout in a warm, damp atmosphere. In the presence of diastase in the malt produced from barley, starch first yields maltose, a sugar which is an isomer of cane sugar; and this sugar ferments in the presence of yeast. *Industrial alcohol* is usually produced in concentrations up to about 10% by fermentation. The growth of the yeast takes place more slowly as the concentration of the alcohol becomes greater and ceases altogether at about 15%. The dilute solution is concentrated to produce the constant boiling solution, containing 95% of alcohol, by fractional distillation. *Absolute alcohol* cannot be obtained by the distillation of the aqueous solution; but it may be produced by adding calcium oxide to combine with the water and then by distilling the alcohol from the lime. It may also be produced by the distillation of solutions containing alcohol, water, and benzene, in carefully regulated proportions. Absolute alcohol is the last fraction distilled from this mixture.

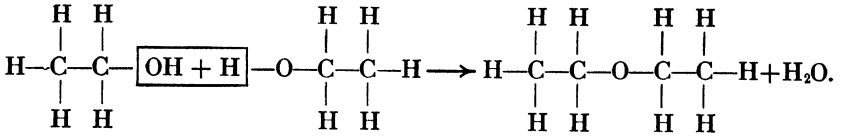
Ethyl alcohol is a colorless liquid with a boiling point of 78°. It is soluble in water in all proportions. It is used in large amounts as a solvent for many substances which do not dissolve in water; and a great many synthetic organic reactions are carried out in alcoholic solution. It is also a raw material from which many other substances are produced. Ethyl alcohol has limited uses as a fuel. Its use in internal combustion engines, either pure or in solution in gasoline, has been urged as a means of aiding in the disposal of surplus agricultural products and conserving the supply of petroleum. For the production of the same amount of energy, it is more expensive than gasoline, so that legal enactments will be necessary to force the inclusion of alcohol in gasoline until such times as economic factors make it a logical procedure.

Ethylene glycol, $CH_2OH—CH_2OH$, is the simplest of the dihydric alcohols. It is produced from ethylene by reaction first with hypochlorous acid and then with sodium hydroxide. It is used as a solvent and in the production of derivatives which are also used as solvents. It is soluble in water in all proportions and is one of the substances suitable for use in the water in automobile radiators to lower the freezing point of the water. The boiling point of ethylene glycol is 197° so that it is not evaporated during the operation of the machine.

Glycerol, $CH_2OH—CHOH—CH_2OH$, is a trihydric alcohol, which is a by-product of the manufacture of soap from animal fats and vegetable oils. It is used in the preparation of cosmetics and of chewing tobacco because it absorbs moisture and prevents the tobacco drying out. The principal use of glycerol is in the production of the nitroglycerines which are used as plastics and as explosives.

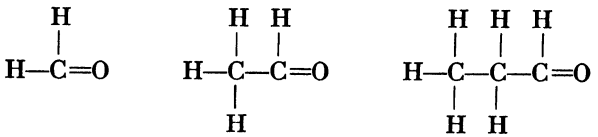
The Ethers. The ethers are an important class of compounds prepared from the alcohols. The ethers contain two carbon-hydrogen organic radicals in combination with an atom of oxygen. They may be represented by the type formula ROR' in which R and R' may be the same or may be different radicals. They are the organic counterpart of the metal oxides, in that they bear the same relation to the alcohols that the metal oxides bear to the metal hydroxides. The ethers, however, do not exhibit basic properties and do not unite with water to form alcohols. The common ether is di-ethyl ether. It is prepared by the dehydration

of ethyl alcohol by sulfuric acid at a temperature of 140°. At higher temperatures, ethylene is produced.



Ethyl ether is used extensively as an anaesthetic. It is a valuable solvent which is nearly insoluble in water and is extensively used in the extraction of organic substances from aqueous solutions. Other ethers may be prepared in a reaction which is similar to that used for the preparation of ethyl ether, by the dehydration of the alcohol. Mixed ethers contain two different organic radicals.

The Aldehydes. The mild oxidation of the primary alcohols, by the use of weak oxidizing agents or by the use of dilute solutions of stronger oxidizing agents, yields a class of compounds known as aldehydes. In this reaction, two hydrogen atoms are removed from the alcohol molecule and the reaction is one of dehydrogenation. One of the hydrogen atoms comes from the hydroxide group and the other from attachment to the carbon atom which carries the hydroxide group. The type formula for the aldehydes is *RCHO*. The characteristic structural group is shown in the following formulas representing the three lower members of the series.



Formaldehyde Acetaldehyde Propaldehyde

Formaldehyde, HCHO, is prepared by mild oxidation when a mixture of the vapor of methyl alcohol and air is passed over copper gauze heated to a temperature of about 300°.

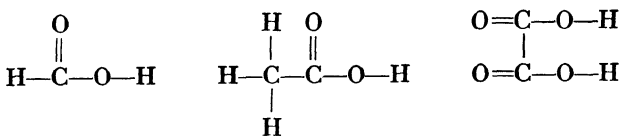
$$2\,CH_3OH + O_2 \longrightarrow 2\,HCHO + 2\,H_2O.$$

Formaldehyde is a gas at room temperature and its forty per cent solution, *formalin*, is used as a disinfectant and as a preservative for biological specimens. Aldehydes have the property of polymerizing, *i.e.*, adding molecule to molecule to build up compounds of higher molecular weights which are multiples of that of the simple substance. Formaldehyde yields a solid condensation

product which does not have the reactions of an aldehyde, showing that the aldehyde group is altered during the condensation reaction. This substance, known as paraformaldehyde, decomposes to produce formaldehyde when it is heated. Formaldehyde also yields condensation products with other substances, producing resins which have great industrial importance as plastics. The most extensive use of formaldehyde is in the production of the synthetic resin, "Bakelite."

Acetaldehyde, CH_3CHO, is a similar compound formed by the mild oxidation of ethyl alcohol. Commercially, it is produced by the addition reaction of acetylene with water; and it is an intermediate product in the formation of a number of important substances.

The Acids. The organic acids may be prepared by the oxidation of the aldehydes and the alcohols. The organic acids may be represented by the type formula *RCOOH*, containing the functional group, —COOH, called the carboxyl group and shown structurally in the following formulas representing formic, acetic, and oxalic acids:



Formic acid Acetic acid Oxalic acid

These acids are slightly ionized and exhibit the usual reactions of weak acids. The hydrogen atom of the carboxyl group shown in the formulas of the acids is the replaceable hydrogen of the molecule.

Formic acid, $HCOOH$, is found in nettles and in ants. It is commonly prepared from sodium formate, which is itself produced by the reaction of carbon monoxide under pressure with sodium hydroxide.

$$CO + NaOH \longrightarrow HCOONa.$$

$$2\,HCOONa + H_2SO_4 \longrightarrow 2\,HCOOH + Na_2SO_4.$$

If an excess of sulfuric acid is added, the formic acid is dehydrated and carbon monoxide is the product.

Acetic acid, CH_3COOH, is prepared by the atmospheric oxidation of hard cider in the presence of the enzyme in the microorganism, *bacterium aceti*. The acid is also a product of the

destructive distillation of wood. Calcium acetate is formed by neutralizing the crude, acidic distillate with lime. The solid salt is recovered from the solution and acetic acid is produced by heating it with sulfuric acid. Industrially, acetic acid is prepared in large amounts by the atmospheric oxidation of acetaldehyde, produced synthetically from acetylene. ***Acetic anhydride,*** $(CH_3CO)_2O$, is also produced from acetylene by passing it into acetic acid containing a metallic catalyst. Acetic acid and acetic anhydride are used extensively in the production of compounds such as cellulose acetate.

The Esters. The esters make up a class of organic compounds which are products of the reactions of the alcohols with acids. There are a number of reactions which yield esters, but the direct reaction of the alcohol with the acid is the most important of these. The reaction is known as *esterification* and is illustrated by the following equations.

$$HCl + C_2H_5OH \rightleftharpoons H_2O + C_2H_5Cl.$$
$$CH_3COOH + C_2H_5OH \rightleftharpoons H_2O + CH_3COOC_2H_5.$$

The reaction does not go to completion but yields an equilibrium mixture. The rate of the reaction is increased by the presence of the mineral acids. The reverse reaction is hydrolysis. The hydrolysis of an ester may be carried to completion by the addition of a base to neutralize the acid and prevent the esterification reaction. This reaction in which a base is used to decompose the ester into an alcohol and a salt is called *saponification.*

Some of the esters have pleasant odors to which the characteristic fragrance of fruits and flowers is due. Many of the esters are synthesized for use in preparing perfumes and flavors. The natural odors of the flowers are due usually to a mixture of volatile esters, some of which are present in only small amounts. Therefore, the synthetic perfumes usually lack some of the constituents and fail to give the true fragrance of the flower. The fats and oils are esters of the trihydric alcohol, glycerol, with certain organic acids of high molecular weight. A number of the esters are of great industrial importance; *e.g.*, glyceryl trinitrate, in dynamite; cellulose trinitrate, in guncotton; and cellulose acetate, in rayon.

Fats and Oils. These substances are mixtures of the glyceryl esters of organic acids, such as palmitic acid, $C_{15}H_{31}COOH$, stearic

acid, $C_{17}H_{35}COOH$, and oleic acid, $C_{17}H_{33}COOH$. Oleic acid is an unsaturated compound, containing two atoms of hydrogen less per molecule than stearic acid. Palmitin, glyceryl palmitate, $(C_{15}H_{31}COO)_3C_3H_5$, and stearin, $(C_{17}H_{35}COO)_3C_3H_5$, are fats, but olein, $(C_{17}H_{33}COO)_3C_3H_5$, is an oil. Natural products containing large proportions of olein have lower melting points than those which contain large proportions of stearin. Olive oil contains about 75% of olein and lard about 60%. Butter contains all of these substances together with about 8% of the glyceryl ester of butyric acid.

Since olein is an unsaturated compound, it will undergo addition reactions. The combination may be brought about at a temperature of 200° by bubbling hydrogen through the oil in the presence of finely divided nickel as a catalyst. This process is known as the *hydrogenation of the oil.* The hydrogenation of olein converts it into stearin, a solid fat.

$$(C_{17}H_{33}COO)_3C_3H_5 + 3\ H_2 \longrightarrow (C_{17}H_{35}COO)_3C_3H_5.$$

Cottonseed oil, which contains a large proportion of olein, formerly was of little importance; but the hydrogenation of this oil has made it an important substance in supplying the demand for the solid fats employed in cooking.

In addition to the use of fats in foods, they are the sources of glycerol and are necessary to the manufacture of soap. These substances are prepared by heating the fat with a solution of sodium or potassium hydroxide, a reaction of saponification. The reaction of sodium hydroxide with palmitin is represented by the following equation:

$$(C_{15}H_{31}COO)_3C_3H_5 + 3\ NaOH \longrightarrow C_3H_5(OH)_3 + 3\ C_{15}H_{31}COONa.$$

After the reaction is complete, salt is added to coagulate the soap, an effect discussed in connection with colloids. The soap rises to the surface and is removed. Different ingredients are added to the soap, depending on the uses for which it is intended. Glycerol is obtained from the aqueous solution.

Carbohydrates. These complex substances contain carbon, hydrogen, and oxygen, the latter two elements being present in the same proportions as in water. Carbohydrates are formed in plants by the reaction of carbon dioxide and water, with the evolution of oxygen. This reaction takes place in direct sunlight

in the presence of chlorophyll, and the process is known as the photosynthesis of carbohydrates. The proportions in which the carbon dioxide and water react in this process in the formation of dextrose are shown in the following equation:

$$6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2.$$

In certain cases the proportions of the carbon dioxide and water differ somewhat from this ratio, and higher sugars, starch, cellulose, and other products result. These substances possess the characteristic reactions of more than one of the types of derivatives formerly considered. Glucose, for example, is both an alcohol and an aldehyde.

The Sugars. There are two classes of common sugars, the monosaccharoses, such as glucose and fructose, which are isomers having the formula $C_6H_{12}O_6$, and the disaccharoses, such as sucrose, maltose, and lactose, isomers having the formula $C_{12}H_{22}O_{11}$. The later substances are known as disaccharoses because they yield two molecules of monosaccharoses by hydrolysis.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

Fructose is a constituent of many fruits and is known as fruit sugar. *Glucose* is the sweet material of corn syrup, obtained by the hydrolysis of starch in the presence of an acid as a catalyst. The continued presence of glucose in the urine is indicative of the disease called diabetes. *Sucrose, cane sugar,* is obtained by the evaporation of the sap of the sugar cane and the maple tree, or the solution extracted from the sugar beet.

Starch. The substance occurs in many vegetables, such as potatoes, corn, rice, oats, and wheat. The composition of starch is expressed in the formula $C_6H_{10}O_5$. The true formula of starch is some multiple of this unit and starch may be represented by the formula $(C_6H_{10}O_5)_x$. When starch is treated with hot water, the granules of which starch is composed burst and a colloidal suspension, known as a "starch solution," is obtained. Starch is an important constituent of many foods. The substance is used in the laundry, in the manufacture of glucose, and in the production of alcohol. Through the action of the enzyme, diastase, starch is converted into malt sugar, $C_{12}H_{22}O_{11}$. This substance decomposes further in the presence of an acid, with the addition of water and the formation of glucose.

Cellulose. The composition of cellulose also is represented by the formula, $C_6H_{10}O_5$, and its formula is written $(C_6H_{10}O_5)_y$. This substance is the most abundant of the carbohydrates, being a constituent of all vegetable matter. The two most extensive sources of cellulose products are cotton and wood. In addition to the direct uses of wood, large amounts of this material are required for the manufacture of paper. For this purpose wood is disintegrated, either mechanically or chemically, into a pulp. Lignin, the cementing material of the cellulose fibers in the wood, is extracted by the action of calcium acid sulfite, leaving a pulp which is dried and pressed between rollers. Various materials may be added to give body, and the paper is sized by the use of substances which fill the pores and prevent the spreading of ink.

Cotton is extensively used for the manufacture of fabrics. The fibers of cellulose are flat and do not yield a lustrous material, while the surface of the silk fiber is rounded and silken fabrics are lustrous. Transparent curved surfaces reflect a more pronounced line of light than do flat surfaces of the same material. A number of such curved surfaces parallel to each other result in high luster. There are several methods by which cotton can be treated so as to increase the luster of the fiber. All of these methods involve the production of a form of cellulose or cellulose derivative which can be reduced to a pasty mass by a suitable liquid, and extruded through a small circular orifice into a coagulating bath, so as to form a cylindrical fiber. When these fibers are spun and woven, the product is known as *rayon. The viscose process* is the most common of the processes for the manufacture of rayon. If cellulose, either from cotton or from wood, is treated with sodium hydroxide and then with carbon disulfide, a product known as cellulose xanthate is produced. This product is disintegrated by water to form a thick, viscous mass, called *viscose.* Viscose is forced through minute circular orifices into a precipitating bath which removes the xanthate group. The regenerated cellulose coagulates to form lustrous filaments. These filaments are spun into thread and woven into cloth to give a fabric having a silklike appearance. Rayon can be dyed readily and makes a strong and durable fabric, though not so strong as silk. The wet fibers of rayon are weaker than the dry fibers.

The viscose may be forced through a narrow slot into the pre-

cipitating bath to form thin, transparent sheets of cellulose. Under the name "cellophane" this material is now quite familiar as a protective covering for a great number of different objects. The material may be dyed to produce wrapping sheet in many different colors, and it may be made moisture proof by coating it with a thin film of a lacquer.

Esters of Cellulose. The molecules of cellulose contain hydroxide groups, so that they react with acids to produce cellulose esters. There are several nitrates of cellulose. These are formed by the reaction of cellulose with a mixture of nitric and sulfuric acids. In the complete nitration of cellulose, all of the hydroxide groups are replaced by nitrate radicals and the product known as *guncotton*, a high explosive, is produced. The empirical formula of this product is $[C_6H_7O_2(NO_3)_3]_y$.

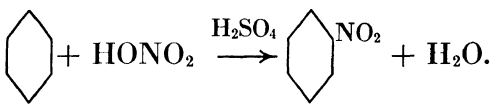
The partially nitrated material, known as *pyroxylin*, may be prepared by regulating the concentration of the acids, the temperature, and the length of time allowed for the esterification reaction. Pyroxylin is soluble in a mixture of ether and alcohol, and the solution is known as *collodion*. This partially nitrated product is soluble in other solvents also. Solutions in butyl acetate, to which various other gums and resins are added, are extensively used as lacquers. When it is mixed with camphor, pyroxylin yields the product known as *celluloid*. This material is used in the production of photographic films. Pyroxylin is not explosive but it is very inflammable, so that photographic films prepared from it are ignited easily and burn rapidly. The partially nitrated products of cellulose are used in one of the processes for the production of rayon. After the formation of the cylindrical fiber, the product is denitrated to re-form cellulose.

Cellulose acetate is made by the reaction of acetic anhydride with cellulose. This ester is soluble in a number of solvents. From cellulose acetate, films which burn with difficulty may be obtained, and these are now extensively used in the motion picture industry. Cellulose acetate is used in a process for the production of rayon. In this process, the product is composed of esters of cellulose rather than regenerated cellulose. Cellulose acetate is also used in the manufacture of safety glass.

Derivatives of Aromatic Hydrocarbons. The derivatives of the aromatic hydrocarbons fall into a large number of classes, each

containing many specific substances. It will, therefore, be necessary to limit the discussion to a few types of these derivatives which are industrially important and to indicate only a few facts about these. Although benzene and its homologues are unsaturated compounds, they enter much more readily into reactions involving substitution than those involving addition. Many of these substitution products have important industrial applications.

Nitro Compounds. One of the important methods of attacking the benzene nucleus so as to form substitution products consists in subjecting the hydrocarbon to the action of a mixture of nitric and sulfuric acids, a reaction known as *nitration.* Sulfuric acid used in the process serves the function of a dehydrating agent. In the course of the reaction, one, two, or three nitro groups are substituted for the same number of hydrogen atoms in the nucleus of the molecule.



The number of nitro groups entering the molecule depends on the concentration of the acids and the temperature. In the dinitro and trinitro derivatives, the nitro groups are linked to alternate carbon atoms in the benzene ring. Many of the derivatives of the aromatic hydrocarbons are synthesized through the production of a nitro compound as the first step in the process. Nitro compounds are used in the production of dyes, drugs, and explosives.

Sulfonic Acids. The reaction of the aromatic hydrocarbons with concentrated sulfuric acid, known as sulfonation, furnishes a second method of replacing hydrogen of the nucleus of the molecule. The products, known as sulfonic acids, contain the characteristic group, —SO_2OH. Most of the sulfonic acids are crystalline substances which are soluble in water. They are useful as intermediate products in the synthesis of many organic compounds. Some of the dyes are sulfonic acids and others are derivatives of these acids.

Halogen Derivatives. The formation of *chlorobenzene* illustrates a third reaction which may be used for the formation of derivatives of the aromatic hydrocarbons, in which one or more of the hydro-

gen atoms of the nucleus is substituted. Chlorobenzene is prepared by the reaction of chlorine with warm benzene in the presence of iron as a catalyst.

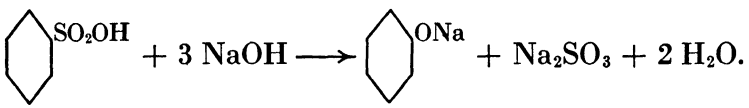
$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl.$$

Some dichlorobenzene is formed during this reaction and the product is purified by distillation.

The reaction of chlorine and bromine with the homologues of benzene in the presence of iron as a catalyst yields products in which the substitution is primarily in the side-chain. Benzyl bromide, $C_6H_5CH_2Br$, and xylyl bromide, $CH_3C_6H_4CH_2Br$, are used as "tear gases," because of their great action on the lachrymatory glands.

Hydroxide Derivatives. There are a number of compounds which contain the hydroxide group in the place of an atom of hydrogen in the nucleus of the molecule of the aromatic hydrocarbon. The simplest of these compounds is *phenol*, C_6H_5OH, also known as *carbolic acid.* The similar compounds of toluene are the three *cresols*, isomeric compounds in which the three hydroxide groups are in the ortho, meta, and para position, respectively, to the methyl group. These substances are weakly acidic and are analogous to the hydroxy-compounds of the non-metallic elements.

Phenol is separated from coal tar and is produced synthetically from benzene. According to one of the methods, benzene sulfonic acid is first formed and this substance is fused with sodium hydroxide to form the sodium salt of phenol and sodium sulfite.



Phenol may be liberated from this salt by the action of carbon dioxide.

$$2\,C_6H_5ONa + H_2O + CO_2 \longrightarrow 2\,C_6H_5OH + Na_2CO_3.$$

Another and more recently developed method is based on the reaction of chlorobenzene with sodium hydroxide solution under a pressure of some 300 atmospheres and a temperature of 350° to 375°. This reaction yields the sodium salt from which phenol is easily liberated. Phenol is a colorless solid which melts at 40°.

It is a corrosive poison which is familiar for use in the preparation of germicidal solutions. Trinitrophenol is the important military explosive, *picric acid.* Large quantities of phenol are used in the manufacture of synthetic resins, dyes, and a number of other commercial products.

Side-Chain Derivatives. The side-chain of a hydrocarbon is a group which contains one or more atoms of carbon, linked to the nucleus of the molecule. Thus, toluene, $C_6H_5CH_3$, contains the methyl group as a side-chain. Alkyl groups may be introduced into the aromatic ring by the reaction of the aromatic hydrocarbon with the alkyl halide and aluminum chloride, called the Friedel and Crafts reaction.

$$C_6H_6 + C_2H_5Br \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HBr.$$

There are a number of derivatives, such as alcohols, aldehydes, acids, and esters, in which the characteristic group is in the side-chain. Side-chain derivatives exhibit the same general reactions which are characteristic of the same variety of derivatives in the methane series. The reactions are, however, influenced and modified by the presence of the benzene nucleus in the molecule.

Synthetic Resins. The most familiar of the synthetic resins which have been developed commercially is "Bakelite." Formaldehyde condenses with phenol in a reaction which is catalyzed by the presence of a base; and the product changes to a hard mass when it is heated under pressure. This resin is not soluble, is not elastic, and is inactive chemically. It may be molded into a great number of useful objects which are in demand by most of the industries. Within the approximate range of 25 years, the annual production of this material has grown to some 50,000,000 pounds.

A number of synthetic resins are now produced by the polymerization of unsaturated compounds. One group of resins is made from the acrylic esters, such as $CH_2{=}C(CH_3)COOR$, which is prepared from ethylene. These resins have good optical properties and may be molded into lenses, and sheets for laminated safety glass. Another series of resins, the vinyl resins, is made from acetylene, through the intermediate formation of vinyl chloride, $CH_2{=}CHCl$, or vinyl acetate, $CH_2{=}CHOOCCH_3$.

Dyes. Formerly, the dyestuffs were obtained entirely from natural products; *e.g.*, alizarin from madder root, and indigo from the indigo plant. Large amounts of the natural product were required to secure small amounts of the dye and the cost was great. In 1856, Perkin, a young British student, while attempting to synthesize the drug quinine, discovered a dye, mauve. Since that time a great number of dyestuffs have been prepared by synthetic processes. These synthetic products have the advantage in comparison with the natural products, that they can be prepared in the pure condition, and can be made in larger quantities and more cheaply than the natural extracts. The color of the dye depends on the manner in which the atoms of the constituent elements are linked together. Certain molecular configurations always yield colored products, while different substituent groups modify the color, thus producing different shades of the same color. By-products from the destructive distillation of coal, separated from the tarry material known as coal tar, and from the volatile gases, are the crude materials used in the synthesis of these substances, so that they are called "coal tar dyes."

Drugs. Great progress has been made in the synthesis of known drugs and in the production of new drugs; but the progress has been much slower than in the field of the dyes. The problem involved in the separation and purification of the active principle in a drug is itself a very complex one. The physiological action of a drug is often the result of several of the substances in the natural product. The active material of many of the drugs has, however, been isolated and the composition and constitution determined. Following this, methods for the synthesis of the products have usually been developed. Thus, adrenalin, formerly obtained only as an extract from the suprarenal gland of the sheep, and thyroxine, an essential substance produced in the thyroid glands of animals, are now produced by synthetic methods.

The work of the chemist goes further than the synthesis of known drugs. Some progress has been made in efforts to determine the particular grouping of the atoms of the constituent elements which is responsible for the physiological action of the drug. When this is known, it may be possible to prepare new drugs which have greater beneficial effects than any drugs known at present, without the harmful effects which accompany the use

of so many of the natural preparations. By this type of research, *procaine*, novocaine, the familiar local anaesthetic, was discovered, and is now largely used instead of cocaine.

Among the synthetic products of the organic chemistry laboratory, many new substances have been found to be useful as drugs. Aspirin is an example of a drug of this type. In the effort to synthesize compounds which are poisonous to the disease organisms but harmless to mankind, some noteworthy successes have been achieved. Ehrlich developed two arsenical drugs, salvarsan and neosalvarsan, which have proved to be of great value in the war on syphilis. Recently, prontosil, containing sulfanilamide which was developed by a German chemist, G. Domagk, has come into great prominence in treating infections caused by four of the major germ enemies, streptococci, pneumococci, meningococci, and gonococci. Sulfapyridine, a derivative of sulfanilamide, shows a more general action against pneumococci than does sulfanilamide. Other derivatives also are coming into use. These chemicals check the growth of the germs so that the body may be able to overcome the infection.

Hormones. There are a number of substances secreted by ductless glands in one part of the body and transferred by the blood or lymph to other organs in the body. The secretions of these endocrine glands aid in keeping the various parts of the body properly adjusted to each other. Adrenaline and thyroxine are examples of hormones which have been obtained in the pure condition and studied so that their structure has been determined. Both of these substances may now be produced by synthetic methods. The hormone, insulin, is necessary for the proper oxidation of carbohydrates in the body. The absence of this hormone causes diabetes, which is recognized by the presence of glucose in the urine.

Foods. In the discussion of the organic substances, one must not lose sight of the fact that the most extensive and normally most important use of these substances is as foods. The animal body requires food for replacing the materials consumed in life processes, in maintaining the body temperature and supplying energy, and in the growth of the immature body. There are three main classes of foods: *the carbohydrates, the fats, and the proteins.* In addition, certain mineral salts and water are required.

With the exception of the mineral salts and sugar, these substances are insoluble and do not pass freely through the lining of the digestive tract to be absorbed into the circulatory system of the body. In the digestion of food many chemical reactions take place inside of the body, for the conversion of these substances into somewhat simpler products which can be absorbed. After the nutritive substances have been absorbed, they are again converted by chemical processes into products which are stored in the cells of the animal body, or are oxidized to furnish heat and energy for work, and the oxidation products are excreted. The normal diet should contain the proper proportions of these classes of foods to meet the needs of the individual. In addition the diet should be a varied one, including fresh vegetables and fruits, butter and milk, to furnish the several classes of vitamins which are required for the normal health of the individual. The specific reactions involved in the digestive processes are in many cases not definitely known; and those which are known are, for the most part, beyond the scope of this book. A large amount of work is being done by the physiological chemist in the endeavor to discover more specifically the chemical reactions involved in life processes, so that derangements of these normal functions, which we call disease, may be treated in the most intelligent manner.

EXERCISES

1. For each of the following classes of substances, select one compound, write its graphic formula, discuss its sources, and name the use or uses which contribute to its economic value: (*a*) alcohols; (*b*) aldehydes; (*c*) acids; (*d*) esters.
2. Discuss two cases in which synthetic methods for the production of organic compounds are threatening the supremacy of the former methods of production.
3. Discuss the process for the production of synthetic methanol, in the light of Le Chatelier's principle.
4. How does esterification differ from neutralization? Show how the law of mass action may be applied in the formation of an ester.
5. What is a fat? An oil? What is the difference between edible oils, fuel oils, and lubricating oils?
6. What principle is employed in the production of rayon? What is "cellophane"?
7. Distinguish between an organic nitrate and a nitro compound. Give an example of each and state how these substances are prepared.

8. Show by equations in which graphic formulas are used two reactions which may be employed for the formation of substituted products from benzene.
9. How is aniline prepared from nitrobenzene? Phenol from benzene sulfonic acid?
10. Discuss the importance of derivatives of the aromatic hydrocarbons in (*a*) drugs; (*b*) dyes; (*c*) explosives.

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PROBLEMS

I. EQUIVALENT WEIGHTS AND FORMULAS

1. The composition of several compounds of silver is given below:

Silver oxide	93.09% of silver
Silver chloride	75.26% of silver
Silver fluoride	85.03% of silver
Silver sulfide	87.06% of silver.

From the data, calculate the equivalent weights of these elements.

2. The weights of each of the non-metals listed below hold in combination 5.04 g. of hydrogen:

Phosphorus	51.70 g.	Nitrogen	23.40 g.
Sulfur	80.15 g.	Chlorine	35.5 g.
Carbon	15.005 g.	Oxygen	40.00 g.

Calculate the equivalent weight of each element.

3. If 3.387 g. of a metal displace 0.378 g. of hydrogen, what is the equivalent weight of the metal?
4. When a strip of iron is suspended in a solution of copper sulfate, it is found to undergo a loss in weight of 3.15 g. while 3.586 g. of copper are displaced. The equivalent weight of iron is 27.92. Calculate the equivalent weight of copper.
5. A one-gram sample of magnesium chloride contains 0.2553 g. of magnesium. The equivalent weight of magnesium is 12.16. Calculate the equivalent weight of chlorine.
6. Magnesium oxide contains 60.32% of magnesium, and magnesium bromide contains 13.20% of magnesium. Calculate the equivalent weight of bromine.
7. The combustion of 10 g. of mercuric sulfide yields 8.62 g. of mercury. This weight of mercury combines with chlorine to form 11.66 g. of mercuric chloride. If the equivalent weight of chlorine is 35.46, what is the equivalent weight of sulfur?
8. A solution contains 1.8962 g. of stannous chloride. By reaction with zinc all of the tin is deposited and is found to weigh 1.187 g. The weight of zinc dissolved is 0.6537 g. The equivalent weight of zinc is 32.68. Calculate the equivalent weight of tin and of chlorine.
9. It is found by experiment that 3.102 g. of phosphorus unite with 10.638 g. of chlorine, and that this chloride can be caused to combine with an additional 7.092 g. of chlorine, forming a second compound of these two elements. The equivalent weight of chlorine is 35.46. Calculate the equivalent weight of phosphorus in each of these compounds. Reduce the ratio of the equivalent weights of phosphorus to an integral ratio.

The atomic weight of chlorine is 35.46; and of phosphorus, 31.02. Find the simplest formula for each compound, and the valence of phosphorus in each compound.

10. Find the simplest formula corresponding to each of the following analyses:

(*a*) Pb	64.11%	C	29.71%	H	6.18%			
(*b*) Ti	38.76	F	61.24					
(*c*) Na	18.33	S	25.83	O	19.36	H_2O	36.28%	
(*d*) N	7.62	H	2.20	Sn	32.30	Cl	57.88	
(*e*) H	0.77	S	62.06	O	37.17			
(*f*) H	2.22	C	26.67	O	71.11			
(*g*) Al	20.30	Cl	79.70					

II. REACTING WEIGHTS OF SUBSTANCES

11. Calculate the weight of potassium nitrite formed by the decomposition of 21.3 g. of potassium nitrate.
12. What weight of slaked lime is required to decompose 5 g. of ammonium chloride and what weight of each product is formed?
13. What weight of silver nitrate is required for the precipitation of all of the chloride in 7.48 g. of ferric chloride?
14. What weight of lead chromate would be precipitated by the addition of an excess of lead acetate to a solution containing 1.5 g. of potassium chromate?
15. Calculate the weight of sulfuric acid which may be produced from 60 g. of iron disulfide.
16. A series of reactions is carried out to produce the following products:

$$S \longrightarrow FeS \longrightarrow H_2S \longrightarrow SO_2 \longrightarrow SO_3 \longrightarrow H_2SO_4 \longrightarrow Na_2SO_4.$$

Calculate the weight of each product formed if one fifth of a gram atom of sulfur is used. Calculate the weight of each of the other materials required for these successive reactions.

17. What weight of concentrated sulfuric acid of specific gravity 1.8, containing 98% of the acid, would be required for complete reaction with 10 g. of sodium chloride?
18. Concentrated hydrochloric acid has a specific gravity of 1.19 and contains 38% of the acid. Calculate the weight of this solution required to prepare one liter of a solution containing one mole of hydrochloric acid.
19. If 10 g. of bromine react with a solution containing 10 g. of potassium hydroxide, what weight of each salt is produced and what weight of potassium hydroxide remains in solution?
20. A two-gram sample of impure sodium chloride is dissolved in water and an excess of silver nitrate solution is added. The precipitate is found to weigh 4.628 g. Assuming that all of the chloride in this precipitate is from sodium chloride, calculate the percentage of sodium chloride in the sample.
21. How many grams of phosphorus are required to produce one liter of phosphoric acid of specific gravity 1.61, containing 75% of phosphoric acid?
22. Calculate the percentage of magnesium carbonate in a magnesite sample if one gram yields 0.43 g. of carbon dioxide.

23. What weight of barium sulfate could be obtained from a one-gram sample of pyrite containing 35% of sulfur?
24. How many pounds of aluminum may be obtained from a ton of bauxite which contains 65% of aluminum oxide?

III. REACTING VOLUMES OF GASES

(In these problems it is assumed that the measurements of the gas volumes are made under the same conditions of temperature and pressure in each instance.)

25. What volume of oxygen would be required for the complete combustion of 500 ml. of acetylene, C_2H_2?
26. What volume of carbon dioxide would result from the combustion of 4.48 liters of ethylene, C_2H_4?
27. Calculate the volume of hydrogen sulfide required to reduce 50 ml. of sulfur dioxide to free sulfur.
28. If 40 ml. of hydrogen are mixed with 50 ml. of oxygen, at a temperature of 100°, and a spark is passed through the mixture, what would be the volume of the resulting gas mixture? What would be the partial pressure of each gas in this mixture?
29. Calculate the volume of oxygen required to oxidize 10 liters of ammonia to nitric oxide and water.
30. Assuming that air contains one fifth by volume of oxygen, what volume of air would be required for the combustion of 100 ml. of hydrogen?

IV. REACTING WEIGHTS AND VOLUMES OF SUBSTANCES

(It is assumed that all gases are measured at standard conditions of temperature and pressure unless otherwise specified.)

31. What volume of oxygen would be produced by the decomposition of 10 g. of potassium chlorate?
32. What volume would the oxygen produced in Problem 31 occupy if collected over water at 20° and 750 mm.?
33. Calculate the volume of hydrogen sulfide produced by the reaction of an excess of hydrochloric acid with 0.2 mole of ferrous sulfide.
34. If 7.78 liters of carbon dioxide are absorbed in an excess of sodium hydroxide solution, what weight of sodium carbonate is formed?
35. If 5.6 liters of chlorine are absorbed in a solution of potassium carbonate, what volume of carbon dioxide is evolved?
36. A sample of crude dolomite contains 55% of calcium carbonate and 42% of magnesium carbonate. Calculate the volume of carbon dioxide evolved by the reaction of hydrochloric acid with a 5-g. portion of this material.
37. If two moles of sodium chloride react with sulfuric acid and the hydrochloric acid formed is oxidized by manganese dioxide, what volume of chlorine is produced?
38. A sample of impure aluminum weighing 0.03 g. yields 35.43 ml. of hydrogen by reaction with hydrochloric acid. Calculate the per cent of aluminum in this sample.

39. What volume of nitric oxide would result from the reaction of 10 g. of copper with nitric acid, assuming that nitric oxide is the only reduction product of nitric acid formed in the reaction? If this nitric oxide is converted into nitrogen dioxide, what would its volume be?
40. Assume that a cylinder of liquid ammonia contains 17 kg. of the liquid.
    (*a*) How many liters of ammonia gas at standard conditions will this liquid yield?
    (*b*) Approximately how many liters of concentrated ammonia solution (28.3%, density 0.9 g. per ml.) can be prepared?
    (*c*) What is the approximate normality of this solution?
    (*d*) How many liters of 3 N. sulfuric acid will be required to neutralize this solution? How many liters of 3 M. sulfuric acid?
    (*e*) In each case, what weight of salt will be formed in the neutralization?

    If this ammonia is "cracked" into its constituent gases, find:

    (*f*) The volume of the mixed gases at standard conditions.
    (*g*) The partial pressure of each constituent of the mixed gases.
    (*h*) If the volume of the original ammonia cylinder was 33.6 liters, find the pressure, in atmospheres, required to force the mixed gases back into the original cylinder.
    (*i*) If the ammonia is treated by the Ostwald process, with subsequent oxidation of the nitric oxide, what weight of nitrogen dioxide would be formed?
    (*j*) What weight of nitric acid could be formed by the absorption of this nitrogen dioxide gas in water in the absence of air?

V. PRODUCTS OF ELECTROLYSIS

41. If an electric current deposits 5.39 g. of silver, what weight of the following substances would be deposited by the same current: copper, mercury, lead, bismuth, chlorine, bromine, oxygen, hydrogen?
42. What weights of cadmium and iodine would be deposited from a solution of cadmium iodide by the passage of a 2-ampere current through the solution for 3 hours?
43. What volumes (S. T. P.) of hydrogen and oxygen would be liberated by the passage of a 2.5-ampere current through a solution of sodium sulfate for 30 minutes?
44. If a current deposits 10.78 g. of silver from a solution of a silver salt, what weight of copper from copper sulfate, of mercury from mercurous sulfate, and of cadmium from cadmium sulfate would be deposited by the same current? What volumes (S. T. P.) of hydrogen and of oxygen would be liberated from sulfuric acid solution by this current?
45. What weight of copper would be deposited from cupric chloride by 3214 coulombs of electricity? What weight and volume (S. T. P.) of chlorine?
46. How long must a 5.58-ampere current flow through a solution of sodium chloride in a Nelson cell in order to cause the formation of 5 moles of sodium hydroxide?

47. It is found that the same electric current passed through a series of cells deposits 10.78 g. of silver, 6.9666 g. of bismuth, 3.1785 g. of copper, 0.56 liters of oxygen, and 1.12 liters of chlorine. Calculate the equivalent weight of each of these elements.
48. What must be the amperage of a current in order to deposit 1.589 g. of copper in 1 hour and 20 minutes?

VI. MOLECULAR AND ATOMIC WEIGHTS

49. The weight of a liter of oxygen at standard conditions is 1.429 g. The same volume, under like conditions, of other gases weighs: (*a*) 1.17 g.; (*b*) 0.77 g.; (*c*) 1.78 g.; (*d*) 7.14 g.
Calculate the molecular weights of these gases by reference to oxygen.
50. If 34.2 ml. of a certain gas at 20° C. and 700 mm. weighs 0.0447 g., what is the molecular weight of the gas?
51. Calculate the molecular weight of chloroform from the following data: 0.22 g. of chloroform in a Victor-Meyer apparatus displaced 45 ml. of air collected over water at 20° C. and 755 mm.
52. If 0.716 g. of a compound occupy 327.6 ml. in the gaseous state at 200° and 750 mm., what is the molecular weight of the compound?
53. If 0.091 g. of a gas occupy 33.5 ml. at 100° and 770 mm., what is the molecular weight of this substance?
54. If 0.15 g. of a substance yields 30.5 ml. of vapor at 95° and 400 mm., what is its molecular weight?
55. Calculate the density, relative to air, of chlorine, carbon dioxide, and ammonia.
56. Calculate the volume, standard conditions, of 5 g. of acetylene; 6.4 g. of sulfur dioxide; 4 g. of methane; 7.3 g. of hydrogen chloride; and 9.2 g. of nitrogen dioxide.
57. Calculate the freezing point and the boiling point of water from a solution which contains 100 g. of mannitol, $C_6H_{14}O_6$, dissolved in 1000 g. of water.
58. What weights of wood alcohol, CH_3OH, glycerol, $C_3H_8O_3$, and "prestone," $C_2H_6O_2$, respectively, must be added to 100 g. of water to lower the freezing point to − 18.6°, approximately 0° F.?
59. Calculate the molal concentration and the freezing point depression in each of the solutions listed in the following table:

Solute	*Weight*	*Weight of Water*	*Molal Concentration*	*Freezing Point Depression*
$C_{12}H_{22}O_{11}$	17.1 g.	25 g.		
$C_6H_{12}O_6$	0.36	20		
C_2H_5OH	230.0	2500		
CON_2H_4	6.0	250		
C_3H_6O	23.2	100		
H_2O_2	170.0	500		

60. Calculate the molal depression of the freezing point of the several solvents from the data in the following table:

Substance Dissolved	*Weight of Solute*	*Weight of Solvent*	*Observed Lowering of Freezing Point*	*Molal Depression*
$C_{12}H_{22}O_{11}$	171 g.	250 g.	3.72	
$C_{10}H_8$	12.8	200	2.56	
$C_{10}H_{16}O$	1.52	25	2.05	
C_6H_6	3.9	50	7.5	
$C_5H_{10}O_2$	25.5	125	7.8	
C_2H_5OH	13.8	100	35.4	

61. Calculate the molecular weights of the substances yielding the following experimental data:
    (*a*) The freezing point of water is depressed 0.62° by 1.08 g. of solute in 100 g. of water.
    (*b*) The freezing point of benzene is depressed 1.28° by 4.0 g. of a solute in 125 g. of benzene.
    (*c*) The boiling point of benzene is raised 0.15° by 8 g. of a solute in 125 g. of benzene.
    (*d*) The boiling point of water is raised 0.26° by 9 g. of a solute in 100 g. of water.
62. Three substances have the composition C 40.00%, O 53.33%, H 6.67%. From data outlined below, find the true formulas:
    (*a*) 250 ml. of "A" at 950 mm. and 91° C. weigh 0.312 g.
    (*b*) 3 g. of "B" in 25 g. of water lower the freezing point 2.48° C.
    (*c*) 0.27 g. of "C" in 10 g. of water raises the boiling point 0.078° C.
63. A metal yields an oxide in which 16 parts by weight of oxygen combine with 20.38 parts of the metal, and a chloride in which 35.46 parts of chlorine combine with 16.98 of the metal. What is the atomic weight of the metal?
64. An oxide of an element contains 23.95% of oxygen and a chloride contains 45.60% of chlorine. Calculate the equivalent weight and the atomic weight of this element.
65. Calculate the approximate atomic weight of the element "Y" from the following data.

Compound of "Y" With	*Weight of 1 Liter of Gaseous Compound (Standard Conditions)*	*Per Cent "Y" in Compound*
Oxygen	3.036 g.	52.94
Chlorine	6.869	7.80
Sulfur	3.398	15.77
Oxygen	1.250	42.86
Hydrogen	1.250	85.72
Nitrogen	2.322	46.13

66. Calculate the exact atomic weight of the element "X" according to the following data.

Compound of "X" With	*Molecular Weight of Compound*	*Per Cent of "X" in Compound*
Iron	161.8	65.6
Copper	134.1	52.8
Mercury	235.2	15.1
Aluminum	132.5	79.8
Phosphorus	136.6	77.5
Phosphorus	207.7	85.1
Silicon	168.9	83.5
Tin	260.3	54.4
Carbon and hydrogen	84.7	83.5

Two grams of a compound of this element with hydrogen contain 1.9447 g. of "X."

VII. CONCENTRATIONS OF SOLUTIONS

67. Calculate the gram equivalent weights of the following substances:
HCl, $Ca(OH)_2$, H_2SO_4, $Pb(NO_3)_2$, $AgNO_3$, H_3PO_4, $Al_2(SO_4)_3$.
68. How many moles of each of the following substances are required to prepare 500 ml. of one molar solution: phosphoric acid; potassium hydroxide; magnesium sulfate? What is the normality of each of these solutions?
69. Calculate the molarity of the following solutions:
(*a*) One mole of Na_2SO_4 in 500 ml. of solution.
(*b*) Five gram equivalent weights of KCl in two liters of solution.
(*c*) Two grams of $CaSO_4(H_2O)_2$ in 1000 ml. of solution.
(*d*) 8 g. of NaOH in 250 ml. of solution.
(*e*) 73 g. of HCl in 750 ml. of solution.
(*f*) 5 g. of $Al_2(SO_4)_3$ in 432 ml. of solution.
(*g*) 0.025 g. of Ag_2SO_4 in 1000 ml. of solution.
70. The common laboratory reagents have the following specific gravity and composition:
Concentrated sulfuric acid, specific gravity 1.8, contains 98% of H_2SO_4.
Concentrated hydrochloric acid, specific gravity 1.19, contains 38% of of HCl.
Concentrated nitric acid, specific gravity 1.42, contains 70% of HNO_3.
Calculate the approximate normality of each solution. What volume of each solution would be required to make one liter of a solution which is approximately 3 N.?
71. What volume of 0.5 N. sulfuric acid is required for the neutralization of a solution containing 10 g. of sodium hydroxide?
72. What volume of 0.2 M. hydrochloric acid is required for the complete decomposition of 5 g. of calcium carbonate?
73. If 25 ml. of a 0.38 N. acidic solution are equivalent to 30 ml. of a basic solution, what is the normality of the base?

74. If 21.2 g. of anhydrous sodium carbonate are treated with the minimum volume of acid required for complete reaction:
   (*a*) What volume of half-molar sulfuric acid is required?
   (*b*) What would be the normality of the sodium sulfate solution formed, assuming that the volume of solution after reaction is the same as that of the acid taken in (*a*)?
   (*c*) If all the carbon dioxide is driven out, dried, and collected at 27 C. and 750 mm., what volume will it occupy?
75. Enough calcium oxide is used to convert 10.6 g. of sodium carbonate into calcium carbonate and sodium hydroxide, and the calcium carbonate is removed by filtration.
   (*a*) To what volume must the resulting sodium hydroxide solution be diluted in order that a tenth-molar solution be prepared?
   (*b*) It is found that 15 ml. of this tenth-molar sodium hydroxide solution are neutralized by the following volumes of different acids, respectively:
      (1) 30 ml. hydrochloric acid.
      (2) 15 ml. sulfuric acid.
      (3) 10 ml. phosphoric acid.
      What are the molarity and normality of each of the acids?
76. Calculate the *p*H of the solutions in which the ion concentrations are:
   (*a*) H^+, 0.8 M. (*b*) H^+, 0.085 M. (*c*) H^+, 0.00136 M.
   (*d*) H^+, 0.0095 M. (*e*) OH^-, 0.8 M. (*f*) OH^-, 0.0016 M.
77. Calculate the concentration of the hydrogen ion in solutions having the following *p*H values: (*a*) 0.1; (*b*) 2.06; (*c*) 13.07; (*d*) 11.27.
78. Calculate the apparent degree of ionization of the following solutes from the freezing point depression in aqueous solution:
   (*a*) 0.2 M. HCl, freezing point − 0.708°.
   (*b*) 0.5 M. KCl, freezing point − 1.657°.
   (*c*) 0.1 M. $MgCl_2$, freezing point − 0.494°.
   (*d*) A solution containing 1.5 g. of KCl in 100 g. of water begins to freeze at − 0.684°.
   (*e*) A solution containing 5.64 g. of NaCl in 100 g. of water begins to freeze at − 3.216°.
79. From the degree of ionization, calculate the ionization constant of each of the following weak electrolytes:
   (*a*) HCN, 0.1 M., 0.01%.
   (*b*) H_2S, 0.1 M. ($H^+ + HS^-$), 0.07%.
   (*c*) H_2CO_3, 0.1 M., ($H^+ + HCO_3^-$), 0.17%.
   (*d*) HF, 0.1 M., 8.5%.
   (*e*) $NH_3 + H_2O$, 0.1 M, ($NH_4^+ + OH^-$), 1.34%.
80. Calculate the value of the ionization constant of acetic acid according to the per cent ionization at each of the following concentrations: 1 M., 0.42%; 0.1 M., 1.33%; 0.01 M., 4.1%; 0.001 M., 12.5%.
81. Calculate the concentration of the hydrogen ion and the *p*H in solutions of the following acids from the numerical values of the ionization constants given in the appendix:

(*a*) 0.5 M. $HC_2H_3O_2$; (*b*) 0.1 M. HClO; (*c*) 1 M. HF;
(*d*) 0.5 M. HNO_2; (*e*) 0.1 HIO.

82. Calculate the concentrations of hydrogen ions in each of the following solutions of acetic acid if enough sodium acetate is added to each solution to maintain the concentration of the acetate ion 1 M.:
(*a*) 0.1 M.; (*b*) 0.5 M.; (*c*) 1 M.
83. Calculate the concentration of sulfide ions in solutions containing the concentrations of hydrogen ions listed below:
(*a*) 2 M.; (*b*) 0.5 M.; (*c*) 0.1 M.; (*d*) 1×10^{-7} M.; (*e*) 1×10^{-10} M.
84. What is the concentration of the hydrogen ion in the solutions which result from the addition of 50 ml. of 2 N. HCl to each of the following solutions:
(*a*) 50 ml. of 2 N. NaOH; (*b*) 50 ml. of 2 N. Na_2S; (*c*) 50 ml. of 2 N. NaCN; (*d*) 50 ml. of 2 N. Na_2CO_3; (*e*) 50 ml. of 2 N. NH_3.
85. From the solubility data in the appendix, calculate the solubility products of the following substances:
(*a*) AgCl; (*b*) AgBr; (*c*) $BaSO_4$; (*d*) $PbCl_2$; (*e*) $Mg(OH)_2$.
86. From the solubility product data, calculate the solubility in moles per liter of the following substances:
(*a*) ZnS; (*b*) AgI; (*c*) $BaCrO_4$; (*d*) Ag_2SO_4; (*e*) AgCN.
87. What is the maximum concentration of the carbonate ion which may be used in the precipitation of the calcium group of cations without precipitating magnesium carbonate, if the concentration of the magnesium ion is 0.1 M.?
88. What is the maximum concentration of the hydroxide ion which may be present in a solution in which the concentration of the magnesium ion is 0.1 M.?
89. Calculate the maximum concentration of the chromate ion which may be used for the separation of barium and strontium ions in a solution which is 0.1 M. with respect to each of these ions.
90. Calculate the concentration of hydrogen ions required to regulate the sulfide ion concentration so as to effect the separation of cadmium and zinc ions in a solution in which they are each present in 0.1 M. concentration.

APPENDIX

I. UNITS OF MEASUREMENT

Length

1 kilometer	= 1000 meters (m.)	= 0.6214 mile.
1 meter	= 100 centimeters (cm.)	= 39.37 inches.
1 centimeter	= 0.3937 in.	
1 inch	= 2.54 cm.	

Volume

1 liter	= 1000 milliliters (ml.)	= 1.06 quarts, fluid.
1 liter	= 1000.027 cubic centimeters (cc.).	
1 fluid ounce	= 29.5737 cc.	
1 cubic foot	= 28.32 liters.	

Gram molecular volume of a gas at 0° and 760 mm. = 22.4 liters.

Weight

1 gram (g.)	= weight of 1 ml. of water at 4°.
1 kilogram (kg.)	= 1000 g. = 2.2 pounds avoirdupois.
1 pound	= 453.6 g.
1 ounce avoirdupois	= 28.35 g.
1 short ton	= 2000 pounds.
1 long ton	= 2240 pounds.
1 metric ton	= 1000 kilograms = 2204.6 pounds.

Temperature

0° Centigrade	= Freezing point of water = 32° Fahrenheit.
100° Centigrade	= Boiling point of water = 212° Fahrenheit.

Electricity

96,500 coulombs	= Quantity of electricity required to deposit 1 gram equivalent of an element = 1 faraday.
1 ampere	= 1 coulomb per second.
1 coulomb	= Quantity of electricity required to deposit 0.0011180 g. of silver from a solution of a silver salt.
1 ohm	= Unit of resistance. The resistance at 0° offered by a column of mercury 106.300 cm. in length of such cross section that it weighs 14.4521 g.
Volt	= Unit of potential difference. The amount of the electromotive force required to cause a current to flow at the rate of one ampere through a resistance of one ohm.

II. VAPOR PRESSURE OF WATER

Temperature	*Pressure, mm.*	*Temperature*	*Pressure, mm.*
0°	4.57	22°	19.63
5°	6.50	23°	20.86
10°	9.14	24°	22.15
15°	12.67	25°	23.52
16°	13.51	26°	24.96
17°	14.39	27°	26.47
18°	15.33	28°	28.06
19°	16.32	29°	29.94
20°	17.36	30°	31.51
21°	18.47	100°	760.00

III. OXIDATION STATES OF COMMON POSITIVE IONS

(The ions are shown in unhydrated form)

1+	*2+*	*3+*
Ammonium, NH_4^+	Barium, Ba^{++}	Aluminum, Al^{+++}
Cuprous, Cu^+	Calcium, Ca^{++}	Antimony, Sb^{+++}
Hydrogen, H^+	Cupric, Cu^{++}	Bismuth, Bi^{+++}
Potassium, K^+	Ferrous, Fe^{++}	Chromic, Cr^{+++}
Silver, Ag^+	Lead, Pb^{++}	Ferric, Fe^{+++}
Sodium, Na^+	Magnesium, Mg^{++}	
	Mercuric, Hg^{++}	
	Stannous, Sn^{++}	
	Strontium, Sr^{++}	
	Zinc, Zn^{++}	

IV. OXIDATION STATES OF COMMON NEGATIVE IONS SHOWN IN FORMULAS OF POTASSIUM SALTS

1−		*2−*		*3−*	
Acetate	$KC_2H_3O_2$	Carbonate	K_2CO_3	Arsenite	K_3AsO_3
Bromide	KBr	Chromate	K_2CrO_4	Arsenate	K_3AsO_4
Chlorate	$KClO_3$	Dichromate	$K_2Cr_2O_7$	Phosphate	K_3PO_4
Chloride	KCl	Metasilicate	K_2SiO_3	Phosphate	K_3PO_3
Hydroxide	KOH	Sulfate	K_2SO_4	*4−*	
Hypochlorite	$KClO$	Sulfide	K_2S	Orthosilicate	K_4SiO_4
Nitrate	KNO_3	Sulfite	K_2SO_3	Ferrocyanide	$K_4Fe(CN)_6$
Nitrite	KNO_2				

V. NON-METAL OXIDES AND CORRESPONDING ACIDS AND SALTS

Element	*Oxide*	*Acid*		*Salt*	
Nitrogen	N_2O_3	Nitrous	HNO_2	Nitrite	$NaNO_2$
	N_2O_5	Nitric	HNO_3	Nitrate	$NaNO_3$
Carbon	CO_2	Carbonic	H_2CO_3	Carbonate	Na_2CO_3
Sulfur	SO_2	Sulfurous	H_2SO_3	Sulfite	Na_2SO_3
	SO_3	Sulfuric	H_2SO_4	Sulfate	Na_2SO_4
Silicon	SiO_2	Metasilicic	H_2SiO_3	Metasilicate	Na_2SiO_3
	SiO_2	Orthosilicic	H_4SiO_4	Orthosilicate	Na_4SiO_4
Phosphorus	P_2O_3	Phosphorous	H_2HPO_3	Phosphite	Na_2HPO_3
	P_2O_5	Phosphoric	H_3PO_4	Phosphate	Na_3PO_4
Arsenic	As_2O_3	Arsenious	H_3AsO_3	Arsenite	Na_3AsO_3
	As_2O_5	Arsenic	H_3AsO_4	Arsenate	Na_3AsO_4
Boron	B_2O_3	Boric	H_3BO_3	Borate	Na_3BO_3
Chlorine	Cl_2O	Hypochlorous	$HClO$	Hypochlorite	$NaClO$
	Cl_2O_7	Perchloric	$HClO_4$	Perchlorate	$NaClO_4$
Manganese	MnO_3	Manganic	H_2MnO_4	Manganate	Na_2MnO_4
	Mn_2O_7	Permanganic	$HMnO_4$	Permanganate	$NaMnO_4$
Chromium	CrO_3	Chromic	H_2CrO_4	Chromate	Na_2CrO_4

VI. ELECTROMOTIVE SERIES OF THE METALS[1]

These electrode potentials are expressed in volts referred to the standard reference hydrogen electrode at 25° and unit activities.

Lithium	− 3.02	Iron, ferrous	− 0.44
Rubidium	− 2.99	Cadmium	− 0.402
Potassium	− 2.922	Cobalt	− 0.277
Barium	− 2.90	Nickel	− 0.25
Strontium	− 2.89	Tin, stannous	− 0.136
Calcium	− 2.87	Lead	− 0.126
Sodium	− 2.712	Hydrogen	0.000
Magnesium	− 2.34	Antimony, antimonyl	+ 0.212
Aluminum	− 1.67	Copper, cupric	+ 0.345
Manganese	− 1.05	Mercury, mercurous	+ 0.7986
Zinc	− 0.762	Silver	+ 0.7995
Chromium	− 0.71	Gold, auric	+ 1.42

[1] The data are from Latimer and Hildebrand: *Reference Book of Inorganic Chemistry* (The Macmillan Company).

VII. OXIDIZING AGENTS. TYPICAL HALF REACTIONS

Non-Metals

$$Cl_2 + 2\,\epsilon \longrightarrow 2\,Cl^-.$$
$$S + 2\,\epsilon \longrightarrow S^{--}.$$

Metal Ions

$$Fe^{+++} + 1\epsilon \longrightarrow Fe^{++}$$
$$2\,Hg^{++} + 2\,\epsilon \longrightarrow Hg_2^{++}$$
$$Cu^{++} + 2\,\epsilon \longrightarrow Cu$$

Oxyions in Acidic Solution

$$NO_3^- + 4\,H^+ + 3\,\epsilon \longrightarrow NO + 2\,H_2O$$
$$NO_3^- + 2\,H^+ + 1\,\epsilon \longrightarrow NO_2 + H_2O$$
$$NO_3^- + 10\,H^+ + 8\,\epsilon \longrightarrow NH_4^+ + 3\,H_2O$$
$$ClO_3^- + 6\,H^+ + 6\,\epsilon \longrightarrow Cl^- + 3\,H_2O$$
$$MnO_4^- + 8\,H^+ + 5\,\epsilon \longrightarrow Mn^{++} + 4\,H_2O$$
$$Cr_2O_7^{--} + 14\,H^+ + 6\,\epsilon \longrightarrow 2\,Cr^{+++} + 7\,H_2O$$

Molecular Oxidizing Agents in Acidic Solution

$$HClO + H^+ + 2\,\epsilon \longrightarrow Cl^- + H_2O$$
$$H_2SO_4 + 2\,H^+ + 2\,\epsilon \longrightarrow SO_2 + 2\,H_2O$$
$$H_2SO_4 + 8\,H^+ + 8\,\epsilon \longrightarrow H_2S + 4\,H_2O$$
$$H_2SO_3 + 4\,H^+ + 4\,\epsilon \longrightarrow S + 3\,H_2O$$
$$H_2O_2 + 2\,H^+ + 2\,\epsilon \longrightarrow 2\,H_2O$$

Oxyions in Basic Solution

$$ClO^- + H_2O + 2\,\epsilon \longrightarrow Cl^- + 2\,OH^-$$
$$Na_2O_2 + 2\,H_2O + 2\,\epsilon \longrightarrow 2\,Na^+ + 4\,OH^-$$
$$O_2 + 2\,H_2O + 4\,\epsilon \longrightarrow 4\,OH^-$$
$$MnO_4^- + 2\,H_2O + 3\,\epsilon \longrightarrow MnO_2 + 4\,OH^-$$
$$CrO_4^{--} + 4\,H_2O + 3\,\epsilon \longrightarrow Cr(OH)_4^- + 4\,OH^-$$
$$BiO^+ + H_2O + 3\,\epsilon \longrightarrow Bi + 2\,OH^-$$

VIII. REDUCING AGENTS. TYPICAL HALF REACTIONS

Metals

$$K \longrightarrow K^+ + 1\,\epsilon$$
$$Ca \longrightarrow Ca^{++} + 2\,\epsilon$$
$$Al \longrightarrow Al^{+++} + 3\,\epsilon$$
$$H_2 \longrightarrow 2\,H^+ + 2\,\epsilon$$
$$Cu \longrightarrow Cu^{++} + 2\,\epsilon$$

Low Valent Metal Ions

$$Hg_2^{++} \longrightarrow 2\,Hg^{++} + 2\,\epsilon$$
$$Fe^{++} \longrightarrow Fe^{+++} + 1\,\epsilon$$
$$Sn^{++} + 6\,Cl^- \longrightarrow SnCl_6^{--} + 2\,\epsilon$$
$$CuCl_2^- \longrightarrow Cu^{++} + 2\,Cl^- + 1\,\epsilon$$

Simple Negative Ions

$$S^{--} \longrightarrow S + 2\,\epsilon$$
$$2\,I^- \longrightarrow I_2 + 2\,\epsilon$$
$$2\,Cl^- \longrightarrow Cl_2 + 2\,\epsilon$$

Non-Metals with Acidic Oxidizing Agents

$$P + 4\,H_2O \longrightarrow H_3PO_4 + 5\,H^+ + 5\,\epsilon$$
$$S + 4\,H_2O \longrightarrow SO_4^{--} + 8\,H^+ + 6\,\epsilon$$
$$I_2 + 6\,H_2O \longrightarrow 2\,IO_3^- + 12\,H^+ + 10\,\epsilon$$

Non-Metals with Basic Oxidizing Agents

$$S + 8\,OH^- \longrightarrow SO_4^{--} + 4\,H_2O + 6\,\epsilon$$
$$P + 8\,OH^- \longrightarrow PO_4^{---} + 4\,H_2O + 5\,\epsilon$$

Oxycompounds in Basic Solution

$$Cr(OH)_4^- + 4\,OH^- \longrightarrow CrO_4^{--} + 4\,H_2O + 3\,\epsilon$$
$$MnO_2 + 4\,OH^- \longrightarrow MnO_4^{--} + 2\,H_2O + 2\,\epsilon$$
$$MnO_4^{--} \longrightarrow MnO_4^- + 1\,\epsilon$$
$$SO_3^{--} + 2\,OH^- \longrightarrow SO_4^{--} + H_2O + 2\,\epsilon$$
$$Sn(OH)_4^{--} + 2\,OH^- \longrightarrow SnO_3(H_2O)_3^{--} + 2\,\epsilon$$

IX. SOLUBILITY OF SOME OF THE COMMON SALTS AND HYDROXIDES[1]

(Moles of Solute in 1000 g. of Water at 20°, unless otherwise noted.)

Chlorides

Calcium chloride	6.70
Sodium chloride	6.13
Magnesium chloride	5.76
Potassium chloride	4.61
Barium chloride	1.72
Mercuric chloride	0.246
Lead chloride	0.0357
Silver chloride	1×10^{-5}

Bromides

Sodium bromide	8.77
Calcium bromide	7.1
Potassium bromide	5.42
Magnesium bromide	5.25
Barium bromide	3.4
Lead bromide	0.012
Silver bromide	4.2×10^{-7}

Iodides

Sodium iodide	11.98
Potassium iodide	8.63
Calcium iodide	7.00
Magnesium iodide	5.03
Lead iodide	0.00139
Silver iodide	1.3×10^{-8}

Fluorides

Potassium fluoride (21°)	16.6
Silver fluoride	13.6
Sodium fluoride	1.0
Calcium fluoride (18°)	3.99×10^{-5}

Sulfates

Zinc sulfate	3.358
Magnesium sulfate	2.88
Ferrous sulfate	1.74
Sodium sulfate	1.33
Cupric sulfate	1.30
Potassium sulfate	0.637
Silver sulfate	0.0254
Calcium sulfate	0.00188
Lead sulfate	2.5×10^{-4}
Strontium sulfate	8.5×10^{-5}
Barium sulfate	1.98×10^{-5}

Nitrates

Silver nitrate	12.3
Sodium nitrate	10.31
Calcium nitrate	7.88
Strontium nitrate	3.34
Potassium nitrate	3.08
Barium nitrate	2.93
Lead nitrate	1.66

Carbonates

Potassium carbonate	8.0
Sodium carbonate	2.09
Potassium bicarbonate	3.32
Sodium bicarbonate (25°)	1.22
Magnesium carbonate	0.0055
Calcium carbonate (18°)	3×10^{-5}
Barium carbonate (18°)	2.5×10^{-5}

Hydroxides

Sodium hydroxide	27.2
Potassium hydroxide	19.9
Barium hydroxide	0.233
Strontium hydroxide	0.0656
Calcium hydroxide	0.0218
Magnesium hydroxide (18°)	1.1×10^{-4}
Zinc hydroxide	2.2×10^{-6}

[1] Based on *International Critical Tables* (McGraw-Hill Book Company).

X. SOLUBILITY PRODUCTS[1]

At 20°. In the dilute, saturated solutions of the slightly soluble substances, it may be assumed without great error that the effective ion concentration is equal to the total ion concentration.

Substance	*Formula*	*Solubility Product*
Aluminum hydroxide	$Al(OH)_3$	1.9×10^{-33}
Barium carbonate	$BaCO_3$	6.2×10^{-10}
Barium chromate	$BaCrO_4$	2×10^{-10}
Barium oxalate	BaC_2O_4	2×10^{-7}
Barium sulfate	$BaSO_4$	4×10^{-10}
Cadmium sulfide	CdS	1.4×10^{-28}
Calcium carbonate	$CaCO_3$	9×10^{-10}
Calcium chromate	$CaCrO_4$	2×10^{-2}
Calcium fluoride	CaF_2	2.6×10^{-13}
Calcium oxalate	CaC_2O_4	4×10^{-9}
Calcium sulfate	$CaSO_4$	3.5×10^{-6}
Chromic hydroxide	$Cr(OH)_3$	6.7×10^{-31}
Cobalt sulfide	CoS	1×10^{-26}
Cobalt sulfide	$CoS\alpha$	7×10^{-23}
Cupric sulfide	CuS	4×10^{-38}
Ferric hydroxide	$Fe(OH)_3$	1×10^{-38}
Ferrous hydroxide	$Fe(OH)_2$	1.6×10^{-14}
Ferrous sulfide	FeS	1×10^{-19}
Lead bromide	$PbBr_2$	7.8×10^{-6}
Lead chloride	$PbCl_2$	1.8×10^{-4}
Lead chromate	$PbCrO_4$	2×10^{-14}
Lead iodide	PbI_2	1×10^{-10}
Lead sulfate	$PbSO_4$	6.2×10^{-8}
Lead sulfide	PbS	1×10^{-29}
Magnesium carbonate	$MgCO_3$	3×10^{-5}
Magnesium hydroxide	$Mg(OH)_2$	5×10^{-12}
Magnesium ammonium phosphate	$MgNH_4PO_4$	2.5×10^{-13}
Manganous hydroxide	$Mn(OH)_2$	7.1×10^{-15}
Manganous sulfide	MnS	1.6×10^{-16}
Mercuric iodide	HgI_2	2.9×10^{-12}
Mercuric sulfide	HgS	1×10^{-53}
Mercurous chloride	Hg_2Cl_2	3×10^{-18}
Nickel sulfide	NiS	1.4×10^{-24}
Nickel sulfide	$NiS\alpha$	3×10^{-21}
Silver bromide	$AgBr$	1.8×10^{-13}
Silver chloride	$AgCl$	1×10^{-10}
Silver cyanide	$AgCN$	1×10^{-13}
Silver iodide	AgI	1.7×10^{-16}
Silver phosphate	Ag_3PO_4	1.8×10^{-18}
Silver sulfate	Ag_2SO_4	6.5×10^{-5}
Stannous sulfide	SnS	8×10^{-29}
Strontium carbonate	$SrCO_3$	4.6×10^{-9}
Strontium chromate	$SrCrO_4$	5×10^{-5}
Strontium oxalate	SrC_2O_4	1.4×10^{-7}
Strontium sulfate	$SrSO_4$	7.2×10^{-9}
Zinc hydroxide	$Zn(OH)_2$	4×10^{-17}
Zinc sulfide	ZnS	4.5×10^{-24}

[1] The data are based primarily on *International Critical Tables* and Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*.

XI. IONIZATION CONSTANTS[1] (25°)

Substance	*Formula*	*Constant*
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}
Boric acid	H_3BO_3	5.8×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
Bicarbonate ion	HCO_3^-	4.7×10^{-11}
Hydrocyanic acid	HCN	4×10^{-10}
Hydrofluoric acid	HF	7.2×10^{-4}
Hypobromous acid	HBrO	2×10^{-9}
Hypochlorous acid	HClO	5.6×10^{-8}
Hypoiodous acid	HIO	1×10^{-11}
Nitrous acid	HNO_2	4.5×10^{-4}
Phosphoric acid	H_3PO_4	7.5×10^{-3}
Dihydrogen phosphate ion	H_2PO^-	6.2×10^{-8}
Monohydrogen phosphate ion	HPO_4^{--}	1×10^{-12}
Sulfurous acid	H_2SO_3	1.2×10^{-2}
Hydrosulfite ion	HSO_3^-	1×10^{-7}
Hydrogen sulfide	H_2S	1.1×10^{-7}
Hydrosulfide ion	HS^-	1×10^{-15}
Water	H_2O	1×10^{-14}
Ammonia water	$NH_3(NH_4^+ + OH^-)$	1.8×10^{-5}

[1] Based on Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*.

XII. PERIODIC SYSTEM BASED ON ATOMIC WEIGHTS (SHORT FORM)

Group →	*0*	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*		
Period ↓											
I		H 1.008									
II Short	He 4.0	Li 6.9	Be 9.0	B 10.8	C 12.0	N 14.0	O 16.0	F 19.0			
III Short	Ne 20.2	Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5			
IV Long	A 39.9	K 39.1	Ca 40.1	Sc 45.1	Ti 47.9	V 51.0	Cr 52.0	Mn 54.9	Fe 55.8	Co 58.9	Ni 58.7
		Cu 63.6	Zn 65.4	Ga 69.7	Ge 72.6	As 74.9	Se 79	Br 79.9			
V Long	Kr 83.7	Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Cb 92.9	Mo 96.0	Ma —	Ru 101.7	Rh 102.9	Pd 106.7
		Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9			
VI Long	Xe 131.3	Cs 132.9	Ba 137.4	La 138.9	Hf 178.6	Ta 180.9	W 184.0	Re 186.3	Os 191.5	Ir 193.1	Pt 195.2
		Au 197.2	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209.0	Po 210	—			
VII Incomplete	Rn 222	—	Ra 226.0	Ac 226?	Th 232.1	Pa 231	U 238.1				

Atomic Weights are to the first place of decimals, only

Fourteen Elements are omitted from this classification. These elements together with lanthanum and hafnium are the "Rare Earths." Their symbols and atomic weights are: Ce, 140.1; Pr, 140.9; Nd, 144.3; Il, —; Sm, 150.4; Eu, 152.0; Gd, 156.9; Tb, 159.2; Dy, 162.5; Ho, 163.5; Er, 167.6; Tm, 169.4; Yb, 173.0; Lu, 175.0.

XIII. LOGARITHMS OF NUMBERS

NATURAL NUMBERS	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10

LOGARITHMS OF NUMBERS (*continued*)

NATURAL NUMBERS	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5

LOGARITHMS OF NUMBERS (*continued*)

NATURAL NUMBERS	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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PERIODIC CLASSIFICATION OF THE ELEMENTS BASED ON ATOMIC NUMBERS.

Group / Period	*I*	*II*	*III–B*	*IV–B*	*V–B*	*VI–B*	*VII–B*	*VIII-B*			*I–B*	*II–B*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*
I 2 Elements	H 1																	He 2
II 8 Elements	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
III 8 Elements	Na 11	Mg 12	*Transition Elements*										Al 13	Si 14	P 15	S 16	Cl 17	A 18
IV 18 Elements	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
V 18 Elements	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	Ma 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
VI 32 Elements	Cs 55	Ba 56	57[1] 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85	Rn 86
VII 6 Elements	— 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	93	94	95	96	97	98	99	100	101	102	103	

[1]The elements having atomic numbers 57–71 are: La, 57; Ce, 58; Pr, 59; Nd., 60; Il, 61; Sm, 62; Eu, 63; Gd, 64; Tb, 65; Dy, 66; Ho, 67; Er, 68; Tm, 69; Yb, 70; Lu, 71. These elements comprise the "Rare Earths." They contain the same number of valence electrons and their atoms differ in the number of electrons in the fourth shell.