INTERNATIONAL

1943

	Symbol	Atomic Number	Atomic Weight
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16.0000
Palladium	Pd	46	106.7
Phosphorus	P	15	30.98
Platinum	Pt	78	195.23
Potassium	K	19	39.096
Praseodymium	Pr	59	140.92
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.10
Selenium	Se	34	78.96
Silicon	Si	14	28.06
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.06
Tantalum	Ta	73	180.88
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

INTERNATIONAL CHEMICAL SERIES
LOUIS P. HAMMETT, PH.D., *Consulting Editor*

GENERAL CHEMISTRY

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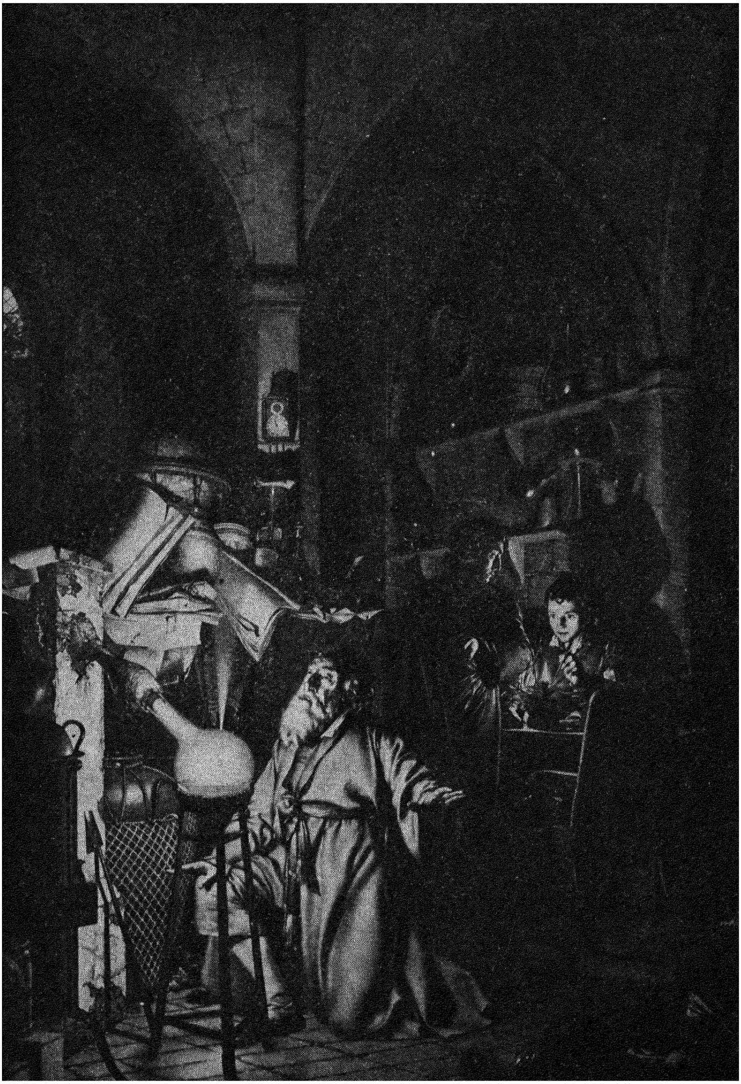

The discovery of phosphorus. (*Courtesy, Fisher Scientific Company.*)

GENERAL CHEMISTRY

by JOHN ARREND TIMM
Professor of Chemistry
Director of School of Science
Simmons College

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PREFACE

Most of the textbooks in general chemistry for college students contain too much material to be taught adequately in a single course. The author, though determined to avoid this fault, has been unsuccessful. There are at least three reasons for this failure. (1) No two teachers will agree on the fundamental topics that must be included or on those items which, although they may not be essential, are needed to add zest to the course and inspiration to the students. Hence a variety of such topics has been discussed so that any resourceful teacher may find and teach what he wants and omit what he does not. (2) If the students are to profit by their study of the text, explanations of important theoretical principles cannot be concentrated to a minimum of words. The author must talk to the reader as he would to his own students, or his efforts will be wasted. Hence the size of this book is in large part the result of its conversational style, which the author hopes will make the task of preparing assignments less arduous to the student. (3) The author believes that new ideas seldom are absorbed on first exposure. Repetition, in which the treatment is progressively quantitative, is needed to fix fundamental principles in the student's mind. For this reason, such topics as atomic structure and oxidation-reduction are introduced early in the text. Later, the introductory discussion is amplified and, finally, a chapter is devoted to a thorough treatment of each of these topics.

Although the importance of atomic structure and of the manner in which atoms combine is unquestioned, in an elementary course this knowledge is rarely applied to topics other than the theory of ionization. In this text the nature of the forces associated with the various types of ion combination is discussed and applied in the explanation of the physical properties of substances that the student meets in the laboratory. In general, an attempt has been made to show the student how the theory may be and has been applied to the solution of practical problems. At a time when results count and theorists are considered impractical, it is well to emphasize how, at least in the physical sciences, theory has made possible many of the spectacular achievements of chemistry in the war effort.

The author wishes to express his gratitude to his colleagues, Prof. Allen D. Bliss, Ina M. Granara, Raymond E. Neal, and Harriet A. Southgate for their many helpful suggestions; to Miss Katherine V. Lally for her help in preparing the manuscript; and again to Dr. Bliss for his help in correcting the proof. He is indebted to those who have taken time to provide the photographs with which this text is illustrated.

JOHN A. TIMM.

BOSTON, MASSACHUSETTS,
August, 1944.

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GENERAL CHEMISTRY

CHAPTER ONE

INTRODUCTION

John and Jane Doe do not have to be impressed by the achievements of applied chemistry. Today in the midst of a global war this is especially true. The Japanese capture our natural source of supply of rubber, and the chemist comes to the rescue. From petroleum, coal, and alcohol there emerges synthetic rubber. Our bombers see through transparent plastics so tough that machine guns are fastened directly to their surfaces. Quinine, with which to combat the malaria of the tropics, becomes scarce, and synthetic atabrine is produced from the chemistry laboratories to take its place. Nitric acid with which to make explosives and nitrogeneous fertilizers to ensure our supply of food is literally plucked from the air. When our soldiers are wounded, sulfa drugs protect their lives. So spectacular have been the contributions of chemistry to the welfare of the nation that the blind faith in the ability of the chemist to solve present and future difficulties is embarrassing. Ask John Doe what will happen when our petroleum resources are exhausted, and he will reply to the effect that the chemist will make gasoline out of water or coal or something. And the chances are that he is right.

1. The Value of Theory.—What John Doe does not realize is the value of the theories of chemistry in the solution of its problems. To him, a theorist is an impractical soul who never comes down to earth to solve practical problems. To the chemist, theories are a map to lead the way to successful solutions of problems. Without them, his experiments would be unguided, hit-or-miss attempts made with a vain hope that one might perchance be successful.

2. The Scientific Method.—The scientific method is the result of the application of a peculiar intellectual attitude to the solution of a problem. The problems need not always be scientific; for those of business, of law, and of government may be solved by methods as scientific as those which are being employed in determining the nature of the electron. No one procedure can be identified as the scientific method; for each problem may suggest a different method of approach for its solution to different individuals. Indeed, there is no major problem in any branch of science today which is not being investigated by many scientists, each of whom is attacking it from a slightly different angle. To its final solution, each investigator will have contributed his share, and the work of the individual will be fitted into the complete mosaic of the solution.

Although it is true that the application of the scientific method may vary with the problem and with the individual who seeks its solution, nevertheless, in its broader aspects it is characterized by a distinctive type of procedure. The first step in applying the scientific method to the solution of a problem involves the *collection of data—the investigation of the facts.* These are the experiences that make a direct impression on our senses, that can be described and measured, but that cannot be changed to suit our inclinations. They must be such that everyone who has proper facilities to investigate them will agree as to their existence and description.

The accuracy and the completeness with which a given fact is described will, of course, vary with the investigator, with his equipment, and with the nature of the problem under investigation. Hence the great importance of independent measurements of the same fact by several investigators. Sometimes, different methods of measurement may be applied, and if their results are identical, we are the more certain of the description of the fact. The solution of certain problems does not require so high an accuracy as others. In the early history of a branch of science, the accuracy with which its facts are described is usually low. At this stage, when investigators are few in a new field of research, it is neither necessary nor expedient that time be taken to attain the highest accuracy. Progress is faster at first if description is more qualitative than quantitative. But as the science grows, the accuracy of its descriptions increases. Many great discoveries have been the result of an increase in the accuracy of measurement. When Lord Rayleigh measured the density of nitrogen prepared by heating ammonium nitrite and that obtained from the air, he found a difference in density amounting to only 0.5 per cent. But the accuracy of his measurements was within 0.02 per cent. The discovery of the inert gases of the atmosphere was the result (37-2).

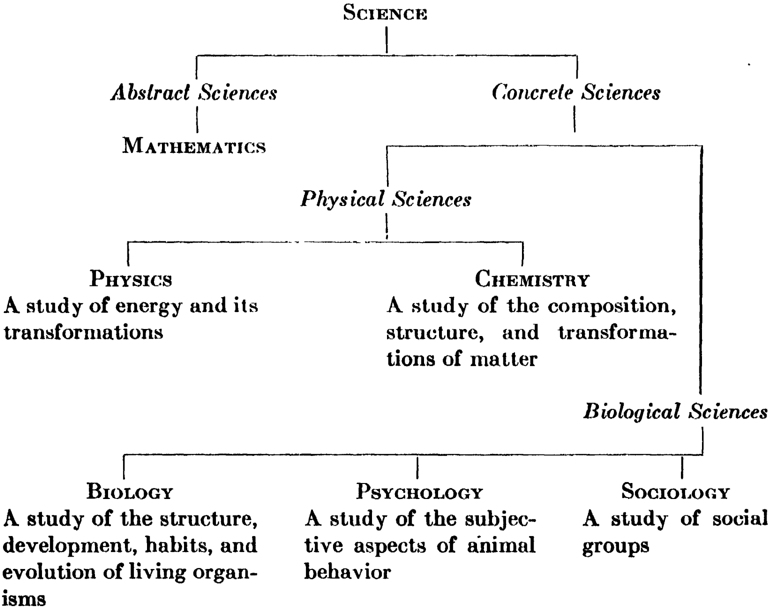
The next step in the application of the scientific method involves the *classification of the facts.* This is done by discovering a resemblance between a number of isolated facts. When this similarity is found, a statement of it is a *law* of nature. For example, when the pressure is doubled on a sample of hydrogen gas, its volume is halved. All other gases behave in the same way. This resemblance is stated as Boyle's law, *viz.*, the volume of a gas is inversely proportional to the pressure. Since *a law is a statement of a resemblance between facts*, a law itself is a fact.

The laws of nature usually suggest a *theory*, or hypothesis, by which they may be explained. These theories are imaginary pictures, or thought models, of the structure of matter and of mechanisms which explain changes in matter. These in a sense explain the facts as summarized by the natural laws. For example, the kinetic theory of matter, which postulates it to be composed of myriads of submicroscopic particles in rapid motion, suggests a plausible explanation of gas pressure and of Boyle's law. Finally, every theory of science suggests experiments by which it may be tested. It suggests new things which should be facts if the theory is true. Experiments can then be carried out to ascertain whether the things suggested by the theory are actually true or false. If every piece of evidence thus obtained substantiates the predictions of the theory, its validity is generally accepted. Many times, however, the facts as revealed by experiment are not in accord with the predictions of the theory. In this case the theory must be discarded. More frequently, experimental testing suggests modifications of the original theory.

3. The Classification of the Sciences.—The classification of the sciences is a matter of convenience only. The danger of such a classification from an educational point of view lies in the fact that the student loses sight of the unity of all scientific knowledge and of the interrelatedness of its various branches. He is apt to consider science as if the facts and theories of its various branches were wrapped up in bundles and as if their contents were entirely unrelated. This attitude is as absurd as that of the child whose knowledge of his country has been confined to the maps of the school geography and who expects to find a neighboring state colored red when he crosses its boundaries. Physics and chemistry, for example, are very closely related branches of science. Certain aspects of the material universe are studied by both physicists and chemists. Their points of view and their methods of attack are usually dissimilar, but in the end their conclusions must be the same. In this text on chemistry, you will find much of physics; yet the transition from one science to the other will, in most cases, be so natural that it will not be noted. Nor is it our intention to emphasize this transition.

Karl Pearson in his "Grammar of Science" first divides science into the abstract and the concrete sciences. The abstract sciences are methodological disciplines such as logic and mathematics. The concrete sciences deal with phenomena that can be investigated through the senses. These are further classified as physical or biological. The physical sciences, physics and chemistry, deal with inorganic phenomena, *i.e.*, with the nature of matter and energy. The biological sciences, biology, psychology, and sociology, study organic phenomena.

TABLE 1.—THE CLASSIFICATION OF THE SCIENCES



PHYSICS
A study of energy and its transformations

CHEMISTRY
A study of the composition, structure, and transformations of matter

BIOLOGY
A study of the structure, development, habits, and evolution of living organisms

PSYCHOLOGY
A study of the subjective aspects of animal behavior

SOCIOLOGY
A study of social groups

Each of these fundamental sciences is further subdivided. For example, biology can be divided into *botany*, the study of plants, *zoology*, the study of animals, and *protistology*, the study of microscopic organisms. There exist also derivative or synthetic sciences which use the methods of some of the fundamental sciences to investigate a specific problem. *Geology*, the study of the structure, structural changes, and history of the earth, is an example of this type. Finally, there are the applied sciences such as *medicine*, *engineering*, and *agriculture*.

4. The Scope of Chemistry.—Chemistry is that branch of science which has the task of investigating the materials out of which the universe is made. It is not concerned with the forms into which they may be fashioned. Such objects as chairs, tables, vases, bottles, or wires are of no significance in chemistry; but such substances as glass, wool, iron, sulfur, and clay, as the materials out of which they are made, are what it studies. Chemistry is concerned not only with the composition of such substances, but also with their inner structure. Further, these materials are constantly undergoing change in nature: iron rusts, wood decays, sugar ferments, coal burns, limestone rock is eaten away by water, and living organisms digest their foods and build up their structures. Chemistry investigates such changes—the conditions under which they occur, the mechanism by which they take place, the new substances that are formed as their result, and the energy that is liberated or absorbed by them. Chemistry also studies the way in which these and similar changes can be carried out in the laboratory or on a larger scale in the chemical plant. As a result of investigations along these lines, chemistry has found how metals can be extracted from their ores; how impoverished fields can be made fertile again; and how the materials that are found in nature can be converted into thousands of new substances to help feed the race, to cure the sick, and to provide such comfort and even luxury for the common man as was not enjoyed by the wealthy of an earlier generation.

5. Scientific Literature.—Once new facts have been discovered or new theories postulated by a scientific investigator, the results must be published so that they may become the common knowledge of all scientists working in the same field of research. Scientific journals exist for this purpose, many of which are published by scientific societies. In this country, the American Chemical Society, whose membership is now nearly 35,000, publishes three journals: *The Journal of the American Chemical*

Society, *Industrial and Engineering Chemistry*, and *Chemical Abstracts*. In the first of these, papers on research in pure chemistry are published. In the second, the results of research in applied chemistry are reported. In *Chemical Abstracts*, the papers that have appeared in scientific magazines all over the world are abstracted. The use of this abstract journal enables the investigator to keep in touch with what has been published in his field of interest. If a given abstract is of particular importance to him, he may then turn to the original paper in the journal in which it was published. In certain other types of journals, such as *Chemical Reviews*, the recent literature in certain fields is reviewed by outstanding authorities in these fields. Further, from time to time, scientific monographs are published in which are gathered the researches of many investigators interpreted by the author of the monograph. Finally, in textbooks the more fundamental aspects of a certain branch of science are presented to the student.

6. References.—It is important for you to learn how to look up the references to scientific literature which you will find in this and other texts. The name of the journal is given first in an abbreviated form, followed by the volume in bold face type, then by the page number, and finally by the year of publication. For example, the reference,

J. Am. Chem. Soc., **51**, 1119 (1929)

means *The Journal of the American Chemical Society*, volume 51, page 1119, published in 1929. You will find the scientific journals, bound by volume, in your college library or in that of the chemistry laboratory. You will find a list of the abbreviations of their names in the Appendix of this text.

Form the habit of looking up the papers that interest you when you are referred to them in the chapters which follow. Nothing will add more to your enjoyment of a course than voluntary collateral reading. Nothing will be a greater stimulant to your intellectual curiosity.

EXERCISES

1. Define the terms fact, law, and theory.
2. What is the scope of chemistry?
3. Make a brief abstract of the paper to be found in *J. Chem. Education*, **20**, 508 (1943).

READING REFERENCES

Thomson: "Introduction to Science," Henry Holt and Company, Inc.

Lucretius: "De rerum natura," translated by W. E. Leonard (Everyman's Library), E. P. Dutton & Company, Inc.

Heimerzheim: Some hints on how to study, *J. Chem. Education*, **20**, 508 (1943).

CHAPTER TWO

MATTER

Since chemistry is the science that studies matter, a clear statement of what this term means would be useful. However, matter is one of the few fundamental concepts along with those of energy, of space, and of time which are difficult to define in a satisfactory manner; for definitions should be stated in simpler, more fundamental terms. The dictionary defines it as "that of which anything is composed," an adequate definition unless one is skeptical enough to look into the meaning of "anything."

1. The Description of Matter.—Granted that matter is an ultimate reality for which there can be no satisfactory definition, nevertheless, it possesses properties by which it makes its presence known and in terms of which it may be described. Most of these properties depend on the conditions to which a given sample of matter is subjected. Thus the temperature determines to a large extent whether water is a solid, a liquid, or a gas. Artisans may fashion wood, glass, or plastics into many useful forms. The color of iron changes when it is heated, and dyed fabrics fade in the sun. But there is one property of matter that does not change however many may be the changes in its other properties. This property is its *mass*, or the quantity of matter. In a closed system, *i.e.*, one from which matter does not escape and to which additional matter is not added, the total mass of the enclosed materials does not change, regardless of other changes that may occur in the system.

2. Weight.—The mass of a given sample of matter may be measured by its weight. This, in turn, depends on the tendency of any two masses in space to move toward each other as if they were impelled by a force acting through the distance between. This force of gravity is directly proportional to the mass of each object but varies inversely as the square of the distance between. When an object is weighed, the magnitude of the force of gravity acting between the mass of the earth and that of the object is measured in terms of arbitrarily defined units such as the pound or the gram. Naturally, the weight of the object will depend upon the distance that separates the object from the earth's center. An object will weigh slightly less at the top of a high mountain than at sea level. Thus although the mass of an object, *i.e.*, the quantity of matter in it, is constant, its weight will vary depending on its position relative to the earth. The mass of a given material is the same in interstellar space as it is at the earth's surface, but its weight at this great distance is practically zero. Since we shall probably never be weighing objects in interstellar space and since the relatively small differences in altitude on the earth's surface make little difference in the weight of an object, we may consider the terms weight and mass as synonymous for our purposes.

3. Elements.—The bewildering array of materials of which the universe is composed made the task of classification, which the science of chemistry faced, a difficult one. Thousands of substances are mixed in such confusion that it must have seemed, to those who first faced the task, that some malicious giant had stirred them up with a gigantic stick. Here and there small samples of a homogeneous material could be collected and described; but the infant science of chemistry could make little progress until the idea came that a relatively few, ultimately simple substances exist of which all that is material is composed. These substances are the elements. The first clear definition of what is meant by an element was given by Robert Boyle in 1661. In the language of the time he wrote, "I mean by elements . . . certain primitive and simple, or perfectly unmingled bodies; which not being made of other bodies or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved." *An element is a substance that cannot be decomposed into nor built up from simpler substances.* A given element is composed entirely of that element. Sulfur is nothing but sulfur, and iron is 100 per cent iron. It follows that any sample of an element must be homogeneous.

To prove that a given substance is an element is not easy. Many substances when heated decompose into simpler substances and, therefore, cannot be elements. However, the fact that a given substance does not decompose when subjected to the highest attainable temperature does not prove that it is an element. Lime, a compound of the elements calcium and oxygen, will not decompose in the flame of an oxyacetylene torch. Yet it can be prepared from its constituent elements. Many substances were at first considered elements until means were discovered by which they could be decomposed or by which they could be synthesized.

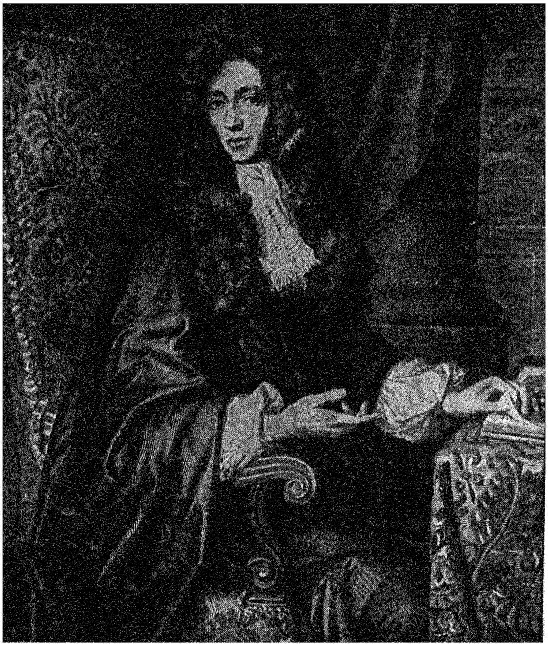


FIG. 1.—Robert Boyle. (*Courtesy of Journal of Chemical Education.*)

4. The Number and Abundance of the Elements.—Ninety-two elements are known today. We shall see later (24-2) that these are related in such a manner that it is possible to say with conviction that these 92 are truly elements. A table of the known elements may be found inside the rear cover of this book.

The 92 elements are not found in equal abundance in nature. F. W. Clarke of the Geophysical Laboratory has made an estimate, given in Table 2, of the relative abundance of the elements in the earth's crust, in the oceans and other bodies of water, and in the atmosphere. The importance of an element does not necessarily depend, however, on its abundance. Thus carbon comprises less than 0.1 per cent of the total, but without this element no life could have developed on the earth, since it is present in all organic compounds.

TABLE 2.—COMPOSITION OF THE EARTH'S SHELL

Element	Per cent	Element	Per cent
Oxygen	46.43	Magnesium	2.09
Silicon	27.77	Titanium	0.63
Aluminum	8.14	Phosphorus	0.13
Iron	5.12	Hydrogen	0.13
Calcium	3.62	Manganese	0.10
Sodium	2.85	All others	0.39
Potassium	2.60		

5. Metals and Nonmetals.—It has been found convenient to classify the elements as metals or as nonmetals. The exact basis of this classification cannot be explained until later, since it depends on the character of the compounds that an element forms. However, the metals, in general, are recognized by their characteristic luster, their high density, and the ease with which they conduct electricity. The names of the common metals are well-known to everyone, *e.g.*, iron, tin, lead, zinc, copper, mercury, silver, and gold. These were discovered early, and their useful properties make them familiar. The less well-known metals were in general discovered later and fortunately after it had been agreed to give them names ending in "um." Thus although scandium, rhodium, and germanium are probably new to the reader, they are easily recognized as metals. The element helium is the one exception to this rule as it is a nonmetal. It should have been called helion. However, since it was discovered in the sun's chromosphere long before its discovery on this earth, we may forgive the scientists who named it originally.

The nonmetals are, in general, less familiar to the average man than the metals. True, he realizes that he has oxygen in his lungs and carbon in his coal bin and perhaps even iodine in his medicine cabinet. Sulfur recalls in a vague way matches, fumigation, and spring tonics to him. If the First World War had not occurred, he would never have heard of chlorine. This lack of knowledge of the nonmetals is due to the fact that their properties, when uncombined with other elements, are not such as to render their use at all common. They are important chiefly as raw materials from which their more directly useful compounds can be prepared. The metals, however, possess attributes that have made them useful and, therefore, familiar. Iron, copper, zinc, lead, and, since Pearl Harbor, especially aluminum and tin are metals for which anyone can name at least half a dozen uses.

6. Compounds.—The material universe is made up of 92 elements each of which is endowed with its own characteristic properties. It must not be assumed, however, that the properties of any sample of matter are a composite of those of the elements of which it is composed. Elements combine with one another to form substances called compounds. Further, each compound is homogeneous even under a microscope, *i.e.*, its properties are the same throughout its entire mass. We are thus unable to distinguish particles of the constituent elements once they have combined to form a compound. More surprising, the properties that characterize the compound are not those of the free elements before combination. The element sodium is a soft metal that looks very much like silver. It rusts very rapidly and enters into a chemical change with water with explosive violence. These are some of the properties of this metal in the free state, *i.e.*, when it is uncombined with other elements. Chlorine, a nonmetal, is a greenish-yellow poisonous gas. A piece of sodium thrown into an atmosphere of chlorine burns with explosive violence, and a dense white smoke is formed which proves to be common table salt. Salt is a compound of the elements sodium and chlorine, and yet its familiar properties are not those which the free elements possess before they combine. Water is a compound of hydrogen and oxygen. Both of these elements in the free state are gases. Hydrogen is highly inflammable, whereas oxygen supports combustion and life. Contrast these properties with those of their compound.

7. Law of Constant Composition.—*In every pure sample of a given compound, the elements are present in the same proportions by weight.* This is the law of constant composition, or of definite proportions as it is sometimes called. When various samples of the same compound are analyzed to determine the percentages by weight of the constituent elements, the result is always the same no matter from what sources the compound may have been obtained and in what way it may have been prepared. Water from the melted snow and ice of the north, from a river in the tropics, from an ocean, or from a puddle in our back yard, provided it has been properly purified, will always be composed of 11.19 per cent of the element hydrogen and 88.81 per cent of the element oxygen by weight. Thus 10 g. of pure water contains 1.119 g. of hydrogen and 8.881 g. of oxygen. This must mean that whenever hydrogen and oxygen combine to form water they do so invariably in the same proportions by weight. Any attempt to persuade these elements to form water in other than these proportions meets with failure. If, for example, a mixture of 1.119 g. of hydrogen and 20.000 g. of oxygen is ignited in the hope of obtaining 21.119 g. of water, when stock is taken after the noise of the explosion is over, only 10.000 g. of water will have been formed and 11.119 g. of uncombined oxygen will be left over.

$$\underset{(1.119\text{ g.})}{\text{Hydrogen}} + \underset{(8.881\text{ g.})}{\text{oxygen}} \rightarrow \underset{(10.000\text{ g.})}{\text{water}}$$

but

$$\underset{(1.119\text{ g.})}{\text{Hydrogen}} + \underset{(20.000\text{ g.})}{\text{oxygen}} \rightarrow \underset{(10.000\text{ g.})}{\text{water}} + \underset{(11.119\text{ g.})}{\text{oxygen}}$$

The law of constant composition is of tremendous significance; for not only does it vastly simplify the study of matter, but it also gives us an insight into the structure of matter, as we shall see in the next chapter.

8. Definition of a Compound.—*A compound may now be defined as a form of matter every sample of which is homogeneous and composed of two or more elements combined in fixed characteristic proportions by weight.*

9. Combination of Elements.—The total number of compounds that 92 elements might form by combining with one another is extremely large, especially since compounds may be made up of any number of elements. Actually, however, and perhaps fortunately for chemistry students, only a relatively small fraction of the number theoretically possible is capable of existence. In the first place, no element will combine with every other element. The inert gases, helium, neon, argon, krypton, xenon, and radon, form no compounds whatsoever. If all elements were equally unsociable, chemistry would be a simple subject to study. Metals form compounds with nonmetals more readily than with other metals, and vice versa. Compounds of more than three elements are rare. If it were not for compounds of the element carbon, the known compounds of the other elements would number only several tens of thousands. The compounds of this element, however, are more numerous than those of all the other elements combined. Several hundred thousand are known, and new ones are being prepared daily. These are the so-called organic compounds, each of which is either found in living organisms or related to those so found. No chemist, no matter how expert he may be, attempts to remember the names and properties of any but a small fraction of the total number of known compounds. Reference books are available in which they may be found.

10. Substances.—We shall use the term substance to refer to either an element or a compound. Each substance has its own characteristic properties that determine its usefulness. The ability to create new substances, many of which may be of the greatest service to mankind, is one of the most interesting functions of chemistry. Sometimes, indeed, compounds that exist in nature may be more cheaply prepared in the chemical laboratory or plant than they can be extracted from natural sources.

11. Mixtures.—Samples of matter as they occur in nature rarely consist of a single substance. Chance operating through the history of the planet has done a thorough job of mixing its ingredients. Frequently, a mixture may be recognized at once because it is heterogeneous, *i.e.*, particles of dissimilar characteristics can be recognized. Sometimes the individual grains are so small that the mixture appears homogeneous to the eye, but under the microscope its heterogeneous character is revealed. Not all mixtures, however, are heterogeneous. For example, when sugar and water are brought together, the resulting mixture is homogeneous even under an ultramicroscope. Such *homogeneous mixtures are called solutions.*

A mixture may be, therefore, either homogeneous or heterogeneous, but it is always made up of more than one substance. Further, these may be mixed in any proportions if the mixture is heterogeneous. Sand, a compound of silicon and oxygen, and the element sulfur may be mixed together in any proportions desired. In the case of certain solutions, there is a limit to the solubility of one substance in another. Thus at 20°C. no more than 204 g.

of sugar will dissolve in 100 g. of water. However, more dilute sugar solutions of any desired composition may be prepared. *The composition of a mixture is*, therefore, *variable.* In this respect, it differs from a pure substance.

Each of the component substances in a mixture retains its identity and, therefore, its characteristic properties. Hence the properties of a mixture are a composite of those of the substances of which it is composed.

SUMMARY

The following definitions are given not with the idea that they should be memorized, but to emphasize the care that must be taken to include in each case at least the minimum information needed to define the term properly. We feel that you should understand and be able to state in your own words the significance of a term or a law rather than to resort to your memory.

Matter is that of which anything is composed.

The *mass* of an object is the quantity of matter of which it is made.

The *weight* of a sample of matter is a measure of the force of gravity acting between its mass and that of the earth.

An *element* is a substance that cannot be decomposed into nor built up from simpler substances.

A *compound* is a substance composed of two or more elements combined in fixed proportions by weight.

A *mixture* is composed of two or more substances that have retained their identity. Its components may be mixed in any desired proportions.

A *solution* is a homogeneous mixture.

EXERCISES

1. What is meant by homogeneous and heterogeneous?
2. What kinds of matter are homogeneous?
3. What is the composition of water?
4. Are liquid water and solid ice composed of the same substance?
5. Is milk a pure substance or a mixture?
6. Give at least one example of an uncombined element, a compound, and a solution found in every motorcar.
7. Name five metals and five nonmetals to be found in your home.
8. State the law of constant composition.

9. How could you distinguish a mixture of iron and sulfur from their compound ferrous sulfide?

10. Classify the following materials: diamond, granite, soil, sugar, cotton, tincture of iodine, molasses, salt, chromium, and brass.

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CHAPTER THREE

ATOMS AND MOLECULES

The system of classification of matter, which was outlined in the last chapter, exerted a tremendous influence on the development of the science of chemistry. More rapid progress has been made since Boyle's definition of an element than in the millenniums of man's history which preceded. It brought order out of a chaos of seemingly unrelated materials. Boyle has been called and is rightly considered the father of chemistry.

1. The Structure of Matter.—The classification of matter into substances, which are either free elements or compounds of elements, and into mixtures of substances suggests certain questions the answers to which are of fundamental significance. Why does each substance possess the properties with which it is endowed? Why are sulfur and salt solids under ordinary conditions? Why are oxygen and carbon dioxide gases? Why does sulfur melt at a much lower temperature than salt? Why do metals conduct electricity whereas nonmetals, in general, do not? Why do elements combine to form a given compound in fixed proportions by weight? These and countless other questions remained unanswered until theories were developed as to the structure of matter in terms of which its properties could be explained.

One of the favorite pastimes of the Greek philosophers was to speculate as to whether matter is continuous or discontinuous. If it be continuous, then a grain of matter may be divided into smaller pieces ad infinitum. Each portion, no matter how small, would possess the same essential properties as the original grain. There would exist no ultimately small particle of that kind of matter. If such a theory were adopted, its usefulness would be extremely limited. If every particle of sulfur, no matter how small, is a yellow solid that melts at a certain temperature, then sulfur is a yellow solid because it is a yellow solid. Such a useless theory has no right to exist. On the other hand, if there be an ultimately small particle of sulfur that possesses very few but extremely significant properties and if all the characteristics by which we recognize the element sulfur can be explained in terms of these few fundamental properties, then we shall have an extremely useful theory.

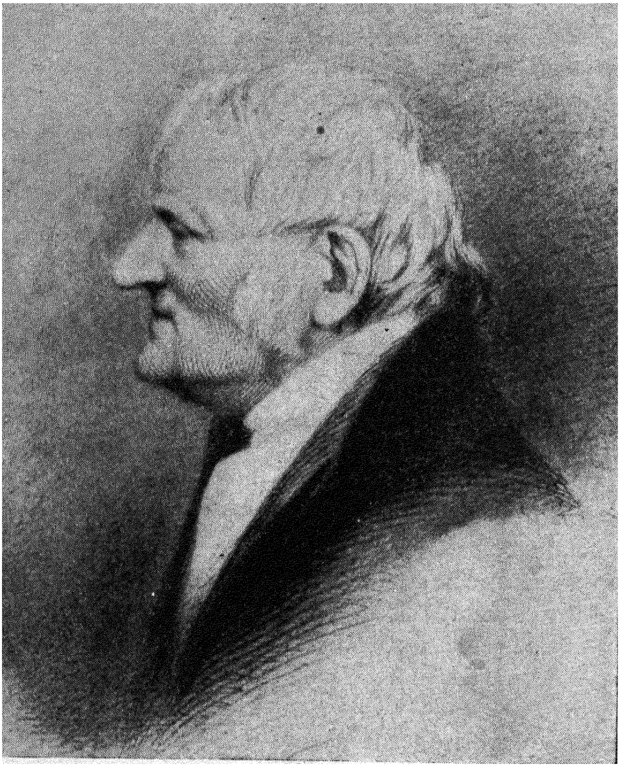

FIG. 2.—John Dalton. (*Courtesy of Journal of Chemical Education.*)

In this chapter, we shall try to give only a survey of some of the essential theories of the structure of matter without attempting to show in detail how each theory is derived from and explains the known facts. A more rigorous treatment will come later. However, an early knowledge of these theories will prove exceedingly useful.

2. The Atomic Theory.—The Greek philosophers were divided into two schools of thought as to the ultimate nature of matter. One group, of which Aristotle (384–322 B.C.) was a leading proponent, believed that matter is continuous, whereas the other school, led by Leucippus and Democritus (460–362 B.C.), held that it is composed of ultimately small particles called atoms which are "indivisible, indestructible, and existent from eternity to eternity." To neither school was available a knowledge of the facts sufficient to establish the essential validity of the atomic theory.

Our modern atomic theory we owe in large measure to William Higgins, an Irishman, and to John Dalton, a Manchester schoolmaster. The former in 1789 and the latter in 1808 based the derivation of this theory on the law of constant composition which had just been established by Proust. The following statement of the theory is essentially that of Higgins and Dalton.

THE ATOMIC THEORY

1. An atom of an element is the smallest particle of that element which can exist.
2. There are as many different kinds of atoms as there are elements.
3. The atoms of a given element are alike in every respect, *e.g.*, each has the same weight.
4. In each of the molecules of a given substance, there are the same number of atoms of each of the elements of which the substance is composed.

Each of these postulates needs further comment. The first statement does not imply that an atom is the smallest particle that can exist or that an atom is indivisible. As a matter of fact, the atoms of the elements have an internal structure built up of particles more fundamental than atoms. These subatomic particles, the electron, the proton, and the neutron, are, however, the same in whatever kind of atom they may be found. Hence the sulfur atom, for example, is the smallest particle of sulfur that can exist despite the fact that it is composed of subatomic particles. For the time being, we need not consider atomic structure further.

Postulates 2 and 3 will have to be modified later (29-1) when we consider isotopes. The modification will be more in the nature of an extension and will not affect the essential validity of these postulates.

3. Molecules of Compounds.—Postulate 4 introduces a new term, molecule. Before attempting a definition, let us consider informally what this term implies. When elements combine, the resulting compound is homogeneous. We are unable to see the dissimilar particles of the constituent elements. Presumably, these particles are the atoms that are far too small to be seen. In order to explain the law of constant composition, we may assume that a given compound is composed of molecules, each of which is the smallest particle of the compound which can exist. Further, we may imagine that each of the molecules of a given compound is composed of the same number of the same kind of atoms. Thus each water molecule is made up of two hydrogen atoms and one oxygen atom. Since all hydrogen atoms are identical and have the same weight and since the same is true for all oxygen atoms, it follows that the ratio by weight of hydrogen to oxygen in water is fixed.

As a matter of fact, it is known that every oxygen atom is very nearly sixteen times as heavy as every hydrogen atom. Hence two weights of hydrogen are combined with sixteen of oxygen in every water molecule. Thus hydrogen makes up $\frac{2}{18}$, or 11 per cent, and oxygen $\frac{16}{18}$, or 89 per cent, of the weight of water. The atomic theory explains very nicely why elements are combined in a given compound in fixed proportions by weight.

4. Molecules of Elements.—Postponing the proof until later, there exists sufficient evidence not only that atoms of different elements are found combined in molecules of compounds, but that molecules of elements exist in which are combined atoms of that element only. The element oxygen, which exists as a gas when uncombined, is made up of molecules each of which is a pair of oxygen atoms. Similarly hydrogen, nitrogen, and chlorine molecules are diatomic. In these gases, each diatomic molecule may be pictured as an island separated by nothing but empty space from its fellow molecules. Molecules of the element sulfur exist as clusters of eight atoms. Not all kinds of atoms are equally sociable. Mention has been made of the fact that the inert gases, helium, neon, argon, krypton, xenon, and radon, form no compounds. Atoms of these elements refuse to combine not only with those of other elements, but also with one another. Their molecules are single atoms.

5. The Size of Molecules.—Molecules are exceedingly minute, much smaller than the smallest particles that the high-powered microscope, working under the best conditions, can hope to resolve. Many attempts have been made to determine molecular diameters by indirect means. Such attempts have all given results which indicate that the approximate diameter of an average molecule must be about 3×10^{-8} cm.[1] This is about 100,000 times smaller than that of the smallest particle visible under a microscope (3×10^{-3} cm.). It is about 10,000 times too small to reflect rays of visible light. Hence molecules can never be resolved by optical microscopes. By means of the electron microscope, however, photographs have recently been made of the giant protein molecules of disease-producing viruses. Such giant molecules, however, are of organic compounds of great complexity which are nearly a million times as heavy as the water molecule.

6. Molecules and the States of Matter.—There are as many different kinds of molecule as there are substances—molecules of uncombined elements and molecules of compounds. The molecules of a substance are the structure units, the "islands in space," of the states in which it may exist. *There are three such states: gaseous, liquid, and solid.* The state in which a substance exists is determined in large measure by the temperature which, in turn, determines the velocity at which its molecules move—the higher the temperature, the greater the molecular velocity. This molecular motion tends to stir up the molecules and to prevent close packing. Dead sardines can be packed close together, but live, wiggling fish need elbowroom. If molecules were not in motion, they could be packed in actual contact like dead sardines in a can. Molecular motion tends to keep the molecules apart. The higher the temperature, the greater will be the average distance between them under a given set of conditions. Of course the molecules in their random movements will collide with one another, but they will rebound with no loss in kinetic energy. At a given instant throughout the mass of a given object, a certain fraction of its molecules may be in contact, in the act of colliding, but the *average* distance, when all the molecules are considered, is a function of the temperature.

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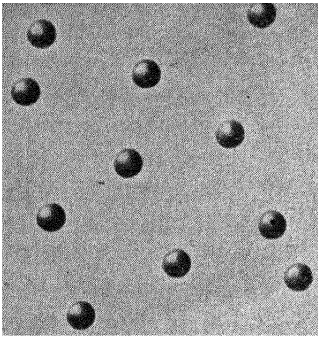
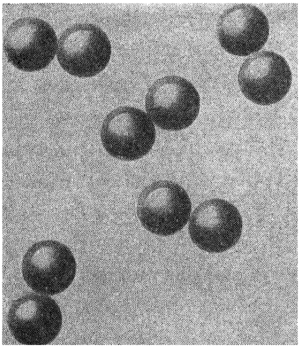
[1] This notation, by which very small or very large numbers are expressed as powers of 10, is explained in the Appendix.

There exist between molecules forces of attraction, *van der Waals forces*, which tend to oppose the "stirring-up effect" of molecular motion. The strength of these forces depends on the kind of molecules between which they are acting. Thus they are stronger between molecules of water than between those of oxygen. Between sugar molecules, they are still stronger. The relative strengths of the tendencies to move together as determined by the van der Waals forces and to move apart owing to molecular motion (temperature) determine whether the substance is a gas, a liquid, or a solid under a given set of conditions. Thus sugar is a solid, water a liquid, and oxygen a gas, under normal conditions.

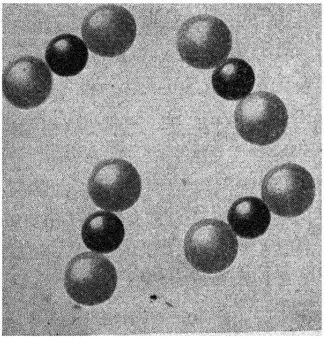
7. The Gaseous State.—In a gas, the molecular motion has gained the upper hand so that a given gas sample has no definite volume but expands to fill uniformly the volume of any container in which it is placed. Unless the gas is compressed into a very small volume, the average distance between its molecules is very great as compared with their dimensions. Study the illustrations of the gases helium, oxygen, and carbon dioxide (Fig. 3). These are not photographs but drawings to illustrate the mental picture that the theory gives us of their structure. They are not



Helium



Oxygen



Carbon dioxide

FIG. 3.—Mental pictures of the structure of three gases given by the kinetic-molecular and the atomic theories.

drawn exactly to scale; for at normal pressures the average distance between molecules in a gas is about ten times greater than the molecular diameter. Note that each molecule of helium is a single atom, that each oxygen molecule consists of a pair of oxygen atoms, and that each molecule of the compound, carbon dioxide, consists of one carbon and two oxygen atoms.

8. The Liquid State.—A given mass of liquid has a definite volume and shows a free surface in a container of greater volume.

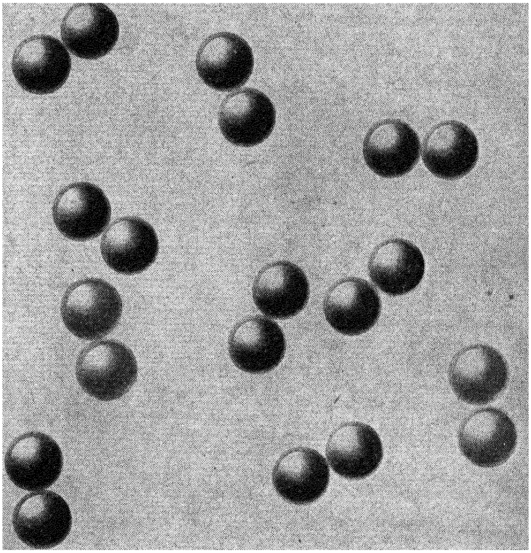


FIG. 4.—Eight nitrogen and two oxygen molecules in a submicroscopic sample of the gaseous mixture, air.

The forces of intermolecular attraction in a liquid exert a greater influence than in a gas, especially since the molecules are closer together. All forces increase rapidly as the distance is reduced. The molecules are in motion. Indeed their kinetic energy is just as great as that of the molecules of a gas at the same temperature. However, the forces of attraction between the molecules of a substance that is a liquid are characteristically greater than between those of a gas at the same temperature. Since the average distance between the molecules of a liquid is much less, the density is correspondingly greater.

9. Solids not only have a definite volume but are characterized by a regular geometric shape. A solid is composed of crystals. Its molecules are frozen into a regular space pattern, or crystal lattice. Each molecule occupies a position in a regular array of molecules. It must not be assumed, however, that the molecules are at rest, but rather that their motion is one of vibration about fixed points in the crystal structure. The kinetic energy due to this vibratory motion becomes greater as the temperature is raised and the molecules demand greater elbowroom. The fact that solids expand when heated is evidence of this demand.

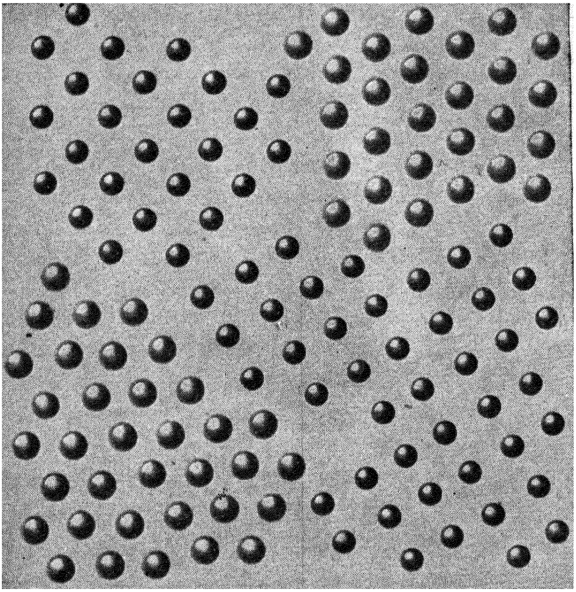


FIG. 5.—A mixture of two solids.

10. Molecules in Mixtures.—When substances are mixed, their molecules do not lose their identity. There is no such particle as the molecule of a mixture. In a true solution, *i.e.*, a homogeneous mixture, each particle is a single molecule. Thus our atmosphere is essentially a solution of nitrogen and oxygen. There are four times as many molecules of nitrogen as of oxygen (Fig. 4). You will fail to find a "molecule of air." In a heterogeneous mixture, in which dissimilar particles may be seen, each particle of a component is made up of an aggregate of molecules of that component (Fig. 5).

In this chapter we have tried to give you a general survey of our ideas about the structure of matter. Many details have been omitted, and we shall have to return to study them more thoroughly later on.

EXERCISES

1. How does the atomic theory explain the law of constant composition?

2. Is the following statement one of fact or of theory? An atom of an element is the smallest particle of the element that can exist.

3. Draw a picture of your concept of the molecules to be found in a solution of iodine in water.

4. If the ratio of the weights of the water molecule to that of the oxygen molecule is 9:16, what weight of water will contain the same number of molecules as there are oxygen molecules in 32 g. of oxygen?

5. What are van der Waals forces?

6. What is the effect of a rise in temperature on molecular motion?

7. What are the three states of matter?

8. Why does mercury rise in a thermometer tube when the temperature rises?

9. Give one reason for believing that the molecules in a solid are not at rest.

10. In terms of the theory of the molecular structure of matter, explain what happens when a solid is heated to the temperature at which it melts.

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CHAPTER FOUR

ATOMIC AND MOLECULAR WEIGHTS

The absolute weight of a single oxygen atom is 2.639×10^{-23} g., or, if you prefer, 0.000,000,000,000,000,000,000,026,39 g. Obviously this weight was not obtained by placing an oxygen atom on the scales. Would anyone ever seriously try to weigh a speck of dust on scales designed for 10-ton trucks? Methods by which the weights of single atoms and molecules may be calculated have been developed only quite recently. However, such absolute weights are so inconveniently small that they are used very infrequently in the routine calculations of chemistry.

1. Atomic Weights.—Methods for determining the relative weights of atoms and molecules were developed earlier, and such relative weights have proved extremely useful in the solutions of all types of problems. Relative weights can be expressed only as ratios of numbers. By stating that the titanium atom is three times as heavy as the oxygen atom, we indicate that the ratio of the weights of these atoms is 3:1, or $\frac{3}{1}$. For every different pair of atoms, there must exist such a ratio. To avoid the necessity of recording a ratio for every possible pair of atoms, a system of atomic weights is in use in which the weight of the atom of each element is compared with the weight of an oxygen atom. To the weight of the atom of oxygen has been assigned the number 16.0000. The unit of weight in this system of atomic weights is, therefore, one-sixteenth of the weight of the oxygen atom. *The atomic weight of an element* may then be defined as *a number that indicates how many times heavier one of its atoms is than one-sixteenth of the weight of the oxygen atom.*

The atomic weight of the element sulfur is 32.06. This is a number and not an actual weight. It does not correspond to any definite amount of sulfur. It does tell us, however, that one sulfur atom weighs 32.06 times as much as one-sixteenth of the oxygen atom. Further, it indicates that the ratio of the weights of the sulfur and the oxygen atoms is as 32.06 is to 16.00, or

$$\frac{\text{The weight of a sulfur atom}}{\text{The weight of an oxygen atom}} = \frac{32.06}{16.00} \cong^{*} \frac{2}{1}$$

The atomic weight of titanium is 47.90. Hence

$$\frac{\text{The weight of a titanium atom}}{\text{The weight of an oxygen atom}} = \frac{47.90}{16.00} \cong \frac{3}{1}$$

We may compare the weight of the sulfur and the titanium atoms directly, as this is simply the ratio of their atomic weights

$$\frac{\text{The weight of a sulfur atom}}{\text{The weight of a titanium atom}} = \frac{32.06}{47.90} \cong \frac{2}{3}$$

Thus the ratio of the atomic weights of any two elements is the ratio of the weights of single atoms of these elements.

2. Weighing Equal Numbers of Atoms.—Chemists are rarely faced with the problem of weighing out a certain number of atoms of a given element. To solve such a problem requires a knowledge of the weight of a single atom. The problem of weighing out equal numbers of atoms of two different elements presents itself far more frequently. Here a knowledge of the relative weights of their atoms, *i.e.*, their atomic weights, is all that is required. *If weights of two elements are in the same ratio as their atomic weights, they must be made up of the same number of atoms.*

The following analogy will help in understanding why this is true. A wholesale dealer in fruit has two large storage bins one full of oranges and one of grapefruit. The fruit was so carefully sorted that each orange weighs exactly 6 oz. and each grapefruit 18 oz. In short, each grapefruit is three times as heavy as each orange. He receives an order for 1 ton of oranges and an equal number of grapefruit. What weight of the latter shall he send? The answer is, of course, 3 tons, since the same number of grapefruit will weigh three times as much. Since we know the weight of each orange and grapefruit, we may check the accuracy of this conclusion by calculating the actual number of oranges in 1 ton and of grapefruit in 3 tons. The number is 5,333 in each case. In general, weights of these fruits, which are in the same ratio as the weight of a single orange is to that of a grapefruit, will contain equal numbers of fruit. Similarly, *weights of two elements will each contain the same number of atoms if they are in the same ratio as the atomic weights of the elements.*

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* The sign ≅ indicates approximate equality.

3. **The gram-atomic weight, or gram-atom,** is that weight of an element which is made up of a number of grams equal to its atomic weight. A clearer but less elegant definition is that a gram-atom of an element is its atomic weight multiplied by 1 g. Thus if the atomic weight of hydrogen is 1.008, of oxygen 16.00, and of iron 55.85, the gram-atomic weights of these elements are 1.008 g., 16.00 g., and 55.85 g., respectively. Since *gram-atomic weights of any two elements* are obviously in the same ratio as their atomic weights, they *must be made up of the same number of atoms.*

4. **Molecular Weights.**—The weight of a molecule of a substance is equal to the sum of the weights of the atoms of which it is composed. Similarly, *the molecular weight of a substance is equal to the sum of the atomic weights of each atom in its molecule.* Thus the molecular weight of water is the sum of two atomic weights of hydrogen ($2 \times 1.008 = 2.016$) and one atomic weight of oxygen (16.000), or 18.016, since the water molecule is made up of two atoms of hydrogen and one of oxygen. The molecule of chemically uncombined oxygen consists of two oxygen atoms. Hence, its molecular weight (32) is twice its atomic weight (16).

We have seen that atomic weights are numbers that compare the weights of other atoms to that of the oxygen atom, whose atomic weight has been arbitrarily set at 16. When we add atomic weights to obtain a molecular weight, the result is again a number that compares the weight of this molecule to the same standard. *The molecular weight of a substance is, therefore, a number that indicates how many times heavier one molecule of the substance is than one-sixteenth of the weight of the oxygen atom.* Atomic and molecular weights are thus comparable. For example, the weight of a water molecule is to that of a sulfur atom as the molecular weight of water (18) is to the atomic weight of sulfur (32).

5. **Gram-molecular Weight, or Mole.**—In a similar fashion to that used in defining gram-atomic weights, we may define *the gram-molecular weight, or the mole, of a substance as the number of grams of that substance that corresponds to its molecular weight.* In short, a mole is the weight of a substance equal to its molecular weight multiplied by 1 g. A mole of water is 18 g., since its molecular weight is 18. A mole of free oxygen is 32 g., corresponding to its molecular weight of 32. *Moles of all substances contain*

the same number of molecules, since they are weights that are in the same ratios as the corresponding molecular weights.

6. Avogadro's Number.—We pointed out that atomic and molecular weights are based on the same standard and hence strictly comparable. It follows that the number of molecules in a mole of any substance is the same as the number of atoms in a gram-atom of any element. This number has been called Avogadro's number after the great Italian physicist whose famous hypothesis (31-2) led to methods by which molecular and atomic weights may be determined. Avogadro's number has been obtained by widely divergent methods, all of which give results that are in substantial agreement. It is equal to 6.023×10^{23}. This is the number of molecules per mole of any substance and also the number of atoms in a gram-atom of any element.

If Avogadro's number is known, it is relatively simple to calculate the weight in grams of a single atom of any element or of a molecule of any substance. For example, the weight of a water molecule may be determined as follows: One mole of water, 18.016 g., is of course the weight of 6.023×10^{23} water molecules. The weight of one water molecule will be, therefore,

$$\frac{18.016 \text{ g.}}{6.023 \times 10^{23}} = 2.990 \times 10^{-23} \text{ g.}$$

Avogadro's number is so large that it staggers the imagination. The total population of the world in 1925 was about 1,750,000,000. If all these people were to share in the counting of 6.023×10^{23} molecules and were paid well enough to make this uninteresting task appear worth while, they would no doubt gladly tackle the job, especially if they were assured that molecules could be counted at a rate of one a second. At first sight this would seem easy money. However, if each had the perseverance to finish the job, he would be 10,000,000 years older at the end.

EXERCISES

1. Define atomic weight, gram-atom, molecular weight, and mole.

2. Why do moles of all substances contain the same number of molecules?

3. What weight of water will be made up of the same number of molecules as there are in two moles of oxygen?

4. What weight of sulfur contains the same number of atoms as there is in 1 g. of hydrogen?

5. A mole of chlorine is twice the weight of a gram-atom of this element. How many atoms are there in the chlorine molecule?

6. One mole of ammonia contains 3 gram-atoms of hydrogen. How many atoms of hydrogen are in the molecule of ammonia?

7. How many molecules are there in 1 g. of water?

8. Calculate the weight of one atom of sulfur.

9. How many oxygen atoms are there in one mole of water?

10. Can you justify the statement that the atomic weight of an element is the smallest weight of the element to be found in a molecular weight of any of its compounds?

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CHAPTER FIVE

THE SYMBOLISM OF CHEMISTRY

Scientists have always been great admirers of brevity. Hence any device that saves time is held in high favor by them. Back in the dim past there arose among the Chaldeans astrology, the mother of astronomy. The Chaldean astrologers believed that the planets exerted a mysterious influence over the metals of the earth. Later, the Greeks and the Romans associated the metals with the gods and goddesses of the pantheon of their mythology. In this way, the metals known to the ancient world were held sacred to the various gods and goddesses. Gold was sacred to the sun; silver, to the moon; copper, to Venus; quicksilver, to Mercury; iron, to Mars; tin, to Jupiter; and lead, to Saturn. During the Middle Ages the alchemists revived this association of the metals with the planets and used the astrological signs of the latter as symbols for the metals. Thus ☽ (*luna*, the moon) was the symbol for silver; ○ (*sol*, the Sun), for gold; ♀ (Venus), copper; ♂ (Mars), iron; ♃ (Jupiter), tin; ♄ (Saturn), lead; and ☿ (Mercury), quicksilver.

1. Modern Chemical Symbols.—Jöns Jakob Berzelius (1779–1848) introduced the modern chemical symbols. Every element has been given a symbol which usually consists of the first letter of its name, *e.g.*, N is the symbol for nitrogen, O for oxygen, and H for hydrogen. In the cases of elements whose names begin with the same letter, two letter symbols are used. Thus since C is the symbol for carbon, we use symbols of two letters for calcium (Ca), cadmium (Cd), cerium (Ce), cesium (Cs), cobalt (Co), chromium (Cr) etc. The second letter should always be small. Thus Co means cobalt, but CO means carbon monoxide. Since the names of most of the elements are the same in every language, the symbols used are also international. However, those elements which were known to antiquity are an exception in that they are known by different names in different languages. Iron becomes *eisen* in German and *fer* in French. In order to prevent international complications, their symbols are derived from their Latin or Greek names. Thus the symbol for iron is Fe from *ferrum;* that of copper, Cu from *cuprum;* of mercury, Hg from *hydrargyrum,* etc. Two symbols, however, Na for sodium and K for potassium, are derived from their German names *natrium* and *kalium,* respectively. In the table on the inside rear cover of this text will be found the symbols of the elements for ready reference.

2. **The Full Significance of a Symbol.**—A symbol has come to mean more than merely an abbreviation for the element for which it stands. Every symbol stands definitely for one atom and for one atomic weight of the element that it represents. Thus the symbol O stands not only for the element oxygen, but also for one atom of oxygen and for 16 weights (an atomic weight) of oxygen.

3. **Formulas.**—A symbol stands for an atom of an element; a formula stands for a molecule of a substance. A formula for a molecule will include the symbols of the elements of which the substance is composed, together with numbers placed below and to the right of each symbol which indicate the number of atoms of the element corresponding to the symbol present in the molecule of the substance. If only one atom of an element is to be found in the molecule, the number 1 is unnecessary and is, therefore, omitted. A few examples will help explain the meaning of formulas. H_2O, everyone knows, stands for water. To the chemist this formula represents the molecule of water which is composed of two atoms of the element hydrogen and one atom of the element oxygen. The molecule of sulfuric acid is represented by the formula H_2SO_4, which indicates that its molecules are composed of two atoms of hydrogen, one of sulfur, and four of oxygen. An element when uncombined with other elements is composed of molecules that contain atoms of that element only. Hence a formula for the molecule of an element will contain the symbol for its atom only, but if there is more than one atom in its molecule, a subnumber will be included in the formula to indicate this fact. Thus O_2 is the formula for the molecule of uncombined oxygen which contains two atoms of this element. Occasionally, formulas will be met which contain parentheses, *e.g.*, $Al_2(SO_4)_3$. In such cases, the number below and to the right of the parenthesis multiplies through the atoms enclosed in it. In the example cited above, the molecule would contain two atoms of aluminum,

three of sulfur, and twelve of oxygen. The reason for including such parentheses in certain formulas will be explained later.

4. Derivation of a Formula.—It will be so easy to take a formula for granted that we must caution you that a great deal of hard work in the laboratories and in the brains of chemists had to be done before the "H_2O," which we so glibly accept today, emerged. Remember, water came into man's knowledge "as the gentle rain from heaven" and not in the bottles labeled "H_2O." The formula of a substance follows once the numbers of the various atoms in one molecule of the substance are known. Our problem then is to see how this may be ascertained. We shall use water as a typical example.

First of all let us assume that water has been decomposed into and synthesized from the elements hydrogen and oxygen—in short that it is a compound of these elements only. Next an analytical procedure must be devised by which the composition of water may be determined quantitatively.[1] In one such experiment, 0.4536 g. of hydrogen and 3.6000 g. of oxygen were formed by the decomposition of a sample of pure water. This sample must have weighed 4.0536 g. (Why?) The fraction by weight of water due to hydrogen is then $0.4536/4.0536 = 0.1119$ and that due to oxygen $3.6000/4.0536 = 0.8881$. These are the relative weights in which the elements are combined in water. They are not, however, the relative numbers of hydrogen and oxygen atoms in which we are most interested, since a formula is expressed in terms of atoms and not weights.

To obtain this information we must use our knowledge of the atomic weights of these elements—hydrogen 1.0008 and oxygen 16.000. Thus the oxygen atom is roughly sixteen times as heavy as the hydrogen atom. In equal weights of these elements, there would be only one-sixteenth as many oxygen as hydrogen atoms. Our analysis shows us that 0.1119 g. of hydrogen is combined with 0.8881 g. of oxygen in every 1 g. of water. If we divide each of these weights by the corresponding atomic weights, we shall obtain numbers that will indicate the relative number of hydrogen and oxygen *atoms* in water molecules.

$$\frac{0.1119}{1.008} = 0.1110$$

$$\frac{0.8881}{16.000} = 0.0555$$

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[1] Such a procedure is discussed on p. 121.

This result means that for every 0.1110 hydrogen atom there is 0.0555 atom of oxygen. Since fractions of atoms cannot exist, we must change this ratio to the simplest one of whole numbers:

$$\frac{0.1110}{0.0555} = \frac{2}{1}$$

Thus there are two hydrogen atoms for every one oxygen atom in water; hence the simplest formula for the molecule of this substance is H_2O.

The simplest formula usually is, but need not be, the correct one. H_4O_2, H_6O_3, etc., would be equally acceptable formulas for water as far as the information considered above indicates. However, a knowledge of the molecular weight of water will enable us to choose the correct formula for its molecule since H_2O corresponds to one of 18, H_4O_2 to 36, and H_6O_3 to 54. Since the results of experiment indicate that the molecular weight of water, at least in the vapor state, is 18, we are confident that H_2O is not only the simplest formula, but also the correct one.

5. Other Examples.—Aluminum oxide is a compound of the elements aluminum and oxygen. A pure sample of this compound, weighing 1.456 g., was found by analysis to contain 0.771 g. of aluminum. What is the simplest formula that may be assigned to this compound? The weight of oxygen in the sample must be the difference between the weight of aluminum and that of the sample.

$$\begin{array}{rl} 1.456 \text{ g.} & = \text{weight of sample of aluminum oxide} \\ -0.771 \text{ g.} & = \text{weight of aluminum in sample} \\ \hline 0.685 \text{ g.} & = \text{weight of oxygen in sample} \end{array}$$

We then divide the weight of each element by its atomic weight to obtain the relative number of atoms of each element.

$$\frac{0.771}{26.97} = 0.0286 \text{ aluminum atoms are combined with}$$

$$\frac{0.685}{16.00} = 0.0428 \text{ oxygen atoms}$$

This ratio cannot be reduced to one of whole numbers by inspection, but if we divide by the smaller number, the simplest integer ratio follows easily:

$$\frac{0.0286 \text{ Al}}{0.0428 \text{ O}} = \frac{1 \text{ Al}}{1.5 \text{ O}} = \frac{2 \text{ Al}}{3 \text{ O}}$$

The simplest formula is Al_2O_3.

As a final example, the percentage composition of sodium sulfate is sodium 32.37 per cent, sulfur 22.58 per cent, oxygen 45.05 per cent; the atomic weights of its elements are sodium 23, sulfur 32, and oxygen 16. The percentage composition gives us the weight ratios in which the three elements are combined. But before the formula can be calculated, we must convert these weight ratios to atom ratios since the formula is expressed in atoms and not in weights. Dividing each percentage by the corresponding atomic weight will give us numbers that express the atom ratios in which the elements are combined:

$$\frac{32.37}{23} = 1.41$$

$$\frac{22.58}{32} = 0.705$$

$$\frac{45.05}{16} = 2.81$$

Based on these atom ratios, a tentative formula might be written $Na_{1.41}S_{0.705}O_{2.81}$, but since the atoms are not split up into fractions, such a formula must necessarily be incorrect. The next step is to find the greatest common factor of these three numbers and, by dividing each by it, obtain the simplest whole number ratio. In this case the smallest number 0.705 is a factor of the other two. Dividing by it, we obtain

$$\frac{1.41}{0.705} = 2$$

$$\frac{0.705}{0.705} = 1$$

$$\frac{2.81}{0.705} = 4$$

The simplest formula for sodium sulfate is, therefore, Na_2SO_4.

6. Molecular Weights from Formulas.—We have seen that in order to obtain the correct formula of a substance we must determine its molecular weight experimentally. However, once the formula is obtained it is convenient to know how to calculate the molecular weight from the formula. Since the molecule is composed of nothing but atoms, the weight of the molecule must be equal to the sum of the weights of its constituent atoms. Since atomic and molecular weights are referred to the same standard (oxygen atom = 16), the atomic weights are additive and the sum of the atomic weights of each atom in one molecule of a substance must be the molecular weight of the substance. Thus the molecular weight of water is the sum of two atomic weights of hydrogen (2 × 1.008) and one atomic weight of oxygen (1 × 16.000), or 18.016. The molecular weight of sulfuric acid can be calculated from its formula in the same way:

$$\begin{array}{lr}
\text{2 atomic weights of H } (2 \times 1.008) & = 2.016 \\
\text{1 atomic weight of S } (1 \times 32.064) & = 32.064 \\
\text{4 atomic weights of O } (4 \times 16.000) & = \underline{64.000} \\
\text{Molecular weight of sulfuric acid} & = 98.080
\end{array}$$

7. Percentage Composition from a Formula.—As we have seen, a formula is derived originally from the results of a chemical analysis. However, once such a formula has been correctly derived, the percentage composition of the compound for which it stands can be very easily calculated from it. In the case of sulfuric acid, which has been discussed in the previous paragraph, the fraction by weight of this acid due to hydrogen is 2.016/98.080, to sulfur 32.064/98.080, and to oxygen 64.000/98.080. Then by multiplying each fraction by weight by 100 per cent, the fractions are converted into percentages:

$$\frac{2.016}{98.080} \times 100\% = 2.06\% \text{ hydrogen}$$

$$\frac{32.064}{98.080} \times 100\% = 32.69\% \text{ sulfur}$$

$$\frac{64.000}{98.080} \times 100\% = 65.25\% \text{ oxygen}$$

8. Law of Multiple Proportions.—It must be apparent to the reader, even at this early stage, that the atomic theory of Higgins and Dalton is of invaluable help in the study of chemistry. Dalton put it to immediate use by predicting in 1803 the existence of the law of multiple proportions. It was a well-known fact in Dalton's day that certain pairs of elements combine to form more than one compound if they were allowed to react under different conditions. There are, for example, three well-known oxides of nitrogen: nitrous oxide, nitric oxide, and nitrogen dioxide. These compounds are composed of the two elements nitrogen and oxygen only; but in each compound these elements are combined in different proportions by weight, as shown in Table 3. At first sight, these analytical results seem to indicate the fact only that these elements combine in different proportions in each of the three compounds. Yet, if we calculate from these data the weight of oxygen that is combined with 1 g. of nitrogen in each case, a relationship is revealed (Table 4). We at once notice that the weights of oxygen, which combine with 1 g. of nitrogen in each of the three compounds, are in a simple ratio to one another, *i.e.*,

TABLE 3

Compound	Composition, per cent	
	Nitrogen	Oxygen
Nitrous oxide	63.63	36.37
Nitric oxide	46.67	53.33
Nitrogen dioxide	30.44	69.57

$$0.5716:1.143:2.286::1:2:4$$

TABLE 4

Compound	Nitrogen, g.	Oxygen, g.
Nitrous oxide	1	0.5716
Nitric oxide	1	1.143
Nitrogen dioxide	1	2.286

This relationship is not a strange coincidence but is the rule whenever two elements form a series of compounds. The relationship was expressed by Dalton as the law of multiple proportions: *If two elements combine to form more than one compound, a fixed weight of one element will be found combined with weights of the other which are in ratios of small whole numbers.*

This law is easily explained by the atomic theory. Let us take a hypothetical case of two elements X and Y which form two different compounds. Let us further assume that every molecule of one of these compounds is made up of 1 atom of X and 1 of Y and that each molecule of the other compound contains 1 atom of X and 2 of Y. Then the number of atoms of Y, which are found combined with 1 atom of X in the two compounds, are to each other as 1 is to 2. It follows that the weights of Y must be in this ratio also. In general, these integer multiples must exist since the atoms of the various elements, which make up the molecule of a compound, are usually few in number. One atom of each element, 1 atom of one and 2 of the other, 1 of one and 3 of the other, and 2 of one and 3 of the other are the proportions generally found in the molecules of compounds that are composed of two elements.

The formulas of the three oxides of nitrogen in our previous example may be determined from the data in Table 3. From these formulas, the reason for the small integer weight ratio is apparent.

TABLE 5

Compound	Formula	Weight, g.		
		Mole	Nitrogen per mole	Oxygen per mole
Nitrous oxide	N_2O	44	28	16
Nitric oxide	NO	30	14	16
Nitrogen dioxide	NO_2	46	14	32

Thus 14 g. of nitrogen, a fixed weight, will be combined with 8, 16, and 32 g. of oxygen, respectively, in the three oxides and these weights are as 1:2:4.

The law of multiple proportions may not be applied to organic compounds of high molecular complexity, in which cases small whole number ratios are obviously impossible.

EXERCISES

1. What are the symbols of the following elements: iron, sodium, potassium, mercury, tin, lead, magnesium, and manganese?

2. For what does a symbol stand?

3. What information is given by a formula?

4. An oxide of aluminum has the following composition: aluminum, 52.89 per cent and oxygen, 47.09 per cent. Determine the simplest formula for this oxide.

5. A sample of a chloride of iron weighing 8.1105 g. was found to contain 2.7920 g. of iron. Calculate its formula.

6. A compound of carbon and hydrogen has a molecular weight of 26. There is 0.7206 g. of carbon in a sample of the compound weighing 0.7811 g. Determine its formula.

7. One gram of a compound of lead, carbon, and oxygen contains 0.7755 g. of lead, 0.0449 g. of carbon, and 0.1796 g. of oxygen. Determine its formula.

8. Calculate the percentage composition of the following substances: ferric nitrate, ammonium nitrate, aluminum sulfate, and acetic acid.

9. Chromium forms the following oxides: CrO, Cr_2O_3, and CrO_3. Use these compounds to illustrate the law of multiple proportions.

10. How many grams of oxygen are there in a mole of sulfur trioxide?

READING REFERENCES

TILDEN: "Famous Chemists," Chap. XI, Berzelius, E. P. Dutton & Company, Inc.

WEEKS: Berzelius, *J. Chem. Education*, **9**, 477 (1932).

CHAPTER SIX

CHANGES IN MATTER

Chemistry is interested in the properties of the elements and their compounds and especially in interpreting these properties and tying them together by means of theories of the structure of matter. To be able to explain the existence of a snow crystal gives as much intellectual satisfaction to the scientist as a description of its beauty gives aesthetic satisfaction to the poet. But the material world is dynamic as well as static. It is far more than a museum of forms, but rather an arena in which interesting and even exciting changes take place. In many of these changes, chemistry is vitally interested.

1. Physical Changes.—It has been found convenient to classify all changes as either physical or chemical. The substance or substances involved in a physical change retain their identity throughout the change. If we remember that the composition of a substance is the unique property that determines its identity, then it becomes apparent that *in a physical change there is no change in the composition of any substance taking part.* When a substance changes its state, *i.e.*, when a solid melts or a liquid freezes, or when a liquid evaporates or a vapor condenses, no change in composition is involved; hence no new substance is formed. Changes of state are, therefore, physical changes. Many of the properties of steam are quite different from those of ice cubes, but both are the substance water composed of 11.19 per cent hydrogen and 88.81 per cent oxygen by weight. The conversion of ice cubes into steam, or vice versa, is a physical change. The breaking of a bottle, the building of a house, the solution of sugar in water, and the mixing of cement, sand, and water are all physical changes. Such changes may be easily reversible as is the melting of ice, or they may be practically irreversible as is the breaking of a bottle, so that reversibility is no criterion of a physical change.

In terms of theory, a physical change must not involve the destruction of molecules. Since both the reactants and the products of a physical change are the same substance or substances, the molecules of which they are composed remain the same. Such changes may involve changes in the distance between molecules as when bottles are broken, wood is chopped, or water evaporates, and they do involve changes in molecular kinetic energy when temperature changes take place. But they do not involve changes in the structure of the molecules themselves.

2. Chemical Changes.—The products of a chemical change are not the same substances as those which entered into the change. The composition of each product is different from that of each reactant. *A chemical change*, therefore, *is one in which changes in composition are involved and the products are not the same substances as the reactants.*

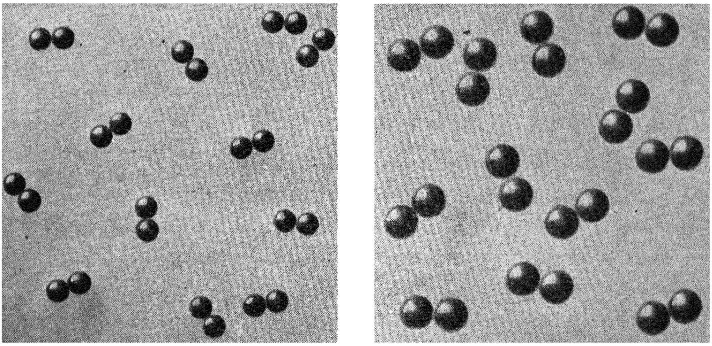

Hydrogen Oxygen

FIG. 6.—The reactants before mixing.

In terms of the molecular and atomic theories, in a chemical change molecules of the reactants break apart and their constituent atoms unite in different combinations to form molecules of the products.

3. The Synthesis of Water.—The formation of water from its elements is a chemical change that we shall now study in some detail as a typical example. We may picture the structures of the gaseous reactants as shown in Fig. 6. These gases may be mixed in a suitable container without reacting. The resulting mixture is homogeneous and, therefore, a solution. We may picture it as in Fig. 7. We have taken care to mix them in the right proportions to form water so that after they have combined there will be no excess of either element left over. The process of

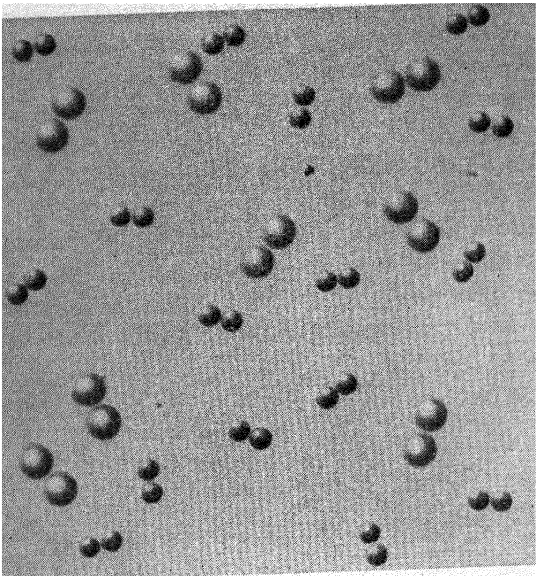


Fig. 7.—A mixture of hydrogen and oxygen before reacting.

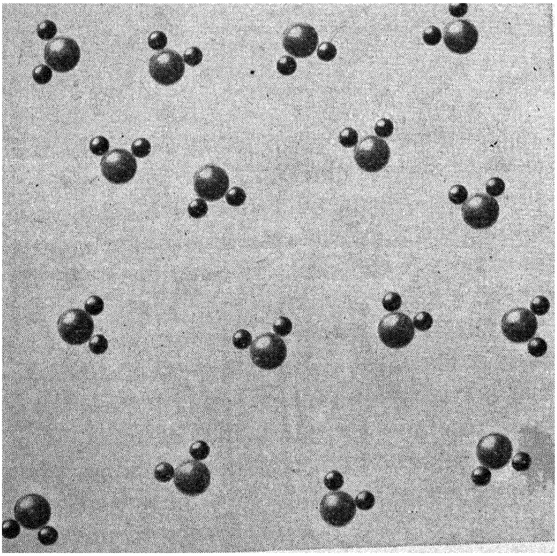
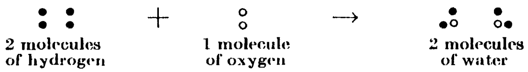


Fig. 8.—The product, water.

mixing was merely a physical change. As yet no chemical change, or reaction, has taken place. The mixture is a dangerous one, however, as a spark will be sufficient to set off the chemical reaction, which in this case goes with explosive violence.

However, we may safely imagine the explosion of the mixture. A large amount of energy is liberated, as sound, light, and heat; and a new substance water is formed as the product of the reaction (Fig. 8). We end up with the same atoms, but they are rearranged in the molecules of the product water.

For this chemical change, we may picture the following unit reaction:



which represents the minimum number of molecules of each kind which can enter into the reaction. Billions upon billions of these unit changes take place when even small amounts of hydrogen and oxygen combine to form water.

4. Equations.—When we replace the pictures of the molecules involved in a unit chemical change by their formulas, the result is a chemical equation. Thus the equation for the synthesis of water is written

$$2H_2 + O_2 \rightarrow 2H_2O$$

In general, the formulas for the molecules of the reactants are placed at the left and those of the products on the right of an arrow which indicates the direction of the change. Wherever necessary, numbers are placed before formulas to indicate the minimum number of molecules of each kind involved in the change. These numbers are determined by the process of balancing the equation to make certain that the number of atoms of each kind on either side of the arrow is the same.

5. Writing and Balancing Equations.—We shall have occasion to study and to write equations for many chemical reactions. Gradually you will acquire a certain facility in writing them and in interpreting their meaning. Many students of elementary chemistry get the idea that they are merely a chemical algebra. This is a dangerous misconception. In algebra, any two quantities may be added; in chemistry, you will be by no means right in assuming that any two substances will enter into a chemical reaction. Every chemical equation is in the last analysis a formulation of an experimental result. No one, not even an experienced chemist, can be absolutely sure whether two given substances will react or, at least, not until he or someone else has gone into the laboratory and proved by an actual experiment that they do. Further, granted that they react, no one can predict with absolute certainty what the products will be until he or someone else has isolated and identified them in the laboratory. Of course anyone who has studied chemistry can hazard a fairly shrewd guess; for he knows that certain classes of substances react characteristically with certain other classes to form certain characteristic products. After he has classified the substances whose reactivity is in question, he can usually predict whether they will react and what the products will be. In this course we shall study some of these fundamental reactions. Until we do, however, do not be concerned if you cannot predict what the products of a certain reaction will be.

For our present purposes, the following information will suffice. Let us assume that we know that when metallic aluminum is treated with hydrochloric acid, HCl, hydrogen gas is evolved and aluminum chloride, $AlCl_3$, is formed. The formulas for the molecules of the compounds involved have been given. We may then start the equation by writing

$$Al + HCl \rightarrow$$

In writing the formula for the molecule of a *free* element, in this case aluminum, it is necessary to remember only that those of hydrogen, oxygen, nitrogen, and chlorine of the common elements are diatomic and hence written H_2, O_2, N_2, and Cl_2. All others are assumed to be monatomic. We might then rush blindly ahead treating a chemical equation as if it were algebra and write

$$Al + HCl \rightarrow AlCl + H$$

This would be wrong. The molecule of no known compound has the formula $AlCl$, and hydrogen atoms never exist alone except in an electric arc. We should write

$$Al + HCl \rightarrow AlCl_3 + H_2$$

The equation must now be balanced. As it stands there are not the same number of hydrogen and chlorine atoms on each side of the arrow. Balancing is accomplished by placing numbers *before* formulas but never by changing the formulas themselves. A 2 in front of the HCl will balance the hydrogen but not the chlorine atoms.

$$Al + 2HCl \rightarrow AlCl_3 + H_2$$

To balance these we must multiply 2HCl by 3 and $AlCl_3$ by 2

$$Al + 6HCl \rightarrow 2AlCl_3 + H_2$$

Then, if a 2 is placed before Al and a 3 before H_2, the equation is balanced

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

6. Kinds of Chemical Reactions.—Chemical reactions have been classified into several types. The simplest type is that of *combination* in which two or more substances combine to form a more complex substance. The general equation of this type is

$$A + X \rightarrow AX$$

A and X may be either elements or compounds as the following examples of combination reactions show:

$$\begin{gathered} 2H_2 + O_2 \rightarrow 2H_2O \\ Zn + Cl_2 \rightarrow ZnCl_2 \\ CaO + CO_2 \rightarrow CaCO_3 \\ H_2O + SO_3 \rightarrow H_2SO_4 \end{gathered}$$

A second type, *decomposition*, is the reverse of the first, involving a breakdown of a more complex molecule into two or more simpler molecules

$$AX \rightarrow A + X$$

Examples of this type are

$$\begin{gathered} 2H_2O \rightarrow 2H_2 + O_2 \\ 2KClO_3 \rightarrow 2KCl + 3O_2 \\ CaCO_3 \rightarrow CaO + CO_2 \end{gathered}$$

A third type involves *displacement* of one kind of atom by another

$$AX + B \rightarrow BX + A$$

specific examples of which are

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$
$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$
$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$

Finally, a fourth type involves an exchange of partners

$$AX + BY \rightarrow AY + BX$$

and is called *double decomposition*. Examples of this type include

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
$$2NaI + HgCl_2 \rightarrow 2NaCl + HgI_2$$
$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

It is a great convenience to be able to classify a certain reaction as belonging to one of these types.

7. Energy and Chemical Reactions.—Every chemical change is accompanied by an energy change. A molecule of a given substance at a given temperature possesses a definite amount of chemical energy by virtue of its structure. Whenever a chemical reaction takes place, the new molecules of the products that are formed also possess an amount of chemical energy; this may be greater or less than that of the molecules from which they are formed. If the energy of the products is greater than that of the reactants, energy must be absorbed from some external source when the reaction takes place. Usually this absorption is one of heat from the surroundings. Chemical reactions that absorb energy are called *endothermic*. On the other hand, if the products possess less energy than the reactants, the excess energy is liberated by the reaction. Such chemical reactions are *exothermic*. Here again the energy is usually evolved as heat. The combustion of coal and the explosion of dynamite are exothermic reactions, whereas the synthesis of nitric oxide from its constituent elements nitrogen and oxygen and the decomposition of water are endothermic changes.

8. Law of Conservation of Mass.—In any change, whether it be chemical or physical, the total mass of the products is the same as that of the substances that enter into the change. This is known as the law of conservation of mass. It may be stated in a slightly different way. In any closed system, the mass of the enclosed substances remains constant whatever changes may occur within the system.

EXERCISES

1. Which of the following involve chemical changes: the rusting of iron, the digestion of food, the electrolysis of water, the vaporization of gasoline, the solution of sugar in water, the melting of paraffin, and the combustion of alcohol.

2. Balance the following equations:

$$Fe + Cl_2 \rightarrow FeCl_3$$
$$H_2 + Cl_2 \rightarrow HCl$$
$$Mg + O_2 \rightarrow MgO$$
$$Cu + S \rightarrow Cu_2S$$
$$Na_2O + H_2O \rightarrow NaOH$$
$$Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2$$
$$CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$$
$$FeO + HCl \rightarrow FeCl_2 + H_2O$$
$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$
$$CH_4 + O_2 \rightarrow CO + H_2O$$

CHAPTER SEVEN

OXYGEN

It has been a good custom in the teaching of chemistry to follow a certain logical order in presenting for study the information about the properties of an element and its compounds. We shall use the following order:

1. *History* of the discovery of the element.
2. Its *occurrence* in nature both as a free element and in its compounds.
3. Its *preparation* by both laboratory and commercial methods.
4. Its *physical properties*, *i.e.*, its color, taste, smell, melting and boiling points, its critical temperature, its solubility in various solvents, etc.
5. The more important *chemical reactions* into which it enters.
6. The *tests* by which it may be recognized.
7. The *uses* to which it may be adapted.
8. The properties of its more important *compounds*.

You will find it helpful in studying to prepare an outline in your notebook in which the information given in the text is presented in a concentrated form. The task of picking out essential information and of boiling this down to as few words as possible will help to fix it in your mind and may make you wonder why the author found it necessary to use so much paper and printer's ink.

Oxygen is perhaps the most important and certainly the most abundant of the elements. Without its presence in the atmosphere, our respiration would be useless and our demise a matter of a few minutes. We are to a large extent composed of oxygen. Without it no fire could burn, no metal rust, and no organic matter decay.

1. History of Its Discovery.—Oxygen has been known for over a thousand years by the Chinese as *yin*, the active component of the atmosphere. Leonardo da Vinci (1452–1519) was the first Occidental to mention the presence of two different gases in the air. Mayow (1669) determined its proportion in the air and discussed at length its relation to the phenomena of combustion, rusting, fermentation, and respiration. He did not, however, prepare a pure sample of it. In 1731, Hales prepared it by heating saltpeter, but did not know that it was to be found in the air. Scheele, a Swedish apothecary, made it in 1771–1772 from no less than seven different substances.

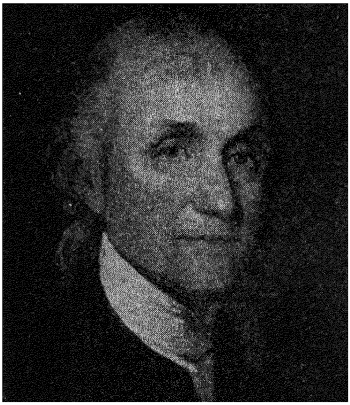


Fig. 9.—Joseph Priestley.

Despite the fact that oxygen had been prepared by so many investigators before him, Joseph Priestley (1733–1804), a nonconformist clergyman of Birmingham, England, is still given credit for having been the first to prepare this gas. On Aug. 1, 1774, he heated mercuric oxide, HgO, by focusing the sun rays by means of a burning glass upon it and found that it gave off great quantities of a gas. He further discovered that a candle burned with extreme brilliance in this gas and also that a mouse was not killed by it but, on the contrary, became very lively—probably because it was frightened.

Because he sympathized with the cause of the French Revolution and because of his heterodox theological views, a mob burned his home and laboratory on July 14, 1791. Priestley barely escaped with his life. Later he came to America to live with some of his children who had settled in Northumberland, Pa.

2. Occurrence.—Approximately one-half the weight of the materials that make up the earth's crust, its waters, and its atmosphere is oxygen. The uncombined element makes up 23.2 per cent of the weight of dry air. Essentially, our atmosphere is a mixture of approximately four parts nitrogen and one part oxygen by volume with less than 1 per cent by volume of inert gases and varying amounts of such substances as water vapor and carbon dioxide. In air there are approximately four nitrogen molecules, N_2, for every one of oxygen, O_2 (Fig. 4). Free oxygen also is found dissolved in water where its presence makes aquatic life possible. Here we must imagine O_2 molecules moving about between the more numerous H_2O molecules of the solvent.

The most abundant compound of oxygen is water. Eight-ninths of its weight is due to oxygen. Pure white sand is made up almost completely of quartz crystals. Quartz is a compound of silicon and oxygen (SiO_2). The vast majority of minerals are compounds of oxygen. The most important ores of iron, tin, aluminum, and manganese are oxides of these metals.

Finally, nearly all organic compounds contain oxygen. All fats, carbohydrates (including starches, sugars, and cellulose), and proteins are compounds of this element.

3. Preparation.—The vast majority of the inorganic compounds of oxygen are so stable that they cannot be decomposed easily by heat. Sand (SiO_2), alumina (Al_2O_3), and magnesia (MgO) make excellent furnace linings. A piece of lime (CaO) may be heated until white-hot in the flame of an oxyhydrogen blast lamp but will not decompose. Relatively few compounds are available from which oxygen may be easily obtained. One of these is the mercuric oxide, HgO, which was Priestley's original source of oxygen. This compound decomposes readily at the temperature of a Bunsen burner into its constituent elements. To obtain the equation for this decomposition, we shall first write the formulas for the molecules of the reactant and the products:

$$HgO \rightarrow Hg + O_2$$

Why is the element mercury written Hg but oxygen O_2 (6-5)? The oxygen atoms may be balanced by taking two mercuric oxide molecules:

$$2HgO \rightarrow Hg + O_2$$

But these two molecules contain two mercury atoms. Hence

$$2HgO \rightarrow 2Hg + O_2$$

is the completely balanced equation. This is not a very useful method for obtaining oxygen as mercuric oxide is too expensive.

LABORATORY METHODS

4. Electrolysis of Water.—Since water is so readily obtainable, its decomposition seems to offer an inexpensive source of oxygen. Heat alone is practically useless in this connection.

Water molecules are so stable that at 2000° C. less than 2 per cent are decomposed into hydrogen and oxygen. A direct current of electricity offers a convenient means of accomplishing this decomposition. In an apparatus such as that pictured in Fig. 10, a direct current is passed through water between two electrodes.

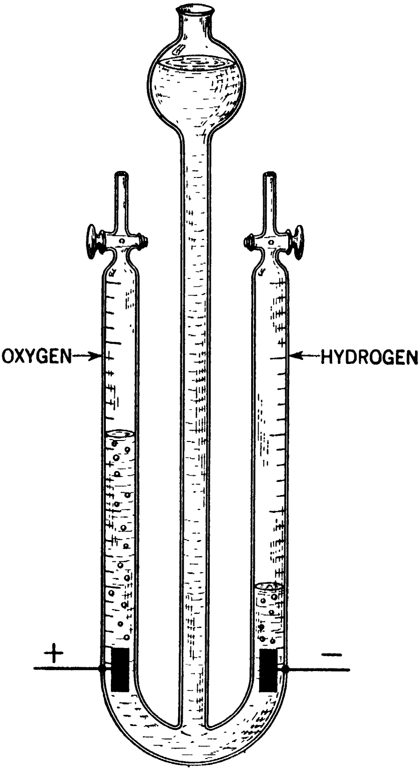


Fig. 10.—Electrolysis of water.

Hydrogen gas is formed at the cathode, or negative electrode, and oxygen at the anode, or positive electrode.

$$2H_2O \rightarrow 2H_2 + O_2$$

This process is an example of *electrolysis*, or a chemical change produced by the passage of a direct current of electricity. The electrolysis of water is a convenient laboratory method of preparing both hydrogen and oxygen in a high state of purity.

5. The Decomposition of Potassium Chlorate.—This substance ($KClO_3$) is a white solid composed of potassium, chlorine, and oxygen. It must be heated above its melting point (368°C.) before its rate of decomposition is high enough to give a positive test for oxygen. At about 400°C., its decomposition is so rapid as to be dangerously violent. It would not be considered as a safe source of oxygen were it not possible to accomplish its decomposition at temperatures below its melting point by the use of a catalyst. If the black solid manganese dioxide, MnO_2, is mixed with potassium chlorate, oxygen is evolved at temperatures as low as 200°C. The mixture is heated in a test tube (Fig. 11), and the oxygen is collected by the displacement of water. This reaction is as follows:

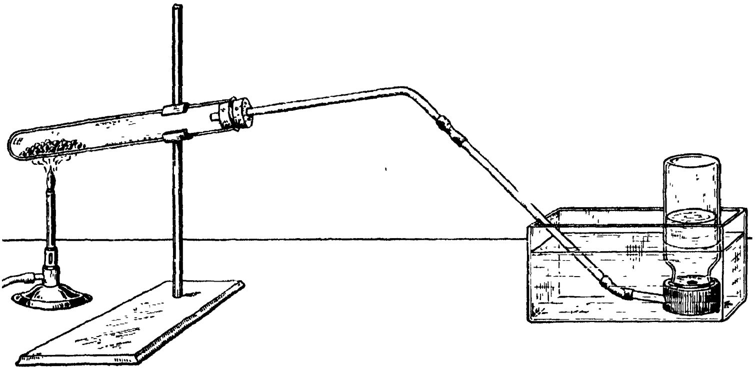


FIG. 11.—Preparation of oxygen from potassium chlorate.

$$\underset{\text{potassium chlorate}}{2KClO_3} \rightarrow \underset{\text{potassium chloride}}{2KCl} + \underset{\text{oxygen}}{3O_2}$$

6. Catalysts.—The function of the manganese dioxide as a catalyst needs careful consideration. After the reaction is complete, the manganese dioxide may be separated from the potassium chloride *absolutely unchanged.* At 200°C. without this substance the rate of decomposition of the potassium chlorate is extremely slow. With the catalyst, the evolution of oxygen is uniform and rapid. A *catalyst is* defined as *a substance that will change the rate of a chemical reaction without itself being changed.* Implied in this definition are several features of catalytic action which it is well to emphasize.

1. A catalyst will not start a reaction that would not occur of itself.

2. Catalysts may speed up or slow up a reaction. Those which slow up reactions are called negative catalysts, or inhibitors.

3. A catalyst is not to be considered as one of the reacting substances as it is not permanently changed by the reaction it catalyzes. It has been aptly called the oil on the machinery of a reaction.

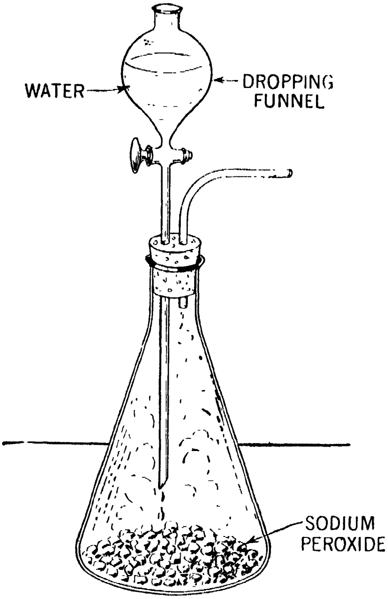


FIG. 12.—Oxygen from sodium peroxide.

4. Catalytic action is specific, *i.e.*, a catalyst for one reaction may not be one for another. You will search in vain for a bottle labeled "catalyst" which can be used as an "oilcan" on any chemical reaction.

7. **The action of water on sodium peroxide** offers another convenient laboratory preparation and does not require the use of heat. The reaction is as follows:

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

In the apparatus shown in Fig. 12, the rate at which water is allowed to drop from the funnel on the peroxide determines the rate at which oxygen is evolved.

8. Commercial Preparation.—The atmosphere is the most obvious source of oxygen. Here the element is uncombined so that it need only be separated from the nitrogen with which it is mixed. This is done on a large scale commercially by a process that involves the liquefaction of air. Carbon dioxide and water vapor are removed by suitable absorbents, and the air is liquefied by compression and cooling. Since liquid nitrogen boils at a lower temperature (−194°C.) than liquid oxygen (−183°C.), the former boils away more rapidly than the latter and a separation is possible. This process will be discussed in detail later (15-7). The oxygen is shipped in steel cylinders under high pressure. When oxygen is needed in quantity in a chemistry laboratory, these cylinders are used.

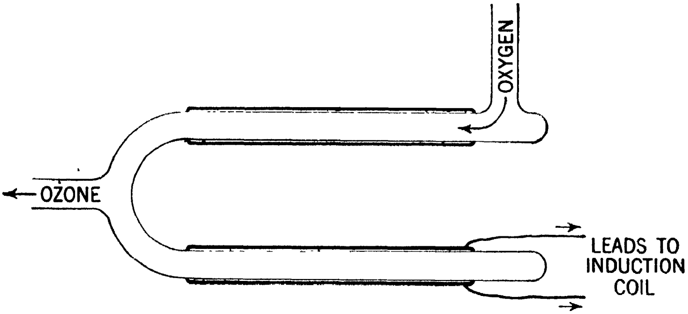


Fig. 13.—An ozonizer.

9. Physical Properties.—Oxygen is a colorless, odorless, and tasteless gas under normal conditions. It may be liquefied only if it is first cooled to below −118°C., its critical temperature (15-1), and compressed. In the liquid state, it has a pale blue color and boils at −183°C. under atmospheric pressure. Below −218°C. it is a white solid. It is only very sparingly soluble in water, some five volumes of the gas dissolving in 100 volumes of water at 0°C. and atmospheric pressure.

10. Ozone.—When oxygen is passed between metal plates, which are connected to an induction coil as in the apparatus shown in Fig. 13, an interesting change in its properties takes place. The current passing through the coil should be enough to produce a silent discharge of electricity but not great enough to produce sparks. The diatomic molecules of oxygen absorb energy, and triatomic molecules of a more active form of oxygen are formed:

$$3O_2 \rightleftarrows 2O_3$$

This form of oxygen is called *ozone*. It is unstable at room temperature, returning to the stable diatomic form with a liberation of energy. Oxygen is not unique among the elements in being able to exist in more than one form. The various forms of an element are called *allotropic modifications*.

In general, the reactions of ozone are the same as those of oxygen which we shall discuss in the next chapter. However, they proceed more rapidly and with the liberation of greater amounts of energy. Ozone may be recognized by its odor which is noticeable wherever electric discharges occur through air. As an active oxidizing agent, it is used to a certain extent to sterilize water and remove odors from air.

EXERCISES

1. What are the four most abundant elements in the earth's crust?

2. Write equations for four methods of preparing oxygen.

3. Is the commercial method for the preparation of oxygen based on a physical or a chemical change?

4. Since water and sand are so inexpensive, why is not oxygen prepared by heating these substances?

5. What is a catalyst?

6. After heating a mixture of potassium chlorate and manganese dioxide to obtain oxygen, how would it be possible to prove that the manganese dioxide acted as a catalyst?

7. How many grams of oxygen are obtained by the decomposition of 100 g. of potassium chlorate?

8. What can be deduced about the relative densities of oxygen and hydrogen from the fact that twice as great a volume of hydrogen as of oxygen is obtained when water is decomposed by electrolysis, although the weight of oxygen obtained is eight times as great as that of hydrogen?

9. What are allotropic modifications?

10. Name two substances that have the same composition.

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CHAPTER EIGHT

REACTIONS OF OXYGEN

Oxygen plays such a unique role in the combustion of fuels and the rusting of metals that the greater part of this chapter will be devoted to these topics. Our modern civilization, for better or for worse the product of the machine, draws its nourishment from an intelligent use of power created by the combustion of coal or petroleum products. A knowledge of the nature of combustion is vital to its proper utilization.

1. The Phlogiston Theory.—During the first part of the seventeenth century, a theory of the nature of combustion was developed in Germany by Becher and Stahl which was destined to be generally accepted for over a century. Few of the fundamental theories that are accepted today have had as long a life. The phlogiston theory assumed that every combustible substance was composed of phlogiston and a calx. When the substance burned, phlogiston, the fiery principle, escaped in the flame, leaving the calx behind as an ash. Substances which left little ash were conceived of as being nearly pure phlogiston. Hydrogen gas, which on burning left no ash, was considered to be pure phlogiston. The rusting, or calcining, of metals was assumed to be of the same nature, although even at that time it was a well-known fact that the rust, or calx, weighed more than the metal from which it was formed. Stahl himself said, "With calcining, the phlogiston departs, but it does not take any weight with it." The ridiculous explanation was actually put forward that phlogiston had a negative weight the loss of which by a metal increased its weight.

2. Lavoisier and the Modern Theory of Combustion.—As a result of the discovery of oxygen in 1774 by Priestley and Scheele and of the experimental proof that substances burned more vigorously in oxygen than in air, the modern theory of combustion soon followed. In November, 1772, before the discovery of oxygen, the great French chemist Lavoisier sent a communication to the French Academy in which he stated that in every combustion and calcination reaction a certain amount of air combined with the combustible substance which accounted for its gain in weight. In the cases of such substances as carbon and sulfur, which appeared to burn completely and leave no ash, he was able to show that the products of combustion were gases which, when collected, were found to weigh more than the carbon or sulfur from which they were formed. Lavoisier's experiments proved further that when the calxes of certain metals were decomposed by heat a gas was set free. Describing one of his experiments he said, "I have carried out the reduction of litharge [an oxide of lead] in a closed vessel, and I have found that in the moment when the calx changes to a metal a considerable amount of air is given off, a thousand times the litharge in volume."

FIG. 14.—Antoine Laurent Lavoisier.

Then Priestley discovered oxygen and shortly afterward visited Lavoisier in Paris, telling the latter of his discovery. Lavoisier immediately saw the significance of the newly discovered gas to his theory of combustion and calcination, although Priestley, until his death in 1804 in this country, remained an active champion of the phlogiston theory. Lavoisier was a great believer in following the course of a chemical reaction quantitatively as well as qualitatively. He was in large measure responsible for the introduction of the balance in chemical research, and with its aid he established the law of conservation of matter which lies at the foundation of all chemical philosophy. For this reason, he is often called the father of modern chemistry. With the aid of the balance, he was able to prove beyond a shadow of doubt that combustion is a process in which combination of the combustible material with the oxygen of the air takes place and that the rusting of metals is a similar process.

In 1794, Lavoisier met his death on the guillotine. A member of the aristocracy and a former government official, he had incurred the hatred of Marat and Fourcroy of the revolutionists. He was brought to trial; false accusations were made against him; and he was sentenced to die with the infamous words, "*La République n'a pas besoin de savants. Il faut que la justice suive son cours.*" As Lagrange afterward remarked, "A moment was all that was necessary in which to strike off his head, and probably a hundred years will not be sufficient to produce another like it." "Compared with the growth of science, the shiftings of governments are minor events," Prof. C. S. Minot once said. "Until it is clearly realized that the gravest crime of the French Revolution was not the execution of the King, but the execution of Lavoisier, there is no right measure of values; for Lavoisier was one of the three or four greatest men France has produced."

3. Chemical Reactions of Oxygen.—Oxygen is a moderately active nonmetal and will combine directly with nearly every other element to form an oxide. The only exceptions to this rule are the inert gases, which form no compounds (37-2); the noble metals silver, gold, and platinum; and the halogens, a group of very active nonmetals, fluorine, chlorine, bromine, and iodine.

4. Metallic, or Basic, Oxides.—Rusting is essentially a slow union of a metal with the oxygen of the air. The rust formed is, therefore, an oxide of the metal. The very active alkali metals, *e.g.*, sodium, Na, and potassium, K, rust so rapidly that they are kept under kerosene or sealed in air-free containers. Active metals like aluminum and magnesium rust readily also, but their oxides form an airproof surface that protects the metal underneath.

Rusting is a comparatively slow oxidation, but it may be accelerated by heating the metal and by substituting pure oxygen for air. Since rusting is an exothermic reaction, heat may be evolved so rapidly under these conditions that the metal burns. The combustion of a metal is the same reaction as its rusting. However, combustion is a rapid oxidation, whereas rusting is slower. Sodium, potassium, and magnesium burn readily when heated in air.

$$2Na + O_2 \rightarrow Na_2O_2$$
$$2K + O_2 \rightarrow K_2O_2$$
$$2Mg + O_2 \rightarrow 2MgO$$

Flashlight bulbs contain aluminum foil in pure oxygen. Here combustion is almost instantaneous:

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

When iron rusts, the familiar brown ferric oxide is formed:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

However when iron wire or powder burns in oxygen, magnetic oxide of iron is the product:

$$3Fe + 2O_2 \rightarrow Fe_3O_4$$

The product of the rusting or the combustion of a metal is invariably a metallic oxide, *i.e.*, a binary compound of the metal and oxygen. Such oxides of metals are frequently called *basic oxides*. A ternary compound, one of three elements, is not an oxide even though it may contain oxygen, *e.g.*, $KClO_3$.

5. Nonmetallic, or Acidic, Oxides.—Nonmetals combine with oxygen to form *acidic oxides*. Here the rate of reaction is usually extremely slow until the temperature is high enough for the nonmetals to take fire. Carbon, sulfur, and phosphorus burn to form carbon dioxide, sulfur dioxide, and phosphorus pentoxide, respectively.

$$C + O_2 \rightarrow CO_2$$
$$S + O_2 \rightarrow SO_2$$
$$4P + 5O_2 \rightarrow 2P_2O_5$$

6. The Combustion of Hydrogen.—Of all the elements, hydrogen is unique. More like the metals in its reactions, it is, nevertheless, a gas under normal conditions. Its oxide, water, is also in many respects a unique compound. The combustion of hydrogen is a strongly exothermic reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

Oxyhydrogen flames were used for welding and cutting metals before the advent of the oxyacetylene torch.

7. The combustion of carbon and its compounds is of particular importance since these substances make up the bulk of our modern fuels. Coal, coke, and charcoal are essentially carbon. This element forms two oxides: the monoxide, CO, and the dioxide, CO_2. The former contains relatively more carbon and less oxygen than the latter. Hence if any carbonaceous fuel is burned in a rather limited supply of air, carbon monoxide is the chief product:

$$2C + O_2 \rightarrow 2CO$$

If the supply of oxygen (air) is generous, the monoxide will burn to the dioxide:

$$2CO + O_2 \rightarrow 2CO_2$$

The compounds of hydrogen and carbon, the so-called hydrocarbons, form another class of substances which are important commercial fuels. The simplest hydrocarbon is the gas methane, CH_4. It is the most important component of natural gas, one of the best of the fuel gases. It also occurs wherever vegetal matter decays in swampy places. Hence it is found as marsh gas and as the firedamp of the coal mines. When a hydrocarbon burns, first of all the hydrogen in its molecules combines with the oxygen of the air and forms water. Then, if there is a sufficient supply of air, the carbon will burn either to carbon monoxide or to carbon dioxide. In a very limited supply of air, therefore, methane will burn as follows:

$$CH_4 + O_2 \rightarrow C + 2H_2O$$

The carbon, set free in this way, is in the form of a very finely divided soot. It is called lamp black and is used in making India ink, printers' ink, and black varnish.

When the supply of air is less limited, carbon monoxide is formed

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$

and when the air is in excess, the following reaction takes place:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Petroleum and its distillation products, gasoline, kerosene, etc., are composed mainly of hydrocarbons. When these important fuels burn, the reactions are similar to those of methane. For example, the hydrocarbon heptane, C_7H_{16}, is one of the components of gasoline. Equations for its combustion are as follows:

$$C_7H_{16} + 4O_2 \rightarrow 7C + 8H_2O$$
$$2C_7H_{16} + 15O_2 \rightarrow 14CO + 16H_2O$$
$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$

Many fuels are composed of carbon, hydrogen, and oxygen, *e.g.*, wood and alcohol. Wood is composed mainly of a compound, cellulose, whose formula is some multiple of $C_6H_{10}O_5$. The formula for grain alcohol is C_2H_5OH. When these and other substances of a similar nature burn, water and carbon dioxide are the products:

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O$$
$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

8. The Danger of Incomplete Combustion.—We have learned that carbon monoxide is a product of the incomplete combustion of a fuel. This colorless, odorless gas is a deadly poison. Inhaled, it attacks the red blood corpuscles and so causes asphyxiation and death. The exhaust of an automobile engine is heavily charged with this gas. To run a motor in a small garage with the doors closed is suicidal. The victim usually is not aware of his danger until it is too late to help himself. An improperly designed or broken furnace may allow this gas to escape into the house in sufficient concentration to do damage especially after the fire has been banked for the night. When fresh coal has been shoveled onto the fire, the carbon dioxide, formed in the lower layers of burning coal, is changed to carbon monoxide by the coal that banks the fire:

$$CO_2 + C \rightarrow 2CO$$

The illuminating gas of most city gas plants contains a high percentage of carbon monoxide.

Resuscitation involves the administration of a mixture of 95 per cent oxygen and 5 per cent carbon dioxide to the victim. The carbon dioxide is needed to stimulate respiration.

9. Factors Influencing the Rate of a Reaction.—We are all aware of the fact that substances vary widely in the ease with which they can be set on fire and in the energy with which they burn. Some materials, like water, brick, and stone, will not burn at all. Others, like most of the metals, can be burned only with great difficulty. On the other hand, phosphorus must be kept under water out of contact with the air; otherwise it would catch fire at room temperature. The factors that determine the rate of a combustion reaction are those which influence reaction velocity in general. We know, of course, that the molecules must be in actual physical contact before they can react. That reaction does not occur every time they collide we have ample proof. Certain kinds of molecules will not react with certain other kinds at all.

In all other cases, only a certain percentage of the collisions between molecules results in interaction. In short, any condition which will increase the frequency with which molecules of the reactants collide and will increase the fraction of the collisions which result in reaction will increase reaction velocity.

10. Temperature.—An increase in temperature will increase the rate at which chemical reactions in general take place. We have seen (3-6) that a rise in temperature results in an increase in the velocity with which molecules move. Hence they will collide more frequently and with greater energy. The increased violence of the collisions tends to jar atoms apart and makes easier their rearrangement into molecules of the products. Combustion reactions are no exception. All combustion reactions are also exothermic so that the faster they go, the more heat they liberate and the higher the temperature. There is, therefore, an accumulative effect. Once started, fires are difficult to put out. Combustible materials, in general, can be safely stored in contact with the oxygen of the air although even at room temperature they are combining with it. However, at this temperature the reaction is so slow that, except under extraordinary circumstances, the heat liberated is conducted and radiated away from the fuel as fast as it is formed, and the temperature does not rise. However, if for some reason the heat of reaction is prevented from escaping, the temperature will rise, the reaction will go

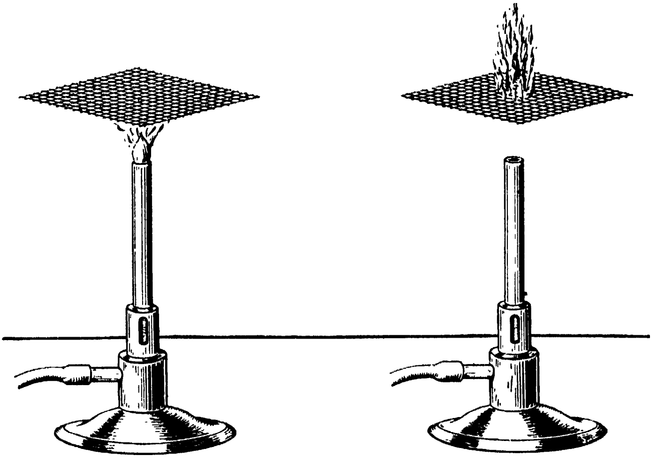

FIG. 15.—The heat-conducting and radiating properties of iron-wire gauze.

faster and faster, producing increasingly greater amounts of heat and a fire will be the result. Spontaneous combustion of oil-soaked rags, of newly cut hay, or even of coal in poorly ventilated coalbins is of such an origin.

However, a combustible substance must usually be heated before it will take fire. A given fuel must be heated to a certain temperature before its combination with the oxygen of the air proceeds so rapidly that the heat of reaction is sufficient to maintain a temperature at which the reaction is self-sustaining and emits light. This temperature is called the ignition point, or kindling temperature, of the substance and depends to a great extent on its state of subdivision. If a burning substance is cooled below its kindling temperature, combustion ceases. This can be easily demonstrated by a simple experiment with a piece of wire gauze and a Bunsen burner (Fig. 15). If the gauze is held some two or three inches above the tip of the burner, the gas turned on, and a burning match applied to the gas stream above the gauze, the gas will ignite above the gauze but not below it. The heat of the burning gas is conducted and radiated away so rapidly by the gauze that the gas underneath is below its kindling temperature. If the gauze is brought downward into a Bunsen flame, no flame will appear above the gauze although unburned gas passes through as can be demonstrated by applying a lighted match.

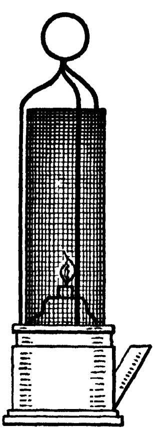

Fig. 16.—Miner's safety lamp.

The cooling power of a piece of wire gauze was appreciated by Sir Humphry Davy and incorporated in his miner's safety lamp (Fig. 16). The wire gauze permits the oxygen of the air, necessary for the flame of the lamp, to pass freely through, but prevents explosive mixtures of firedamp and air outside the lamp from being heated to their kindling temperature by the flame of the lamp.

11. Surface.—The combustion of a solid fuel is a reaction that takes place at the interface between two phases, *viz.*, the solid fuel and the gaseous oxygen. The rate of any such reaction is proportional to the extent of surface between the two phases, as this is the only area at which the reacting molecules are in contact. Consequently, the more finely divided a fuel is, the greater will be the speed at which it burns. A match burns more readily than a log of wood, and straw burns faster than either. Pots and pans made of aluminum or iron do not burn, but these metals in powdered form burn readily in air at the temperature of the Bunsen burner. A fire is easier to start with pea coal than with egg coal. Powdered coal ought to give the hottest fire of all were it not for the fact that it packs and actually offers less surface to the air than the larger sizes. However, if powdered coal is blown out of a suitable nozzle, it can be burned very efficiently almost as if it were a gaseous fuel. Liquid fuels are more efficiently burned when mixed with air and blown out as a fine spray into the combustion chamber. This is the function of the carburetor in the motorcar engine.

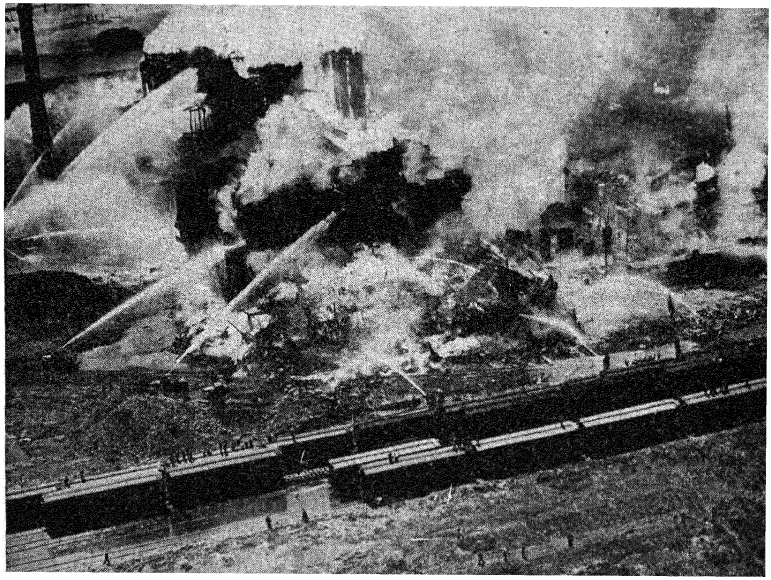

Fig. 17.—A series of grain dust explosions resulted in the loss of nine lives and caused a property loss of $3,500,000. (*Courtesy of National Fire Protection Association.*)

A very finely divided combustible dust suspended in air forms an explosive mixture that needs only a lighted match or an electric spark to set it off. The surface of the solid particles in such a dust is so enormous that their combustion is practically

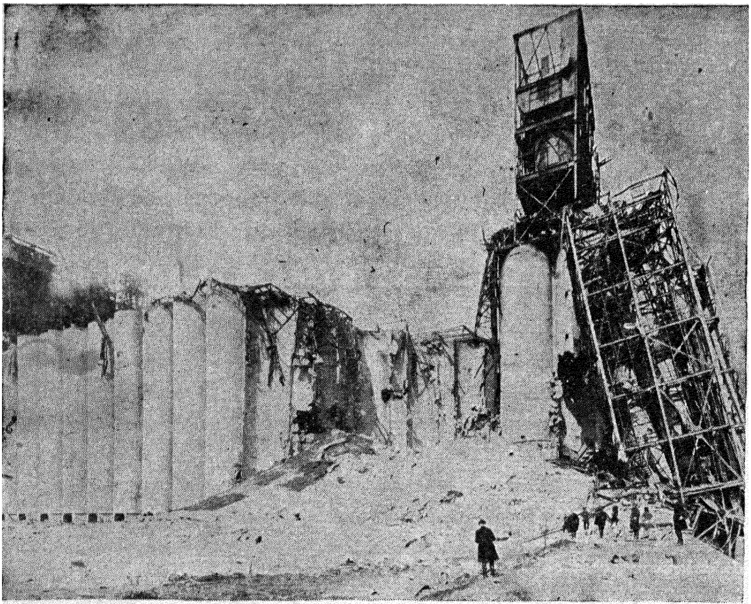

FIG. 18.—What a dust explosion did to the world's largest grain elevator. (*Courtesy of U.S. Department of Agriculture.*)

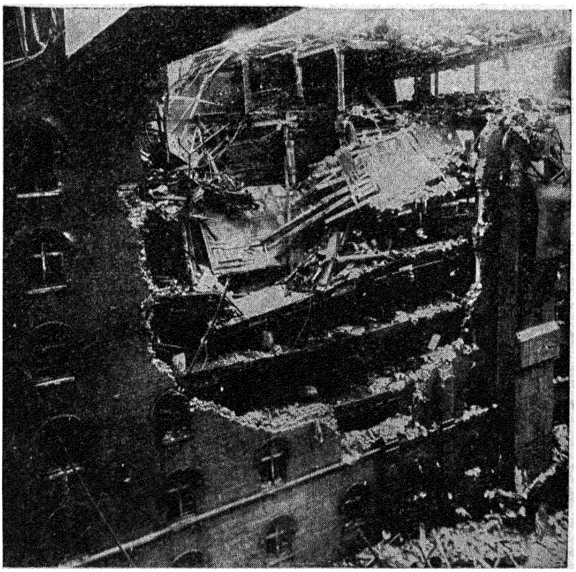

FIG. 19.—Sugar dust caused this explosion. Twelve men lost their lives. (*Courtesy of U.S. Department of Agriculture.*)

instantaneous. In 1924, forty-five lives were lost and about $3,000,000 worth of property was destroyed by dust explosions. Explosions of the dusts of coal, flour, starch, aluminum, bronze, dyestuffs, leather, spices, cork, hard rubber, and even dry milk have been reported.

12. Concentration.—Priestley's classic experiments with oxygen, which demonstrated that substances burn more readily in this gas than in air, are among the first recorded experiments on the influence of the concentration of oxygen on the rate of combustion. Air is only one-fifth oxygen. Hence oxygen in the pure form is five times as concentrated as it is in air at the same pressure. Oxygen molecules strike the surface of the burning substance proportionally more frequently, and the combustion takes place more vigorously. A piece of iron wire, which will not burn in air, burns brilliantly in pure oxygen.

The concentration of the combustible material, if it is a solid or a liquid, cannot be changed. However, if it is a gas, its concentration can be varied. Here again the greater its concentration, the greater its combustion rate. To burn a gas in air, we must first obtain a mixture of the two, which will burn, and then raise this mixture to its ignition temperature. An inflammable mixture may be regarded as one whose combustion will proceed rapidly enough with the liberation of sufficient heat to be self-supporting when once raised to its ignition temperature. The limits of inflammability of certain gas-air mixtures are given in Table 6.

TABLE 6.—LIMITS OF INFLAMMABILITY OF GASES IN AIR

Gas	Lower limit mixture, per cent	Upper limit mixture, per cent
Hydrogen	6.2	71.4
Carbon monoxide	6.3	71.2
Methane	5.8	13.3
Coal gas	7.0	21.0

The first gas burner consisted probably of a metal tube with a round opening. The gas in the tube leading to this burner contained so little air that it was not inflammable. At the opening, the fuel gas mixed with the air and inflammable mixtures were formed. Bunsen introduced the idea of mixing air with the gases prior to their ignition. The Bunsen burner, however, must not admit enough air through the hole near its base to produce an inflammable mixture in the tube for, if it does, the flame will strike back and burn at the base. This it often does when the gas is turned down to such an extent that proportions of gas and air are obtained which are inflammable. The average city gas requires the admixture of slightly more than four volumes of air to every one of gas for its complete combustion, whereas in the Bunsen burner these proportions are reversed. A burner of the Meker type is more efficient since it succeeds in mixing a greater proportion of air with the gas and yet in preventing the mixture from striking back. This is accomplished by a metal grid inserted at the burner outlet and by maintaining an outflow of the gas-air mixture greater than the rate at which a flame is propagated in the reverse direction.

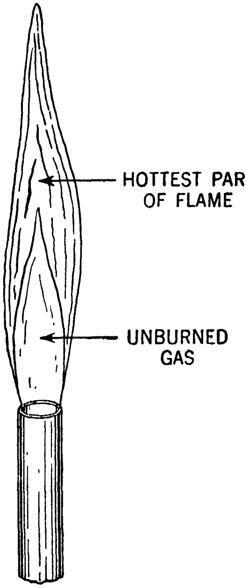

Fig. 20.—Bunsen burner flame.

13. Flames.—A flame is produced whenever an exothermic reaction between gases takes place so rapidly that they become luminous. The familiar form which a flame takes is the result of the way in which the gases are brought together. When a fuel gas is to be burned, it is projected out of a suitable burner into the air. Under such circumstances, the zone in which the fuel gas reacts with the oxygen of the air is marked by the flame. When we speak of a fuel gas burning and of air as supporting combustion, we do so because of the accident of circumstance that originally placed oxygen in the atmosphere. If our atmosphere were illuminating gas, we should be storing air in gas tanks and burning it from Bunsen burners.

The shape of the gas flame is that of a hollow cone, surrounded by a luminous envelope (Fig. 20). The inner cone consists of gas, as yet unburned, which has not come in contact with the oxygen of the air. The luminous envelope marks the zone in which the combustion reactions are taking place. This is the part of the flame where the temperature is the highest. All flames are more or less luminous. Some, however, like those of burning hydrogen and carbon monoxide, are nearly invisible in a brightly lighted room and give out only a pale bluish light in a dark room. Such flames are spoken of as nonluminous. Another type of flame is more brilliantly luminous, giving out a bright yellow light. These are opaque and hence more readily seen. They contain solid particles of carbon which have been heated to incandescence. Nonluminous flames are very poor radiators of heat. On the other hand, luminous flames, because of the incandescent solid particles suspended in them, are good radiators. The flames in gas stoves, used to heat rooms, should be of this type or should consist of nonluminous flames which are directed against asbestos or firebrick.

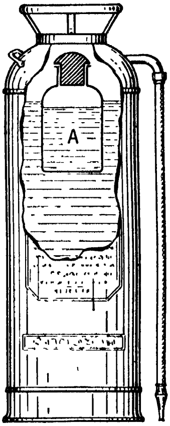

FIG. 21.—A soda-acid fire extinguisher.

14. Extinguishing Fires.—We have seen that two things are necessary in order that a fuel burn—the oxygen of the air and a temperature greater than its kindling temperature. Conversely, to put a fire out one has only to prevent in some way the air from coming in contact with the burning material or to lower the temperature to below the kindling temperature. Water acts in both ways. The first type of fire extinguisher invented shot out of its nozzle a stream of water, heavily charged with carbon dioxide. The former cooled the burning substance and the latter, a very dense gas, blanketed it from the oxygen of the air. Such an extinguisher is shown in cross section in Fig. 21. The bottle A is filled with sulfuric acid and the rest of the container with a concentrated solution of sodium bicarbonate, $NaHCO_3$. When the extinguisher is inverted, the chemicals mix and the following reaction takes place:

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O + 2CO_2$$

A later type is filled with a noninflammable liquid, carbon tetrachloride, CCl_4, which vaporizes when squirted on a fire, forming an exceedingly dense blanket of vapor over the burning material. Its vapors are poisonous, however, so that a room should be well aired out after such an extinguisher has been used.

Yet another type puts out a fire with a foam of carbon dioxide bubbles which is generated by mixing solutions of sodium bicarbonate and aluminum sulfate with a little licorice to make the form more stable. Recently, cylinders of liquid carbon dioxide have been put on the market as fire extinguishers. Their success in extinguishing fires is due to the blanketing effect of carbon dioxide gas and to the intense chilling effect of carbon dioxide snow which forms when the gas is liberated. After doing its bit, the carbon dioxide evaporates away completely, spoiling nothing with which it has been in contact.

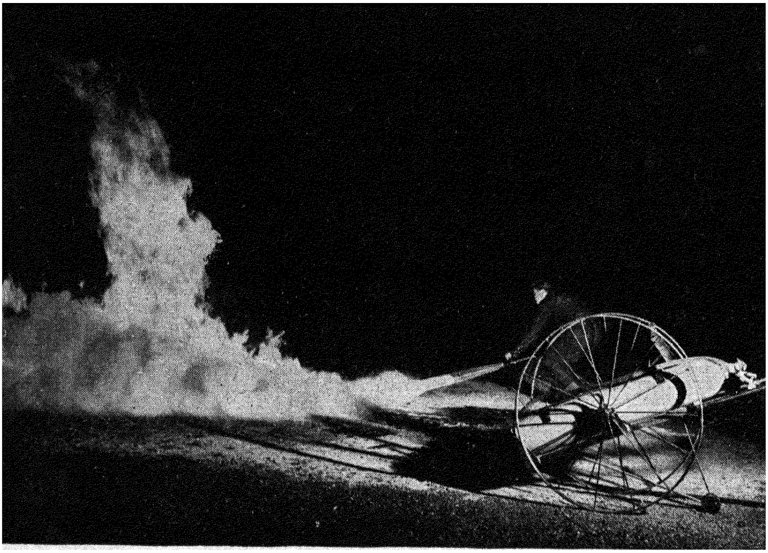

FIG. 22.—Carbon dioxide fire extinguisher in action. (*Courtesy of Walter Kidde & Company.*)

15. Fireproof Substances.—Only those substances which are made up of elements combined with the maximum amount of oxygen atoms that they can hold in chemical combination are absolutely fireproof. Water and carbon dioxide cannot burn, for they are the products of the complete combustion of hydrogen and carbon, respectively. Sand (SiO_2) and all the silicates derived from it are noncombustible for the same reason. These substances in the form of brick, glass, building stone, cement, etc., are the most important fireproof building materials. The structural ironwork of a skyscraper is scarcely to be considered as combustible, yet, in a more finely divided form iron will burn readily in oxygen and even in air. On the other hand, wood, rubber, and many other organic substances contain carbon atoms capable of uniting further with oxygen and are, therefore, combustible.

EXERCISES

1. From the following equation, calculate the weight of magnesium oxide formed when 1 g. of this metal burns:

$$2Mg + O_2 \rightarrow 2MgO$$

Does the calx weigh more or less than the metal of which it is the combustion product? Does your result substantiate the phlogiston theory?

2. Why was Lavoisier one of the most important men of his time?

3. What is a basic oxide? An acidic oxide?

4. Write formulas for 10 basic and 5 acidic oxides.

5. Give one reason for believing that water is a stable compound.

6. What poisonous gas is found among the products of combustion of a carbonaceous fuel?

7. Write equations for the combustion of the hydrocarbon hexane, C_6H_{14}, in a very limited supply, a moderate amount, and an excess of oxygen.

8. Why does sulfur burn more rapidly in pure oxygen than in air?

9. Why do wood shavings burn more rapidly than a log?

10. A chemical reaction takes place between two liquids which do not dissolve in each other. Suggest two methods by which the rate at which they react may be increased.

11. A small amount of gasoline is burning in a beaker. How would you put out the fire?

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CHAPTER NINE

VALENCE

The formula for the molecule of every compound had to be determined originally by methods that we have discussed in Chap. 5 (page 35). Here the information required is an analysis of the compound, the atomic weights of its constituent elements, and, if possible, its molecular weight. Each new compound, after it has been isolated from natural materials or prepared for the first time in chemistry research laboratories, must be subjected to analysis and its molecular weight determined before its formula may be established. If the formulas so determined had to be memorized with no additional help, the plight of a chemistry student would be sad indeed. However, this is not the case. A knowledge of valence comes to our aid and enables us to write formulas of inorganic compounds without committing each to memory. Hence the subject of this chapter will prove essential to our study of chemistry.

1. Valence.—A study of the formulas of the compounds in the following table, all of which were originally derived by methods that we have been discussing, will reveal an interesting relationship, a knowledge of which will be of great value. The formulas in the first column show clearly that the elements chlorine, oxygen, nitrogen, and carbon possess different powers of holding the atoms of hydrogen in combination. The oxygen atom, for example, evidently possesses twice the combining power of chlorine, for it can hold in chemical union twice as many hydrogen atoms. Similarly, nitrogen and carbon atoms possess, respectively, three and four times the combining power of chlorine.

I	II
HCl, hydrogen chloride	$NaCl$, sodium chloride
H_2O, hydrogen oxide	$CaCl_2$, calcium chloride
H_3N, hydrogen nitride	$AlCl_3$, aluminum chloride
H_4C, hydrogen carbide	$SnCl_4$, tin chloride

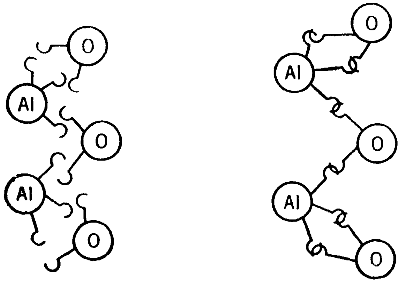
With a little thought, it will also become apparent that hydrogen and chlorine have the same combining power since one atom of one is combined with one atom of the other. In the same way, hydrogen has half the combining power of oxygen, one-third that of nitrogen, and one-fourth that of carbon. Since no compound of hydrogen and another element has ever been found in whose molecules one atom of hydrogen is combined with more than one atom of the other element, no other element has a lesser combining power than hydrogen. Many elements have the same combining power, *e.g.*, chlorine, but none has a lesser one. The combining power of the atom of an element is called its *valence.* To hydrogen has been assigned a valence of 1; and on this basis the valence of the other elements may be defined. Oxygen, for example, has a valence of 2, since it combines with two univalent hydrogen atoms; nitrogen, on the same basis, is trivalent; and carbon, tetravalent. All elements, however, do not combine with hydrogen. Certain metals, for example, form no hydrides. Fortunately, these elements will combine with chlorine and, since the latter is univalent, their valence may be defined on this basis. The formulas in column II show that sodium is univalent; calcium, divalent; aluminum, trivalent; and tin, tetravalent. *The valence of an element, therefore, is equal to the number of hydrogen or chlorine atoms with which one of its atoms combines.*

2. Derivation of Formulas from Valences.—The formula for every compound must originally be derived by methods that we have already discussed. The valence of an element is then derived from a knowledge of the formulas of its compounds. Nevertheless, after the valences of the elements have been determined, it is possible to derive the formulas for their compounds from this knowledge. Let us see how this can be done. We have just learned that the valence of calcium is 2 and that chlorine is univalent. How is it possible to derive the formula for their compound, calcium chloride, from this information? One atom of calcium, with its valence of 2, will combine with two univalent chlorine atoms. Hence the formula is $CaCl_2$. As another example, let us derive the formula for aluminum oxide from our knowledge that the valence of aluminum is 3 and that of oxygen, 2. In this case, two trivalent aluminum atoms will combine with three divalent oxygen atoms and, therefore, the formula is Al_2O_3. In general, the rule to follow is that the valence of each element multiplied by the number of its atoms is the same in each case. Thus the valence of aluminum, 3, times the number of its atoms, 2, is equal to the valence of oxygen, 2, multiplied by the number of its atoms, 3.

3. Elements of More Than One Valence.—In developing the law of multiple proportions, it was pointed out that in some instances two elements will combine in more than one proportion to form more than one compound. Iron and chlorine, for example, form two compounds: ferric chloride, $FeCl_3$, and ferrous chloride, $FeCl_2$.* In this and in similar cases, one of the elements will have a different valence in each compound. In the example given, iron is trivalent in ferric chloride and divalent in ferrous chloride. The behavior of iron in this respect is not limited to its compounds with chlorine alone, but gives rise to two more or less complete series of compounds in one of which iron is divalent and in the other, trivalent. There are, for example, two oxides of iron, FeO and Fe_2O_3; two bromides, $FeBr_2$ and $FeBr_3$; etc.

4. Valence Bonds.—In order to picture how the elements are joined in a compound, chemists in the past imagined that each atom possesses a number of hooks equal to its valence and that, when atoms unite, they are held together by means of these hooks. Thus a graphical picture of the hydrogen chloride, water, and aluminum oxide molecules could be represented as follows:

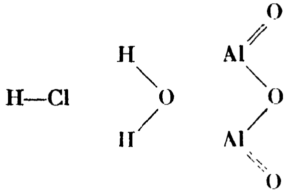
HYDROGEN CHLORIDE WATER



ALUMINUM OXIDE

FIG. 23.—Valence bonds.

A linkage between atoms, formed in this way, is called a valence bond. The hooks are usually omitted and the bonds represented by a straight line.



Such graphical pictures of how atoms are joined are called structural formulas. In such formulas the number of bonds attached to each atom must be equal to its valence. It must not for a moment be supposed that atoms are actually linked by any such physical hooks or bonds as we have just discussed. Such linkages give only a convenient thought model of the structural framework of a molecule.

5. A Survey of Atomic Structure.—Until recently, scientists had no clear picture of the nature of valence bonds. With an increasing knowledge of the structure of atoms, there has come a theory of the nature of valence which is of the greatest interest and significance. Although this theory will be discussed in detail in a later chapter, we may borrow from it certain ideas that will make it easier to apply our knowledge of valence.

We have mentioned (3-2) that three subatomic particles, the proton, the electron, and the neutron, are the structure units in the atoms of all the elements. The proton bears a unit charge of positive electricity and the electron an equal negative charge. The neutron, as its name implies, is not charged. The neutron and the proton are of nearly equal weight, but the electron is much lighter. Every atom is very much like a miniature solar system. Its nucleus, corresponding to the sun, is made up of protons and neutrons and hence is positively charged (Why?) and the massive part of the atom (Why?). In the uncombined atom, electrons, equal in number to the protons in the nucleus, are arranged more or less like planets about the nucleus. The uncombined atom is, therefore, electrically neutral since the number of positive charges on the nuclear protons is exactly equal to the number of negative charges on the planetary electrons. As we shall see later, the number of charges on the nucleus determines the element to which the atom belongs. With this hasty survey, we may consider further the nature of valence.

6. Electrovalence.—When atoms combine, their planetary-electron systems but not their nuclei are involved. When metals combine with nonmetals, each metal atom *loses* a number of electrons equal to its valence and hence acquires an equal *positive charge.* Each nonmetal atom *gains* a number of electrons equal to its valence and hence acquires an equal *negative charge.* Since oppositely charged particles attract one another, the oppositely charged metal and nonmetal atoms are held together in the compound by this electrical force of attraction known as a *Coulomb force.* The *charged metal and nonmetal atoms are called ions.* This type of bonding is called ionic valence, or electrovalence.

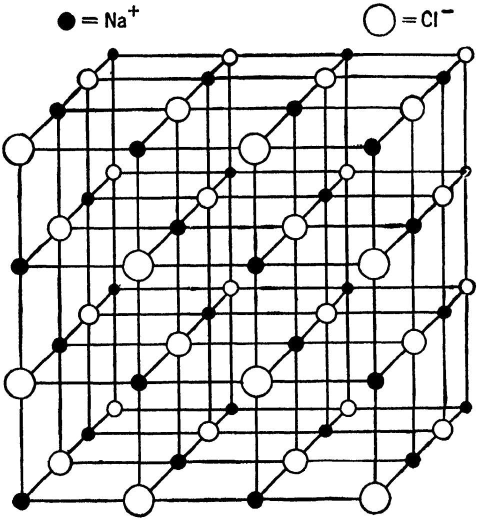


FIG. 24.—Crystal structure of sodium chloride.

When the metal sodium combines with the nonmetal chlorine, each univalent sodium atom loses a single electron which some chlorine atom gains, and a sodium ion (Na^+) and a chloride ion (Cl^-) are formed. The compound sodium chloride must be composed of equal numbers of sodium and chloride ions. When the divalent metal calcium reacts with chlorine, each calcium atom loses two electrons and becomes a calcium ion (Ca^{++}). Since chlorine is univalent, its atom can gain only one electron. Hence two chlorine atoms gain the two electrons lost by a single calcium atom. Therefore, the compound calcium chloride is made up of twice as many chloride ions as calcium ions.

The Coulomb forces of attraction, acting between the oppositely charged ions of an electrovalent compound, are relatively strong. Hence such compounds are invariably solids under normal conditions. Methods have been developed by which the spacing and arrangement of the structure units in the crystal lattice of a solid may be determined. When crystals of sodium chloride are thus analyzed, the structure shown in Fig. 24 is revealed. Here, sodium and chloride ions are arranged alternately at the corners of cubes. Each sodium ion is equidistant from six chloride ions and vice versa. Obviously, the ions are not paired in molecules of NaCl, although there are equal numbers of each kind of ion in the whole crystal. The formula NaCl is strictly speaking not that of the molecule of sodium chloride since *no molecules exist in the crystal structure of an electrovalent compound.* Rather, NaCl means that there are equal numbers of sodium and chloride ions in the crystals of sodium chloride. Similarly, $CaCl_2$ indicates that there are twice as many chloride as calcium ions in the electrovalent compound calcium chloride. Electrovalent compounds are called *salts.*

7. **Covalence.**—Atoms may combine in another way by sharing a pair of electrons. The reasons why such a shared electron pair should serve as a bond to hold atoms together will be discussed later, but some information as to the properties associated with such bonds will be useful now. Usually each atom contributes one electron to the shared pair. If the pair is located halfway between the atoms that it holds together (Fig. 25*a*), each atom may be considered to have lost half the charge on its electron and to have gained half the charge on the electron that the other atom contributes to the pair. This is the case when the same kind of atoms are linked by covalent bonds as, for example, in molecules of uncombined hydrogen (H_2). If, however, the atoms are dissimilar, the electron pair will be nearer one of the atoms. This atom will have lost less than half of its electron and gained more than half of the electron from the other atom. Hence, it is the more negative of the two atoms. However, it will not be a negative ion since it has not gained complete possession of the electron from the other atom. On the other hand, the atom from

which the electron pair is more remote will have lost more than half its electron and will bear a residual positive charge.

In the molecule of hydrochloric acid (Fig. 25*b*), the shared electron pair is nearer the chlorine atom. Hence the latter is more negative and the hydrogen atom, more positive. Molecules like hydrochloric acid in which one part is more positive and the other more negative are *dipoles.* Valence bonds with shared electrons nearer one atom than the other are called *polar bonds.*

Compounds whose atoms are linked by covalent bonds are made up of neutral molecules. Between such molecules, relatively weak van der Waals forces operate so that molecular compounds tend to be gases or liquids under normal conditions. The more polar the molecules and the greater their weight, the greater are the van der Waals forces between them.

(*a*) NON-POLAR (*b*) POLAR

FIG. 25.—Two types of covalence. All electrons have been omitted except the pair which form the bond.

Hydrogen atoms are invariably linked to other atoms by covalent bonds. Thus many hydrogen compounds, *e.g.*, hydrochloric acid, HCl, ammonia, NH_3, and methane, CH_4, are gases. Nonmetal oxides are also molecular compounds.

8. Valence Number.—We have pointed out that the charge on an ion is its valence. In molecular compounds the valence of an atom is equal to the number of electron pairs that it shares with the atoms attached to it. Further, if the covalence is polar, a positive or negative sign is attached to the numerical value of its valence. We then have so-called *valence numbers* for atoms in molecules. Thus the valence numbers of hydrogen and chlorine atoms in hydrochloric acid molecules are +1 and −1, respectively. We must emphasize, however, that neither atom is an ion.

RULES FOR THE SIGN OF THE VALENCE

1. The valence of a free, uncombined element is zero.
2. The valence of a metal atom is positive in all its compounds.
3. The valence of a nonmetal atom is negative in its compounds with metals but positive in its compounds with oxygen.

The valence numbers of the common elements are given in Table 7. A knowledge of these valences will help you to derive the formula of any binary compound if you remember that *the molecule of a covalent compound is always electrically neutral* and that *the algebraic sum of the charges on the ions in the formula of a salt is zero.*

A few examples will illustrate the use of the table. The formula for aluminum chloride must be $AlCl_3$ since one aluminum atom, +3, will neutralize three chlorine atoms, each −1. Here we use the negative valence of chlorine since it is combining with a metal.

TABLE 7.—VALENCE NUMBERS OF THE COMMON ELEMENTS[1]

Metals	Valence	Nonmetals	Valence
Hydrogen (H)	+1	Chlorine (Cl)	−1
Sodium (Na)	+1	Bromine (Br)	−1
Potassium (K)	+1	Iodine (I)	−1
Silver (Ag)	+1	Oxygen (O)	−2
Magnesium (Mg)	+2	Sulfur (S)	−2, +4, +6
Calcium (Ca)	+2	Nitrogen (N)	−3, +3, +5
Zinc (Zn)	+2	Phosphorus (P)	−3, +3, +5
Lead (Pb)	+2	Carbon (C)	−4, +4
Aluminum (Al)	+3	Silicon (Si)	−4, +4
Mercurous (Hg)	+1		
Mercuric (Hg)	+2		
Cuprous (Cu)	+1		
Cupric (Cu)	+2		
Ferrous (Fe)	+2		
Ferric (Fe)	+3		
Stannous (Sn)	+2		
Stannic (Sn)	+4		

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[1] A more complete table will be found in the Appendix.

The formula for aluminum sulfide is Al_2S_3 since two aluminum atoms, each +3, will be needed for three sulfur atoms, each −2. When we try to derive the formula for an oxide of sulfur, we face a new problem. Since the valence of oxygen is −2, the valence of sulfur must be positive, or a neutral molecule would be impossible. There are two positive valences of sulfur, +4 and +6. Hence sulfur forms two oxides SO_2 and SO_3 in which its valences are +4 and +6, respectively.

9. Valences of Groups of Atoms.—The problem of deriving the formulas of ternary compounds, or those of three elements, seems at first sight to offer difficulties. The nitrate group, NO_3, is found in many different compounds of which the following are typical: HNO_3, $NaNO_3$, $Mg(NO_3)_2$, $Al(NO_3)_3$. If we assign to this group of atoms a valence of -1, formulas in which it appears are as easily derived as those of binary compounds. Compare the following series:

$\overset{+1}{\text{H}}\overset{-1}{\text{Cl}}$	$\overset{+1}{\text{H}}\overset{-1}{\text{NO}_3}$
$\overset{+1}{\text{Na}}\overset{-1}{\text{Cl}}$	$\overset{+1}{\text{Na}}\overset{-1}{\text{NO}_3}$
$\overset{+2}{\text{Mg}}\overset{-1}{\text{Cl}_2}$	$\overset{+2}{\text{Mg}}\overset{-1}{(\text{NO}_3)_2}$
$\overset{+3}{\text{Al}}\overset{-1}{\text{Cl}_3}$	$\overset{+3}{\text{Al}}\overset{-1}{(\text{NO}_3)_3}$

The nitrate group is in every respect equivalent to the chlorine atom. Note that only when more than one such group appears in a formula are parentheses used. Table 8 contains the names and valence numbers of the common group atoms. A more complete table will be found in the Appendix.

TABLE 8.—VALENCES OF COMMON GROUPS

Group	Valence	Group	Valence
Ammonium (NH_4)	+1	Sulfite (SO_3)	−2
Hydroxide (OH)	−1	Sulfate (SO_4)	−2
Nitrite (NO_2)	−1	Carbonate (CO_3)	−2
Nitrate (NO_3)	−1	Silicate (SiO_3)	−2
Chlorate (ClO_3)	−1	Phosphite (PO_3)	−3
Acetate ($C_2H_3O_2$)	−1	Phosphate (PO_4)	−3

These groups, except in the compound in which they are combined with hydrogen, are ions. The atoms within the group are linked by covalent linkages. However, the group as a whole has either completely lost (*e.g.*, NH_4^+) or gained (*e.g.*, NO_3^-) one or more electrons.

It must always be remembered that such a charged group of atoms is obviously not a neutral molecule of a substance but only part of a substance. Thus, although there are many metallic nitrates, *e.g.*, $NaNO_3$ and $Al(NO_3)_3$, which may be found on reagent shelves or in the stockroom, you will never find a bottle of nitrate.

Another point that will be of use later on is that the valence of a group of atoms is equal to the algebraic sum of the valence numbers of the atoms in the group. Thus in the nitrate group there are three oxygen atoms, each -2, and one nitrogen atom, $+5$. Thus

$$\begin{array}{rcr} 3 \times -2(\mathrm{O}) & = & -6 \\ 1 \times +5(\mathrm{N}) & = & +5 \\ \hline \mathrm{NO_3} & = & -1 \end{array}$$

Conversely, the valence of any nonmetal in an oxygen-containing group may be easily determined from the valence of the group and the knowledge that the valence of oxygen is always -2. Thus, the valence of the sulfur atom in the sulfate group must be $+6$ since the combined valence numbers of the four oxygen atoms is -8 (4×-2) and that of the group as a whole, -2:

$$\begin{array}{rcr} 4 \times -2(\mathrm{O}) & = & -8 \\ (\mathrm{S}) & = & ? \\ \hline \mathrm{SO_4} & = & -2 \end{array}$$

10. Nomenclature.—The rules for naming compounds are easily mastered. They are as follows:

1. In naming a compound, the name of the positive atom or group is given first followed by that of the negative atom or group.

2. Since positive atoms are usually those of metals, the name of the free metal is used unless it may exist in either of two valences. In such cases, the suffix *-ous*, added to the stem of the classical name of the metal, indicates the lower valence and the suffix, *-ic*, the higher valence. The chloride of iron, $FeCl_2$, is thus ferr*ous* chloride since $+2$ is the lower valence of iron. $FeCl_3$ is fer*ric* chloride.

3. If the negative part of a substance is composed of one kind of nonmetal atom, the ending *-ide* is used. In those cases in which there exists only one negative group of the nonmetal and oxygen, the suffix *-ate* is used, *e.g.*, $CO_3^{=}$ is carbonate. If two such groups exist, *e.g.*, $SO_3^{=}$ and $SO_4^{=}$, the name of the group with the lesser number of oxygen atoms ends in *-ite* and that of the one with the greater number ends in *-ate*. Thus $SO_3^{=}$ is sulfite and $SO_4^{=}$, sulfate.

EXERCISES

1. Define valence.

2. What are the valence numbers of the elements whose symbols are in italics in the following formulas?

$\mathit{Fe}\mathrm{Cl}_3$, $\mathrm{Fe}\mathit{Br}_3$, $\mathit{Na}\mathrm{Br}$, $\mathrm{Na}_2\mathit{S}$, $\mathrm{Na}\mathit{N}\mathrm{O}_3$, $\mathrm{Fe}\mathit{P}\mathrm{O}_4$, $\mathrm{Na}_2\mathit{S}\mathrm{O}_4$, $\mathrm{Fe}(\mathit{N}\mathrm{O}_3)_3$, $\mathrm{K}\mathit{Mn}\mathrm{O}_4$, $\mathrm{Na}_2\mathit{Cr}_2\mathrm{O}_7$.

3. Write formulas in each of the squares of the following table.

	Cl^{-1}	S^{-2}	NO_3^{-1}	SO_4^{-2}	Br^{-1}	PO_4^{-3}	ClO_3^{-1}	$Cr_2O_7^{-2}$
Na^{+1}								
Al^{+3}								
Ca^{+2}								
Fe^{+2}								
K^{+1}								
Zn^{+2}								
Ag^{+1}								
Fe^{+3}								

4. Distinguish between ionic valence and covalence; also between polar and nonpolar covalence.

5. What is an ion?

6. Define a molecule in terms of the type of valence linking its constituent atoms.

7. What are the properties of salts. How are these properties explained in terms of the type of valence and the forces operating between its structure units.

8. Define Coulomb and van der Waals forces?

9. Explain the characteristic properties of molecular compounds in terms of the theory of the nature of valence.

10. A certain pure compound of carbon and chlorine is a liquid at room temperature. Will it conduct electricity? Explain your answer.

CHAPTER TEN

HYDROGEN

Hydrogen occupies a unique position among the elements. It has the lowest atomic weight, and its atom has the simplest structure, consisting of a single proton and one planetary electron. A gas under normal conditions, its density is the lowest of any substance. In its reactions it acts like metal and has a valence number of +1 in all its compounds. Yet the compounds in which hydrogen is combined with nonmetals differ markedly from the analogous one of metals with nonmetals. The hydrogen atom is invariably linked to other atoms by covalent bonds. Unlike metal atoms, it never completely loses its planetary electron and, therefore, never exists as a simple hydrogen ion.

1. **History.**—Hydrogen is by far the least difficult of any of the elementary gases to prepare. As early as the sixteenth century Paracelsus records the preparation of a gas, which must have been hydrogen, by the action of sulfuric acid on iron. Since this was before Boyle had stated the modern definition of an element, Paracelsus may be forgiven for not recognizing it as such. Lord Henry Cavendish was the first (1781) to prove that this "inflammable air" burned in air to form water. Finally, two years later the great Lavoisier gave it the name hydrogen, or water former.

2. **Occurrence.**—Because of the ease with which it burns, little free hydrogen exists on the earth. Less than one part is found in 200,000 parts of air. At the high temperature of the stars, however, its combustion product, water, is unstable, and therefore, the free element exists. Water is its most abundant compound of which one-ninth by weight is hydrogen. Further, it is found in all acids and metal hydroxides. Combined with the element carbon, it occurs in all hydrocarbons including those of natural gas and petroleum. Finally it is found in nearly all organic compounds.

3. **Laboratory Preparation.**—Hydrogen may be prepared in the laboratory by the following methods:

a. The electrolysis of water offers a convenient method by which both oxygen and hydrogen may be prepared simultaneously.

$$2H_2O \rightarrow 2H_2 + O_2$$

b. The action of water on very active metals, such as potassium and sodium, is too violent to be useful. The metal atoms replace only one of the two hydrogen atoms in the water molecules with which they react:

$$2Na + 2HOH \rightarrow 2NaOH + H_2$$

By writing the formula for water as HOH, the nature of the reaction as one of replacement becomes more apparent.

Slightly *less active metals* like aluminum, iron, and zinc *replace* the hydrogen in water when steam is passed *over the red-hot metal.* In these cases, the oxide of the metal is formed

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2{}^*$$

since metal hydroxides, other than those of sodium and potassium, are unstable at red heat.

c. The action of acids on moderately active metals like zinc and iron is the most convenient method of preparing hydrogen in moderate amounts in the laboratory.

Before we consider this important method in detail, it will be well to learn something about acids.

4. Acids may be recognized by their effect on the color of indicators. These are organic substances that assume characteristic colors in acid solutions. Of these the most familiar is litmus, which assumes a red color in solutions that are acidic. Litmus paper is an absorbent paper that has been dipped in a rather concentrated litmus solution and dried. If the litmus solution is acidic, its color and that of the litmus paper, prepared from it, is red. If the solution is other than acidic, *i.e.*, basic, the resulting litmus paper is blue. Solutions that are acidic turn blue litmus paper red. Those which are basic turn red litmus paper blue.

An acid may be readily recognized by its formula. One or more hydrogen atoms make up the positive part of the formula, and the negative portion is a nonmetal atom or a negative group.

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* The student is urged to write and balance every equation in this chapter. Derive the formula for each compound from the valences of its elements.

Thus HCl, H_2S, HNO_3, H_2SO_4, and H_3PO_4 are formulas for the molecules of acids.

5. Nomenclature of Acids.—A special system is used in naming acids. If the negative portion of its formula is a single nonmetal atom the prefix *hydro-* and the suffix *-ic* are added to the name of the nonmetal followed by the word acid. Thus HCl, HBr, and H_2S are hydrochloric acid, hydrobromic acid, and hydrosulfuric acid, respectively. If the negative part of the formula is an oxygen-containing group of atoms, its name determines that of the acid. If the name ends in *-ate*, the suffix *-ic* is added to the name of the nonmetal in naming the acid. Thus H_2SO_4, in which the name of the negative group ($SO_4^{=}$ = sulfate) ends in *-ate*, is sulfuric acid. If the negative group's name ends in *-ite* the suffix *-ous* is used in naming the acid. H_2SO_3 (hydrogen sulfite) is sulfurous acid.

6. The Reaction of a Metal with an Acid.—We shall now return to a detailed consideration of this important laboratory preparation of hydrogen. Of the common metals only *copper, mercury,* and *silver will not liberate hydrogen* when treated with an acid. Of those which do react, the alkali metals potassium and sodium and the alkaline-earth metals barium, strontium, and calcium react too violently to serve as a practical means of preparing hydrogen. Zinc and iron are best adapted for this method of preparation. Of the common acids, *nitric acid cannot be used.*

TABLE 9.—THE COMMON ACIDS

Formula	Name by groups	Acid name
HCl	Hydrogen chloride	Hydrochloric acid
HBr	Hydrogen bromide	Hydrobromic acid
HI	Hydrogen iodide	Hydriodic acid
HNO_2	Hydrogen nitrite	Nitrous acid
HNO_3	Hydrogen nitrate	Nitric acid
$HClO_3$	Hydrogen chlorate	Chloric acid
$HC_2H_3O_2$	Hydrogen acetate	Acetic acid
H_2S	Hydrogen sulfide	Hydrosulfuric acid
H_2SO_3	Hydrogen sulfite	Sulfurous acid
H_2SO_4	Hydrogen sulfate	Sulfuric acid
H_2CO_3	Hydrogen carbonate	Carbonic acid
H_2SiO_3	Hydrogen silicate	Silicic acid
H_3PO_3	Hydrogen phosphite	Phosphorous acid
H_3PO_4	Hydrogen phosphate	Phosphoric acid

It attacks metals, and a gaseous oxide of nitrogen is the usual product (39-8). Because of its low cost and availability, dilute sulfuric acid is commonly used.

In the apparatus shown in Fig. 26, this acid and metallic zinc react according to the following equation:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$

and the hydrogen, which escapes as a gas (↑), is collected by the displacement of water. No heat is needed to start the reaction, but a few drops of cupric sulfate solution will act as a catalyst.

7. Commercial Preparation. Water offers a low-cost source for the commercial preparation of hydrogen. The cost and availability of a direct current of electricity usually preclude its commercial use in the electrolysis of water. However, if steam is passed through a bed of red-hot coals the following reaction takes place:

$$C + H_2O \rightarrow CO + H_2$$

The mixture of gaseous products, carbon monoxide and hydrogen, is used extensively as a fuel under the name of water gas. However, if hydrogen is desired, this mixture, enriched with more steam, is passed over a catalyst, a mixture of the oxides of iron, chromium, and thorium, at a temperature of about 500°C.

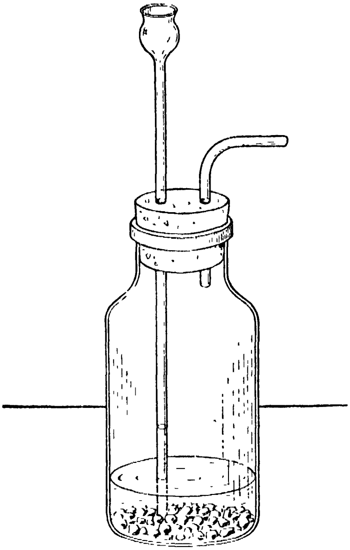

FIG. 26.—A hydrogen generator.

$$CO + H_2O \rightarrow CO_2 + H_2$$

Thus additional hydrogen is produced. The carbon dioxide in the resulting mixture is removed by bubbling the gas through a suitable absorbent.

Natural gas, mainly methane, CH_4, and other hydrocarbon gases, which are abundant products of petroleum refining, serve as rich sources of hydrogen. Mixed with steam, they are passed over suitable catalysts:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

The carbon monoxide in this mixture, as in the water gas, will react with more steam and yield additional hydrogen.

8. Properties of Hydrogen.—Hydrogen is a colorless gas which has no odor. However, impurities in the zinc and the sulfuric acid, used for its laboratory preparation, do release unpleasant-smelling gases which lead many students to associate their odor with hydrogen. Its density, *i.e.*, the weight of a unit volume, is the lowest of any gas under the same conditions. It is liquefied with difficulty since it must be cooled to below −239.9°C., its critical temperature (15-1), before liquefaction by increased pressure is possible. It is colorless as a liquid and as a solid. Hydrogen is only very sparingly soluble in water. Its molecules are diatomic.

9. The Relative Activity of the Metals.—In general, the ease with which a metal forms compounds and the energy liberated in the process is a rough measure of its activity. Reactions of the general type, by which hydrogen is prepared by the action of a metal on an acid, may be used to gain more information as to the relative activity of the metals. Such reactions are displacement reactions of the type

$$B + AX \rightarrow BX + A$$

If the metal B displaces the metal A, B is more active than A. The metals which displace hydrogen from acids are more active than hydrogen. On the other hand, copper, mercury, and silver, which do not displace hydrogen, are less active than hydrogen. This type of reaction is not limited to that of acids with metals. A similar reaction may take place whenever a metal is immersed in a water solution of a salt of another metal. A salt is an ionic compound composed of some metal, other than hydrogen, and some nonmetal or negative group. Thus $NaCl$, $Ca(NO_3)_2$, and $Al_2(SO_4)_3$ are salts. If a piece of zinc is immersed in a solution of cupric sulfate, zinc displaces copper:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

Therefore, zinc is more active than copper. However, when a piece of copper is placed in an aqueous solution of a zinc salt, no reaction takes place. By carrying out similar reactions with other pairs of metals, it is possible to place the metals in a series in the order of their relative activity. This series is called the *electro-*

motive series of metals, because its order can be determined with even greater accuracy by electromotive-force measurements of electrochemical cells (40-11).

In general, any metal will displace a metal, below it in the series, from salts of the latter. This series is a valuable aid to the chemist. In general, the more active a metal is, the less resistant it will be to the action of the weather and to the action of chemicals. The more active the free metal, the more stable are its compounds. On the other hand, the less active the free metal, the easier are its compounds to decompose.

THE ELECTROMOTIVE SERIES OF METALS

Potassium
Calcium
Sodium
Magnesium
Aluminum
Zinc
Iron
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Gold

10. Reactions of Hydrogen.—Hydrogen combines with far fewer elements than does oxygen. More metallic than nonmetallic, it reacts more readily with nonmetals than with metals. At ordinary temperatures it is rather unreactive, but at higher temperatures its reactions with active nonmetals proceed with explosive violence. Metallic hydrides, *e.g.*, NaH and CaH_2, are few in number, unstable, and relatively unimportant.

11. The combustion of hydrogen is a highly exothermic reaction:

$$2H_2 + O_2 \rightarrow 2H_2O + 136{,}740 \text{ cal.}^*$$

Here we encounter for the first time an additional use of equations. The above equation indicates that two molecules of water are formed when two molecules of hydrogen combine with one of oxygen. However, since moles of all substances contain the

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* A calorie is defined as that quantity of heat energy that will raise the temperature of 1 g. of water 1°C.

same number of molecules, the equation also gives us the information that two moles (36.032 g.) of water are formed when two moles (4.032 g.) of hydrogen react with 1 mole (32.000 g.) of oxygen. It is when these two moles of water are synthesized that 136,740 cal. of heat energy is liberated.

This energy was stored as potential energy in the molecules of free hydrogen and oxygen. After combination, the molecules of water must contain an amount of potential energy less by 136,740 cal. than did those of the free elements. When two moles of water are decomposed by electrolysis, an amount of electrical energy must be supplied equal to the heat energy liberated in their formation. Hence water is a stable compound. This is true, in general, of the compounds of active elements.

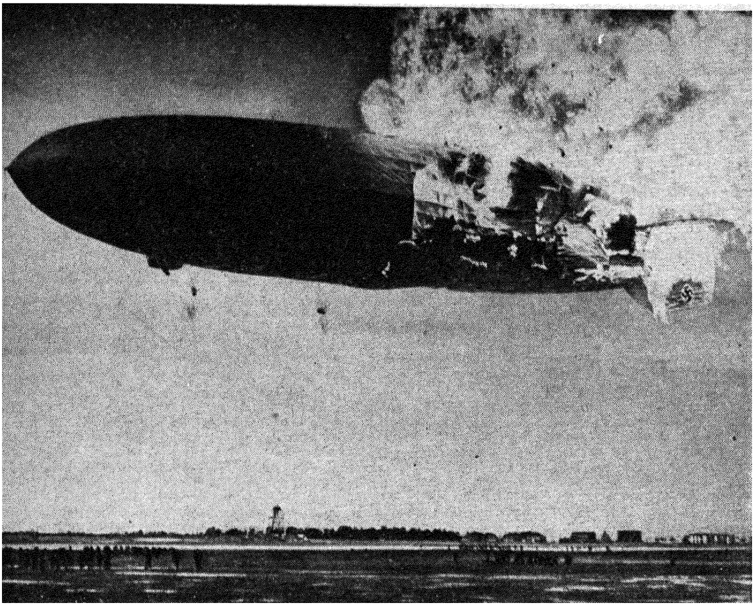

FIG. 27.—The combustion of hydrogen on a large scale. The airship *Hindenburg* was destroyed by fire on May 6, 1937. (*Courtesy of Press Association, Inc.*)

Hydrogen-air and especially hydrogen-oxygen mixtures are explosive. Hydrogen-air mixtures of greater than 71.4 per cent hydrogen contain too little air and those with less than 6.2 per cent contain too little hydrogen to be explosive (8-12). Pure hydrogen burns quietly in air with a blue flame. The burning of the airship *Hindenburg* was an example on a grand but terrible scale of this reaction. If the hydrogen in this ill-fated dirigible had been mixed with more than 29 per cent air, the result would have been a terrific explosion. Hydrogen generators at first contain air and are, therefore, filled with an explosive mixture. Flames should be kept away at this time. Gradually this air is displaced until pure hydrogen remains. Before the gas emerging from such a generator can be safely ignited, a sample should be collected in a test tube by water displacement. If this sample burns quietly at the mouth of the test tube, the gas coming from the generator may be ignited with safety. It is in any case a wise precaution to wrap a towel tightly around the generator. Since two volumes of hydrogen react with one of oxygen, mixtures of these proportions explode with maximum violence.

12. Reactions with Nonmetals.—The halogens fluorine, chlorine, bromine, and iodine are a group of closely related active nonmetals. Their activity decreases in the order named. Each of these elements combines directly with hydrogen:

$$H_2 + F_2 \rightarrow 2HF + 77{,}000 \text{ cal.}$$
$$H_2 + Cl_2 \rightarrow 2HCl + 44{,}000 \text{ cal.}$$
$$H_2 + Br_2 \rightarrow 2HBr + 17{,}000 \text{ cal.}$$
$$H_2 + I_2 \rightarrow 2HI - 13{,}000 \text{ cal.}$$

The product in each case is a gas and also an acid. Fluorine and hydrogen react violently at room temperature. Hydrogen-chlorine mixtures are stable if kept in the dark. Exposure to bright sunlight or to any intense source of light brings about an explosive reaction. Hydrobromic acid is formed when a mixture of bromine vapor and hydrogen is passed through a heated tube. Since hydriodic acid is formed with an absorption of energy, it is less stable than the free elements. Hence its direct synthesis from them is difficult.

Hydrogen combines directly with sulfur vapor to form hydrogen sulfide, or hydrosulfuric acid:

$$H_2 + S \rightarrow H_2S$$

The compound of nitrogen and hydrogen is the gas ammonia. Since this compound is not an acid, its formula is commonly written NH_3. The synthesis of this compound from the nitrogen of the air and hydrogen is one of great importance, since from the ammonia are prepared nitrogenous fertilizers, so essential to ensure our food supply, and nitric acid for the preparation of explosives. A mixture of nitrogen and hydrogen under a high pressure and a moderate temperature is passed over a catalyst:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

13. Reactions with Metal Oxides.—When hydrogen is passed through tubes containing the hot oxides of certain metals, water vapor and the free metals are formed. Oxides of the metals below zinc in the electromotive series behave in this way, *e.g.*,

$$\begin{aligned} Fe_2O_3 + 3H_2 &\rightarrow 2Fe + 3H_2O \\ CuO + H_2 &\rightarrow Cu + H_2O \end{aligned}$$

Although these are displacement reactions, they are not carried out under the same conditions as are those used to determine the order of activity of the metals (10-9). The electromotive series should be used to predict the course of those reactions only which may occur when a free metal is immersed in an aqueous solution of a salt of another metal.

14. Oxidation-reduction.—The majority of the reactions, which we have been considering, have involved valence changes of the elements entering into them. The term *oxidation* meant originally the addition of oxygen to an element. Since oxygen invariably has a valence number of -2 in its compounds, an element combined with it in an oxide must have a positive valence number. An element that unites with oxygen must suffer an increase in valence, since its valence before combination is zero. An element that burns or rusts is oxidized, and its valence is increased:

$$\overset{0}{C} + \overset{0}{O_2} \rightarrow \overset{+4}{C}\,\overset{-2}{O_2}$$

$$4\overset{0}{Al} + 3\overset{0}{O_2} \rightarrow 2\overset{+3}{Al_2}\overset{-2}{O_3}$$

Essentially these reactions are of the same type as the following:

$$2\overset{0}{Al} + 3\overset{0}{Cl_2} \rightarrow 2\overset{+3}{Al}\overset{-1}{Cl_3}$$

although in this reaction no oxygen is involved. The definition of the term oxidation was, therefore, enlarged to include any process in which *the valence number of an element is increased.* Invariably when an element suffers an increase in valence in a reaction, another element has its valence decreased in the same reaction.* Thus oxygen in the first two and chlorine in the last of the above reactions have decreased in valence. *Reduction is such a decrease in valence.* Oxidation and reduction occur simultaneously.

When hydrogen reacts with a metal oxide, *e.g.*,

$$\overset{+2}{\mathrm{Cu}}\overset{-2}{\mathrm{O}} + \overset{0}{\mathrm{H}_2} \rightarrow \overset{0}{\mathrm{Cu}} + \overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}}$$

hydrogen is oxidized and the metal reduced. In a displacement, such as

$$2\overset{0}{\mathrm{Al}} + 3\overset{+2}{\mathrm{Cu}}\overset{-2}{\mathrm{SO}_4} \rightarrow \overset{+3}{\mathrm{Al}_2}\overset{-2}{(\mathrm{SO}_4)_3} + 3\overset{0}{\mathrm{Cu}}$$

the more active metal (Al) is oxidized and the less active metal (Cu) is reduced.

15. Monatomic Hydrogen.—Hydrogen gas under ordinary conditions consists of diatomic molecules. However when this gas is passed through an electric arc, these diatomic molecules absorb enough energy to dissociate into single atoms:

$$\mathrm{H}_2 + 104{,}000 \text{ cal.} \rightleftarrows \mathrm{H} + \mathrm{H}$$

Thus to dissociate a mole (2 g.) of hydrogen into atomic hydrogen, 104,000 cal. of energy must be absorbed. This energy is stored as potential energy in the separated atoms. Such single atoms lead a transitory existence after they emerge from the arc. Colliding with one another, they pair up again and liberate their excess energy. If, however, they burn before recombination has taken place, an extremely hot atomic-hydrogen flame is produced. We can calculate the energy liberated in this reaction as follows:

$$\begin{array}{lr}
 & 2\mathrm{H}_2 + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O} + 136{,}740 \text{ cal.} \\
 & 4\mathrm{H} \rightarrow 2\mathrm{H}_2 \quad + 208{,}000 \text{ cal.} \\
\hline
\text{adding:} & 4\mathrm{H} + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O} + 344{,}740 \text{ cal.}
\end{array}$$

Such flames were first produced by Irving Langmuir of the General Electric Company and are used in welding.

16. Uses of Hydrogen.—Because of its low density, hydrogen has been used to give buoyancy to lighter than air craft. Its inflammability, however, has led to the use of helium in its place in this country (37-5). Its use in the oxyhydrogen blow torch to weld metals has been replaced by the hotter oxyacetylene flame.

The largest amount of hydrogen is used in the synthesis of ammonia (38-8). Large amounts are used in the manufacture of semisolid vegetable shortenings from cottonseed oil. Here hydrogen atoms are added to the molecules of the liquid oil, using metallic nickel as a catalyst. The conversion of low-grade coals into motor fuels and lubricants has been successfully accomplished by a process of catalytic hydrogenation. A similar process has been developed for improving both the yield and the quality of products derived from petroleum.

EXERCISES

1. Write equations for the more important methods by which hydrogen is prepared in the laboratory and commercially.

2. What is an acid?

3. Name the following acids: HCl, H_2SO_4, H_3PO_4, H_2S, $HClO_3$, H_2SO_3, HNO_2.

4. Write formulas for the following acids: nitric, carbonic, acetic, phosphorous, and hydrobromic.

5. How may the relative activity of metals be determined?

6. Which oxide is more readily decomposed by heat, zinc oxide or silver oxide?

7. Define oxidation and reduction.

8. Which element is more readily oxidized, chlorine or iodine?

9. Select the element oxidized and the element reduced in each of the following reactions:

$$2Al + 3Br_2 \rightarrow 2AlBr_3$$
$$Fe + 2AgNO_3 \rightarrow Fe(NO_3)_2 + 2Ag$$
$$2NaI + Cl_2 \rightarrow 2NaCl + I_2$$
$$3S + 4HNO_3 \rightarrow 4NO + 3SO_2 + 2H_2O$$
$$3NO_2 + H_2O \rightarrow NO + 2HNO_3$$

10. Name at least three reactions of commercial importance involving hydrogen in which catalysts are used.

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CHAPTER ELEVEN

THE PROPERTIES OF GASES

Earlier in this text we made a superficial but we hope useful survey of the theories that postulate the existence of molecules and atoms. It is now time to consider in greater detail the facts upon which these theories are based and the logical reasoning involved in their derivation from these facts. As we have pointed out before, matter may exist in any one of three states: as a gas, as a liquid, or as a solid. No one state can be considered as a characteristic of a given substance, for that in which it exists depends upon such conditions as temperature and pressure. Such unqualified statements as "water is a liquid," "iron is a solid," or "oxygen is a gas" are inaccurate unless normal atmospheric conditions are specified, since each of these three substances may be obtained in any of the three states. All substances that are gases at ordinary temperatures and pressures have been liquefied and even solidified. Nearly all those which are normally solids or liquids have been gasified. The exceptions are those which decompose chemically at temperatures below which they can be vaporized.

The kinetic-molecular theory was evolved from a study of the properties of the gaseous state. In this chapter, we shall consider these properties.

1. History.—The gases known to the ancient and medieval worlds were colorless and, of course, extremely tenuous as compared with liquids and solids. The energy of the wind was recognized and utilized early in man's history. But the fact that gases had weight was first established by the great Galileo Galilei (1564–1642) who was responsible, more than anyone else, for the introduction of the experimental method to the investigation of natural phenomena. Galileo proved that air had weight by weighing a flask filled with air at ordinary pressure and then again after more air had been forced into the flask. At about the same time, Otto von Guericke (1602–1686) invented the air pump with the aid of which many experiments with gases became possible.

The story is told that a delegation of the Florentine Guild called upon Galileo for help in devising pumps that would raise water more than 30 ft. Galileo pointed out that one must first know why water would rise this far only. A member of the group suggested the explanation that nature abhors a vacuum. "Yes," replied the great physicist, "but only a vacuum of 30 ft." Among those present was Torricelli (1608–1647), a pupil of Galileo, who invented the mercury barometer.

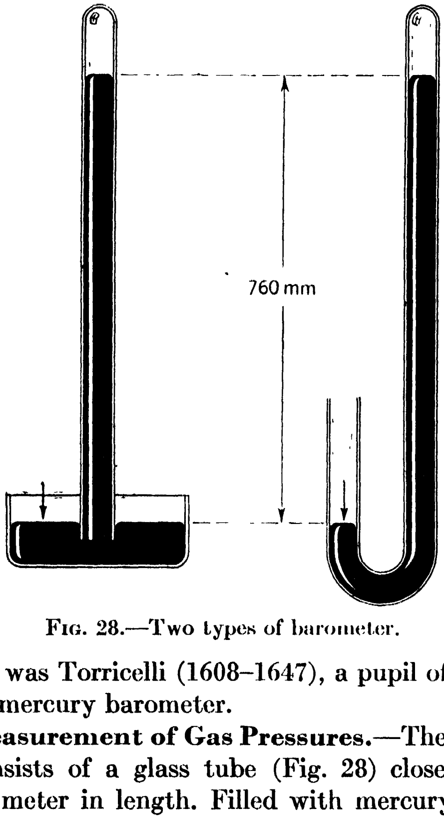

Fig. 28.—Two types of barometer.

2. The Measurement of Gas Pressures.—The barometer of Torricelli consists of a glass tube (Fig. 28) closed at one end and about a meter in length. Filled with mercury, the tube is inverted and its open end placed under the surface of some mercury in a shallow dish. The liquid in the tube falls until its surface is some 76 cm. (30 in.) above that of the mercury in the dish. The closed end of the tube prevents the air pressure from reaching the mercury surface in the tube. The space above is almost a complete vacuum except for the altogether negligible pressure of an exceedingly small amount of mercury vapor. The pressure of the atmosphere on the mercury surface in the dish is supporting a column of mercury 76 cm. high and is, therefore, equal to the weight of the column pressing on a surface equal to the cross section of the tube. If the tube is 1 sq. cm. in cross section, then the volume of the mercury in the column is equal to 76 cc. Its weight is equal to this volume multiplied by the density (the weight of 1 cc.) of mercury (13.6 g./cc.), or 1,033 g. This weight is pressing on an area of 1 sq. cm.

The pressure of the atmosphere is not constant but fluctuates from day to day at a given place and also grows less as the altitude increases. The average height of the mercury column supported by atmospheric pressure at sea level is 76 cm., or 760 mm. This has been defined as *standard pressure.* If the pressures involved are high, it is more convenient to express them in *atmospheres.* One atmosphere is equal to 760 mm.

If a barometer is constructed in which water is used in place of mercury, a column 1,033 cm., or 34 ft., high is supported by atmospheric pressure, since a given volume of mercury is 13.6 times heavier than an equal volume of water.

3. Boyle's Law.—In 1662, Robert Boyle, whom you will remember as the first to define an element, published the results of experiments on various gases and summarized these results in the law that bears his name. *If the temperature of a given weight of gas is constant, the pressure that it exerts is inversely proportional to the volume in which it is confined.* This law may be expressed mathematically as follows:

$$V \propto \frac{1}{P}*$$

To change this variation into an equation, a constant must be introduced:

$$V = k\frac{1}{P}$$

or

$$VP = k \qquad (1)$$

A variation may be changed to a proportion. If V_1 is the volume of a gas sample at the pressure P_1 and V_2 is its volume at P_2 at the same temperature, then

$$V_1 = k\frac{1}{P_1}$$

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* The use of variations is explained in the Appendix.

and
$$V_2 = k\frac{1}{P_2}$$

Dividing, we obtain
$$\frac{V_1}{V_2} = \frac{P_2}{P_1} \tag{2}$$

another method of stating an inverse proportionality and perhaps a more useful one in solving problems.

If the various volumes of a given gas sample are plotted against the corresponding pressures, a curve is obtained as shown in Fig. 29. This curve shows clearly that as the pressure approaches infinity the volume approaches zero, and vice versa.

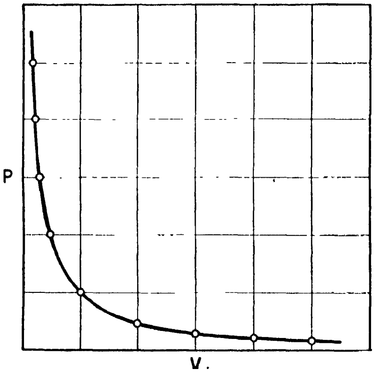

FIG. 29.—The pressure-volume relationship.

Problem.—The volume of a certain gas is 10 liters at a pressure of 3 atm. What pressure will this gas sample exert at the same temperature in a volume of 0.5 liter? It is convenient to summarize the problem as follows:

$$V_1 = 10\text{ l.} \quad P_1 = 3\text{ atm.}$$
$$V_2 = 0.5\text{ l.,} \quad P_2 = x$$

Then

$$\frac{10\text{ l.}}{0.5\text{ l.}} = \frac{x\text{ atm.}}{3\text{ atm.}}$$
$$x = \frac{10}{0.5} \times 3\text{ atm.} = 60\text{ atm.}$$

This is the point at which all good instructors will indulge in what to the student must seem the aggravating habit of using different units of volume or pressure in the same problem. In solving such problems, it must be kept in mind that the same volume units and pressure units must be used in both the numerator and the denominator of each ratio (fraction). Thus if the new volume in the above problem were given as 500 ml. instead of 0.5 liter, it must be converted to liters to agree with the unit used in the numerator.

4. Thermometers.—Temperature is another factor that determines the volume of a gas. In the next chapter, we shall have time to study the significance of the concept of temperature. For our present purposes, however, it will be sufficient to define temperature as a measure of the degree of hotness or coldness of a body. Two bodies are at different temperatures when heat will flow from the one to the other when they are brought in contact. A change in the temperature of a body is accompanied by corresponding changes in many of its properties. Its volume, color, and electrical conductivity are but a few examples of properties that are affected by temperature changes. Its mass is perhaps the only property that remains unaffected. These changes in properties furnish us with a means of measuring temperature changes. We may make a rough estimate of the temperature of a body by its color. A substance becomes red hot before it becomes white hot. In fact, optical pyrometers, which measure high temperatures, make use of this property. Temperatures are frequently measured with the highest precision now obtainable by means of the differences in electrical potential which exist at the junctions of two metals at different temperatures. The commonest temperature-measuring device, however, makes use of the change in volume that accompanies temperature variations. In the modern thermometer, the expansion and contraction of a liquid like mercury or alcohol is used for this purpose.

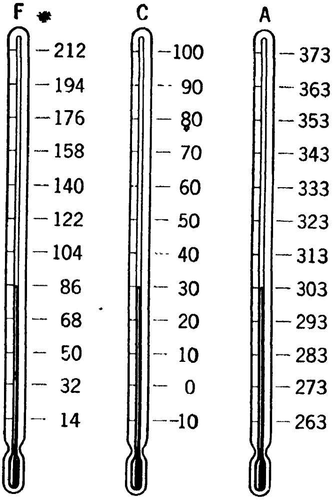

FIG. 30.—Temperature scales.

5. **Temperature Scales.**—To define a degree of temperature on any thermometer, it is necessary to fix two points on the scale arbitrarily. These should represent temperatures that are easily reproducible in the laboratory. Such temperatures are those of melting ice and of water boiling at atmospheric pressure. These fixed points were first adopted by Fahrenheit for the temperature scale that now bears his name. On this scale, a degree is $1/180$ of the distance between these fixed points. Degree divisions of equal length are carried on above and below these points. Fahrenheit chose as zero on this scale the temperature of an ice, water, and salt mixture which to him was the lowest attainable temperature. This was 32° below the fixed point corresponding to the freezing point of water. Hence the latter was assigned a value of 32° and the boiling point of water 212°. Later, in the middle of the

eighteenth century, Celsius, an astronomer, proposed the centigrade scale which has been universally adopted for all scientific work. The fixed points are the same, but the freezing and boiling points of water are 0 and 100°, respectively. In Fig. 30, you will find these two scales compared.

6. Variation of the Volume with the Temperature.—Once reproducible temperature scales had been defined, the investigation of the variation of the volume of a gas with the temperature was made possible. The relationship between these two variables was first studied by the French physicist, Charles, in 1787, and in 1802, by Gay-Lussac, a Frenchman, and Dalton, an Englishman. They found that all gases expand in the same proportion for the same increase in temperature. When we attempt to apply the Fahrenheit or the centigrade scale to the changes in temperature which produce corresponding volume changes in a gas, we find them to be inadequate. As a result of the investigations of Gay-Lussac and Dalton, it was found that any gas will expand $\frac{1}{273}$ of its volume at 0°C. for every degree rise in its centigrade temperature. For example, a gas volume of 273 ml. at 0°C. expands 1 ml. if the temperature is raised to 1°C. The expansion is $\frac{1}{273}$ of 273 ml. Obviously the volume ratio is not that of the temperatures, for 273 ml./274 ml. does not equal 0°/1°. The volume, therefore, does not vary as the centigrade temperature. If the temperature of the same quantity of gas is raised 1 to 2°, there is again a 1 ml. expansion from 274 ml. to 275 ml. This process is reversible. A lowering of 1° in temperature causes a shrinkage of $\frac{1}{273}$ of the volume at 0°C. We must keep in mind that in all these changes we are assuming that the pressure remains constant.

7. Variation of the Pressure with the Temperature.—If a constant amount of gas is confined in a certain volume, its pressure changes in the same way with temperature changes. For every 1° rise in the centigrade temperature, the pressure increases $\frac{1}{273}$ of the pressure of this gas in this volume at 0°C. Cooling produces the opposite effect.

8. The Absolute Temperature Scale.—If a gas at constant pressure could be cooled to a temperature of 273° below zero on the centigrade scale, its volume would presumably shrink $\frac{273}{273}$ of its volume at 0°C. In other words, it would occupy no volume at all. Similarly, a gas in a constant volume cooled to −273°C. would exert no pressure. This (−273°C.) is the lowest possible temperature and is called *absolute zero.* We have seen that neither the volume nor the pressure changes are directly proportional to the centigrade temperature. A temperature scale, however, can be defined which will be directly proportional to these changes. This is called the absolute scale. By adding 273° to a temperature on the centigrade scale, it can be converted to the absolute scale, *i.e.*,

$$t + 273^\circ = T$$

where t is the centigrade temperature and T, the absolute temperature. A comparison of the two scales in Fig. 30 will make this relationship clear. We are now in a position to state in terms of absolute temperatures the laws that govern volume and pressure changes with the temperature.

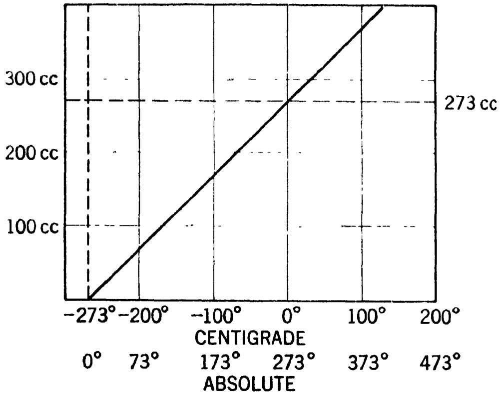

FIG. 31.- The volume-temperature relationship.

Charles's law becomes: *If the pressure of a gas sample is kept constant, its volume will vary directly as the absolute temperature,* or

$$V \propto T$$
$$V = kT \qquad (3)$$
$$\frac{V}{T} = k$$

If the volumes of a gas at two different temperatures are to be compared, we have

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \qquad (4)$$

If the volume of a given mass of gas is kept constant, its pressure varies directly with its absolute temperature, or

$$P \propto T$$

$$P = kT \qquad (5)$$

$$\frac{P_1}{P_2} = \frac{T_1}{T_2} \qquad (6)$$

9. The General Gas Equation.—The three variables volume, pressure, and temperature determine the state of any gas sample completely. We have been considering how one of these varied with another if the third were kept constant. Now we shall consider what is the result when all three factors vary. For example, let us begin with a gas in a state in which its volume is V_1, its pressure P_1, and its absolute temperature T_1 and then change it to a second state in which its volume is V_2, its pressure P_2, and its temperature T_2. What will be the relationship between all these factors? Let us carry out the change from the first state to the second state in two steps. First let us keep the temperature constant at T_1 and raise the pressure to P_2. Let us designate the volume at T_1 and P_2 as V'. Then,

$$\frac{V_1}{V'} = \frac{P_2}{P_1} \qquad (7)$$

Now let us raise the temperature to T_2. Then,

$$\frac{V'}{V_2} = \frac{T_1}{T_2} \qquad (8)$$

Combining equations (7) and (8), we obtain what is known as the *general gas equation:*

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \times \frac{P_2}{P_1} \qquad (9)$$

If any five of the variables are known, the sixth can be calculated by substituting in equation (9). A typical problem will show how this can be done.

Problem.—Ten liters of a gas at a pressure of 5 atm. and at a temperature of 227°C. is heated to a temperature of 327°C. and the pressure is raised to 12 atm. What is the volume under these new conditions?

$V_1 = 10$ l. $\quad P_1 = 5$ atm. $\quad t_1 = 227°$C. $\quad$ or $\quad T_1 = 500°$A.
$V_2 = ?$ $\quad P_2 = 12$ atm. $\quad t_2 = 327°$C. $\quad$ or $\quad T_2 = 600°$A.

Substituting in Equation (9),

$$\frac{10\text{ l.}}{V_2} = \frac{500°}{600°} \times \frac{12\text{ atm.}}{5\text{ atm.}}$$

$$V_2 = 5\text{ l.}$$

10. Standard Temperature and Pressure.—It has been found convenient to define a standard temperature and pressure to which volumes of gases can be referred. Zero degrees centigrade, or 273° A., has been defined as the standard temperature and 760 mm., or 1 atm., as the standard pressure. The abbreviation S.T.P. is frequently used for standard temperature and pressure.

11. Alternate Method of Solving Gas-law Problems.—It is unnecessary to commit the general gas equation to memory in order to solve problems. These can be solved by a method based on logical reasoning only. Consider the problem given in paragraph 9:

$$\begin{array}{lll} V_1 = 10\text{ l.} & P_1 = 5\text{ atm.} & T_1 = 500^\circ\text{A.} \\ V_2 = ? & P_2 = 12\text{ atm.,} & T_2 = 600^\circ\text{A.} \end{array}$$

The new volume V_2 will be equal to the old volume multiplied by pressure and temperature correction factors:

$$V_2 = 10\text{ l.} \times \underline{\qquad} \times \underline{\qquad}$$

Since the pressure is increased, the new volume will be less than the old for this reason. Hence we multiply by a fraction in which the smaller pressure is in the numerator:

$$V_2 = 10\text{ l.} \times 5/12 \times \underline{\qquad}$$

Since the temperature is raised, the new volume will be greater than the old owing to this change; therefore the old volume must be multiplied by a fraction in which the higher temperature is in the numerator:

$$V_2 = 10\text{ l.} \times 5/12 \times 600/500 = 5\text{ l.}$$

12. Law of Partial Pressures.—In 1801, Dalton found that *each gas in a mixture of gases exerts the same pressure that it would exert if it alone occupied the volume of the mixture at the same temperature.* The total pressure in such a mixture is equal to the sum of the partial pressures of each gas in the mixture.

A knowledge of this law is especially useful in solving problems that involve the collection of gases by the displacement of water. Such gases are saturated with water vapor, and the total pressure of such a mixture is the sum of the partial pressures of the gas and of the water vapor. Fortunately, the partial pressure of the water vapor depends on the temperature only and not on the size of the vessel in which the gases are confined. We shall see the reason for this later (14-5). This constant partial pressure of the water vapor at a given temperature is known as its *vapor pressure.* Values for the vapor pressure of water at various temperatures may be found in the Appendix.

Problem.—Let us suppose that a sample of hydrogen is collected at 20°C. by the displacement of water (Fig. 32) until the water levels inside the inverted bottle and outside in the water pan are the same. Under these conditions, the total pressure inside the bottle is the same as the atmospheric pressure of 767 mm. Ten liters of moist hydrogen is collected. The problem is to calculate the volume that this sample of hydrogen will occupy under standard conditions after it has been dried. The partial pressure of the water vapor is its vapor pressure at 20°C., or 17 mm. Hence the partial pressure of the hydrogen under the original conditions must be the difference between 767 and 17 mm., or 750 mm. Thus we dry the hydrogen by a calculation on paper. The solution now is relatively simple:

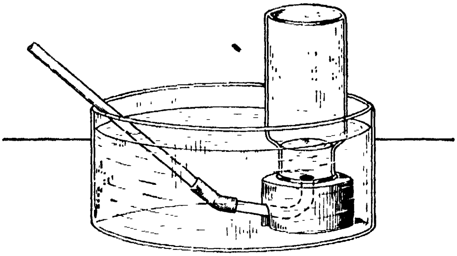

Fig. 32.—A gas collected over water.

$$V_1 = 10 \text{ l.} \qquad T_1 = 293^\circ \qquad P_1 = (767 - 17) \text{ mm.} = 750 \text{ mm.}$$

$$V_2 = x \qquad T_2 = 273^\circ \qquad P_2 = 760 \text{ mm.}$$

$$\frac{10 \text{ l.}}{x} = \frac{293^\circ}{273^\circ} \times \frac{760 \text{ mm.}}{750 \text{ mm.}}$$

$$x = 9.2 \text{ l.}$$

13. Graham's Law of Diffusion.—One gas diffuses readily into a space already occupied by another gas, until in the resulting mixture, both gases are uniformly distributed throughout the entire volume. Nor do differences in the densities of the gases make any difference in the ultimate result. However, the rates at which gases diffuse do vary widely with different gases. In 1829, Graham published the law that summarizes his results on gaseous diffusion. *The rates at which gases diffuse at the same* *temperature are inversely proportional to the square roots of their densities.* Thus,

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \tag{10}$$

where r_1 and r_2 are the diffusion rates of gases that have the densities d_1 and d_2, respectively. Since the density of oxygen is sixteen times greater than that of hydrogen, its rate of diffusion is one-fourth as great.

$$\frac{r_H}{r_O} = \frac{\sqrt{d_O}}{\sqrt{d_H}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Hydrogen has the highest rate of diffusion of any gas, because its density is lowest at a given temperature and pressure. This can be illustrated by an amusing experiment. A bell jar filled with hydrogen is placed around the porous cup of an apparatus shown in Fig. 33. Hydrogen diffuses into the cup through the pores faster than air diffuses outward, thus increasing the gas pressure inside the apparatus. This increased pressure forces the water through the jet tube and creates a miniature fountain.

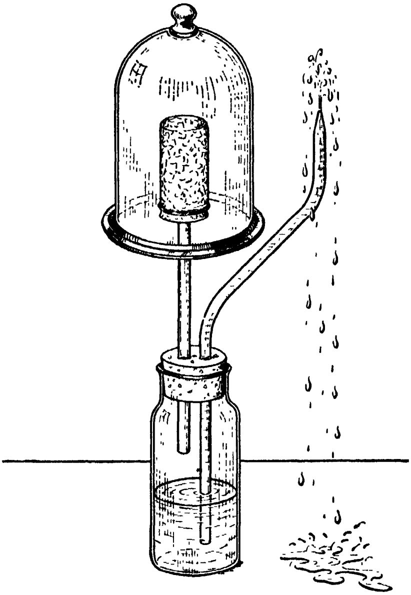

FIG. 33.—Diffusion of hydrogen.

14. Deviations from the Gas Laws.—The gas laws, which we have been considering, are not of the same order of accuracy as, for example, the law of definite composition or the law of conservation of mass. In 1825, Despretz discovered that gases which are near condensation are more compressible than they should be according to Boyle's law. Later, after a series of very comprehensive experiments, Regnault found that no gas obeys the gas laws perfectly, but that in the cases of the difficultly liquefiable gases, such as, hydrogen, nitrogen, or oxygen, the deviations from the ideal behavior, demanded by the gas laws, are slight except at low temperatures or high pressures.

EXERCISES

1. What are the fixed points on the centigrade temperature scale?

2. How is it possible to measure gas pressures in terms of the length of a column of mercury?

3. A sample of gas occupies a volume of 10 liters at a temperature of 91°C. and a pressure of 380 mm. Calculate its volume under standard conditions.

4. A gas, which exerts a pressure of 3 atm. at 27°C. in a volume of 10 ml., is transferred to a vessel of 5 ml. capacity and cooled to −73°C. What pressure does it exert under these conditions?

5. At 77°C. and in a volume of 5 cu. m., a gas exerts a pressure of 30 lb./sq. in. To what temperature must it be cooled to reduce its pressure to 20 lb./sq. in. in a volume of 1 cu. m.?

6. One liter of hydrogen is collected over water at 27°C. and at a pressure of 750 mm. What volume does the dry gas occupy under standard conditions?

7. Five moles of a gas in a steel cylinder exerts a pressure of 2 atm. at 127°C. What would be the pressure within the cylinder if 10 additional moles of the gas is pumped into the cylinder and the temperature is reduced 50°?

8. At a pressure of 190 mm. and a temperature of 27°C., a gas sample occupies a volume of 300 ml. If the pressure were doubled and the temperature were reduced to −23°C., what would be the new volume?

9. The ratio of the densities of two gases under the same conditions is 36:16. What is the ratio of their rates of diffusion?

10. Ten liters of hydrogen and 5 liters of nitrogen under standard conditions are forced into a volume of 1 liter. What are the partial pressures of each gas and the total pressure if the temperature remains constant?

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CHAPTER TWELVE

THE KINETIC-MOLECULAR THEORY

The fact that all gases behave in such a strikingly similar way toward temperature and pressure changes suggested early in their study that their structure is much the same and invited attempts to construct thought models of this structure. The modern theory of the structure of gases was first proposed by Daniel Bernoulli as early as 1738. Later, toward the end of the nineteenth century, the scope of this theory was broadened and made quantitative by the work of Clausius and Maxwell. We shall now try to follow the footsteps of these scientists and derive this theory from the experimental data that were available to them.

In attacking the problem of constructing in our minds a picture of how a gas would look and behave under a hypothetical microscope, whose power of magnification must be greater than any we know how to construct, let us first consider qualitatively some of the characteristics that laboratory investigation shows are possessed by all gases. Then, from these experimental facts, let us try to imagine a picture of the structure of gases which will explain why they have these properties. This picture will be a theoretical one only; we shall test it in many ways before we are confident that it is close to a true one.

1. A Possible Structure of Gases.—In the first place, all gases behave in the same way toward changes in volume, temperature, and pressure regardless of whether they are elements, compounds, or, as in the case of air, a mixture of gaseous substances. From this we can deduce that all gases probably have the same structure. To be on the safe side, we say "probably." Perhaps in the future some gas will be discovered which will not behave like all other gases. This is not at all probable, but it is, nevertheless, possible.

Another property that all gases possess *is the ability to diffuse into a space that is already occupied by another gas.* This plainly indicates that gases have a *porous structure.* Matter in the gaseous state at least is discontinuous, *i.e.*, there are open spaces between the particles of which the gas is composed.

The peculiar nature of gas pressure gives us our best insight as to the structure of a gas. *This pressure is exerted uniformly in all directions.* To picture a mechanism that could exert such a pressure, we must fall back on our experience as to the ways in which pressures can be exerted. Then, by a process of analogical reasoning, we must apply these ways to gases to see whether gas pressure can be explained thus. Perhaps the commonest form of pressure is that of a weight resting on a certain area. This pressure, however, can be exerted downward only, since it depends on the gravitational attraction of the earth. Obviously it cannot be used to explain gas pressure. A pressure exerted by a spring can be exerted along one line only, whereas gas pressure is equal in all directions. Pressure can be caused by the impact of a moving object. Now we are nearer to a plausible explanation. Let us imagine a space in which millions of tiny, submicroscopic particles are moving with high velocities in every direction. Their motion is perfectly random. Will this picture of the structure of a gas explain its pressure? We can visualize the particles raining a shower of blows on every surface of the containing vessel and on every object in the vessel. If the motion of these particles is perfectly random, the number of them moving in any one direction will be on the average the same as that moving in any other, and the pressure exerted will be uniform in all directions. These particles are *molecules*. Owing to the facts that gases are capable of diffusing into one another and of expanding and being compressed, we must also assume that at all ordinary pressures there must be relatively large spaces separating these gas molecules.

2. **Temperature and Molecular Velocity.**—We have learned that *an increase in the temperature of a gas in a constant volume is accompanied by an increase in its pressure.* What effect that will result in this increased pressure will be noticed in our animated picture of an enormously magnified gas when the temperature is raised? Let us first consider upon what the resultant pressure depends when a single gas molecule strikes an object. It depends not only on the mass of the molecule, but also on the speed at which it is moving. A cannon ball will strike harder than a feather moving at the same velocity. In order to explain the

increase in pressure that accompanies a rise in temperature, we must assume that either the mass or the velocity (or both) of the molecules must be increased. Since we know that the mass is unaffected by any temperature change, *a rise in temperature must be accompanied by an increase in the velocity at which the gas molecules are moving.* Since the rate at which gases diffuse also increases with a rise in temperature, this offers additional evidence that molecular velocity increases as the temperature rises.

3. Perfect Elasticity.—Another characteristic of gases, which is so obvious that its implications are almost never considered, is that *a given sample of a gas kept at a constant volume and temperature maintains its pressure eternally.* Would we have predicted this from our picture of gas structure? Imagine, if you will, a mechanism that could start 100 balls in motion through the space of an empty room with high velocities in all directions. What would happen? After bouncing about for a relatively short time, they would all come to rest on the floor. Why? The obvious answer is, of course, gravity. Their original kinetic energy and their elasticity would determine how soon they would come to rest. A set of tennis balls would remain in motion longer than a corresponding set of baseballs. Why do not the molecules of a gas come to rest in the same way? That they do not, we have proof in the fact that the pressure of a gas remains constant at constant temperature and volume. Can our picture of gas structure explain this anomalous behavior? In the first place, we must assume that *the molecules of a gas are perfectly elastic* and all that this implies. A perfectly elastic body would rebound from a surface with no lower kinetic energy than that possessed before impact. Do we know of any object in our everyday experience which will do this? Even a new tennis ball will not rebound from a stationary wall with the same velocity with which it was thrown. The reason for this is that a certain fraction of the original kinetic energy is lost as heat, or, in other words, as friction. The more perfectly elastic a body is, the less friction is developed when it comes in contact with another object. To be perfectly elastic, an object must lose none of its kinetic energy as heat when it strikes another object. In order to explain gas pressure in terms of our model, we must assume that gas molecules are perfectly elastic—that they cannot lose any fraction of their kinetic energy as heat.

A knowledge of the nature of heat energy will show how absolutely impossible it is for these gas molecules to lose any fraction of their kinetic energy as heat. *Their kinetic energy is heat energy.* Hence none of their kinetic energy can be lost as heat when they collide. They must be, therefore, perfectly elastic.

4. The Effect of Gravity.—The next question which our picture of gas structure must answer has to do with the effect of gravity on the gas molecules. Has gravity any effect on them, and, if so, why are they not concentrated near the bottom of the vessel in which they are confined? Also, in the latter case, why is not gas pressure greater on the bottom than on the top of the vessel? Gravity has an effect on gas molecules, but its effect is inappreciable in a vessel of any ordinary height because of the enormous velocities at which the molecules are moving. Since gas pressure ceases at zero degrees on the absolute temperature scale, molecular motion has also ceased. However, if the temperature is raised 0.001°C. only, they will have sufficient kinetic energy to rebound 7 in. from the bottom of the vessel. At about room temperature, their speed of scarcely less than a mile a second will cause them to bound miles into space. If the container is large enough, it is possible to show the effect of gravity. It is a well-known fact that the earth's atmosphere is some fifty miles high only and that the pressure diminishes rapidly as we ascend into the air. If gravity had no effect on the earth's atmosphere, the latter would meander off into space.

5. An Explanation of Boyle's Law.—This picture of the structure of gases can, therefore, be made to explain qualitatively their characteristic behavior. The gas laws are quantitative descriptions of this behavior. Can the kinetic theory of gas structure explain quantitatively as well as qualitatively the behavior of gases?

To explain Boyle's law, our model must be able to show why the same quantity of a gas in, for example, half its former volume will exert twice its former pressure. Imagine a cylinder *A* (Fig. 34) provided with a piston *B* upon which weights can be placed to exert a pressure on the gas confined in the cylinder. The gas will exert a pressure on the lower side of the piston equal to that of the weights on the upper side. In order that we may visualize the molecules better, let us assume that the whole apparatus is of submicroscopic size and that it contains only

10 molecules. When the gas is under the pressure P_1, its volume is V_1. Now let us double the weight on the piston and so double the pressure. The new volume will be half the old. In this case, the kinetic-molecular theory shows clearly that we have confined the same number of molecules in half their former volume.

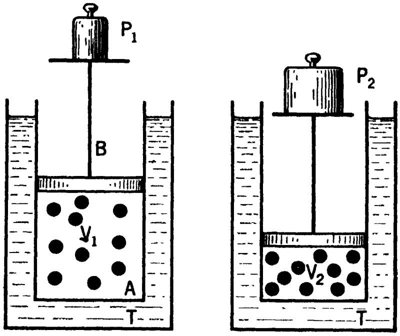

FIG. 34.—An explanation of Boyle's Law.

We have, thus, doubled their *concentration* as there are now twice as many molecules per unit volume. Hence the frequency of molecular impact upon the lower side of the piston will be doubled, resulting in a doubled pressure. The kinetic theory, therefore, postulates that *the pressure exerted by a gas at a given temperature is proportional to its molecular concentration.*

6. The Significance of the Absolute Temperature Scale. When we consider the laws that apply to the variation of the volume or the pressure of a gas with the absolute temperature, we must always remember that these laws are in reality a definition of the absolute temperature scale. This scale is so devised that its temperatures will be proportional to the volume change at constant pressure or the pressure change at constant volume. In a sense, then, these "laws" require no explanation. But it is necessary that we examine the significance of the absolute temperature scale in terms of kinetic-molecular theory. Perhaps the best way to understand this is to consider first the variation of the pressure of a gas at constant volume with the absolute temperature. We have mentioned the fact that the pressure p exerted through the impact of a single gas molecule is determined by its mass m and its velocity u, *i.e.*, is proportional to the product of these factors. This product is what is called the *momentum* of a moving body.

$$p \propto mu$$

The total pressure of all the molecules, P, is proportional to two factors, the momentum of each molecule and the frequency f with which they collide with the walls of the vessels, *i.e.*,

$$[P]_f \propto mu$$

Here the brackets with f as a subletter indicate that the total pressure P is proportional to the momentum of each molecule only if the frequency at which the molecules strike a certain area is constant. If the momentum per molecule is constant, the total pressure will be proportional to the frequency:

$$[P]_{mu} \propto f$$

It follows that when both the momentum and the frequency vary

$$P \propto mu \times f$$

Now the collision frequency f depends only on the velocity of the molecules:

$$f \propto u$$

Therefore, the total pressure is proportional to the mass of each molecule times its velocity squared:

$$P \propto mu \times u \propto mu^2$$

The energy possessed by a moving body, its kinetic energy, is equal to one-half the product of its mass by its velocity squared. Since either side of a variation may be multiplied by a constant without changing its validity, it follows that the pressure must be proportional to the kinetic energy of its molecules,

$$[P]_v \propto mu^2 \propto \tfrac{1}{2}mu^2 \propto \text{K.E.}$$

according to the picture we have been considering of the manner by which gas exerts pressure.

The absolute temperature scale has been defined in such a way that it will vary as the pressure of a gas in a constant volume

$$[P]_v \propto T$$

Hence *the absolute temperature is a measure of the kinetic energy of the molecules of a gas.*

$$\text{K.E.} \propto T$$

In coming to this conclusion, we have assumed that the velocity and hence the kinetic energy of all the molecules of a gas at a given temperature are the same. This is, however, not the case. At a given instant, certain molecules may be in the act of colliding, at which instant their kinetic energy has been changed to potential energy. Other molecules may have acquired additional energy by a fortuitous sequence of collisions. In short, all kinetic energies are possible from zero to infinity, but the average kinetic energy is fixed by the temperature. It is possible to calculate the probability of a molecule having a certain kinetic energy by means of statistical mechanics, but such a calculation is far beyond the scope of this book.

Since it is the average kinetic energy of the molecules that determines the absolute temperature

$$T \propto \tfrac{1}{2} mu^2$$

it follows that it is the *square* of the velocity which varies directly as the absolute temperature:

$$T \propto u^2$$

a result obtained by removing the constants, $\tfrac{1}{2}$ and m, from the variation. Hence, if the absolute temperature is quadrupled, the velocity is doubled.

7. Absolute Zero.—If a gas could be cooled to absolute zero, or −273.13°C., it would cease to exert a pressure. In terms of the kinetic-molecular theory, its molecules have stopped moving and obviously can no longer exert a pressure. Similarly, at absolute zero, the volume of a gas should be zero. Strictly speaking, the volume of the space between the molecules has become zero, as the molecules at rest are in actual contact. Under ordinary conditions, the space between molecules is so large as compared with that of the molecules themselves that the total volume inhabited by the gas is practically the same as the volume of the free space between them.

8. Deviations from the Gas Laws.—We have pointed out that at high pressures and at low temperatures gases, in general, do not obey the gas laws exactly. Easily liquefiable gases, *e.g.*, carbon dioxide, even under ordinary conditions disobey these laws. Such deviations are explained by the kinetic theory by assuming the existence of forces of attraction between molecules. These forces, as we shall see later, are partly gravitational, partly electrical, and partly magnetic. These forces are called van der

Waals forces. They become greater as the average distance between molecules becomes less. Hence at high pressures, *i.e.*, at great concentrations, these forces cannot be neglected, and the behavior of the gas deviates from that demanded by the gas laws. Further, at high pressures, the volume of the molecules themselves becomes appreciable when compared with the space between them. Since the volume mentioned in the gas laws refers to the free space between molecules, this becomes another factor that causes deviation.

We have seen that the tremendous velocities at which molecules move at all ordinary temperatures serve to counteract the forces of mutual attraction between them and cause them to diffuse freely away from one another to fill the space of the containing vessel. At low temperatures, however, the molecules are moving relatively slowly. The effect of the forces of intermolecular attraction under these conditions becomes appreciable, and deviations from the gas laws result.

These forces vary in magnitude according to the nature of the gas. They are greater between the molecules of the easily liquefiable gases than between those of gases that can be liquefied only at low temperatures. A hypothetical gas between whose molecules there are no forces of attraction and whose molecules are merely points in space is called a perfect gas. Such a gas would obey the gas laws in every particular of its behavior. No known gas will behave in such an ideal way, although the inert gas helium (37-5) approaches in its behavior that of the perfect gas.

9. Summary.—It will be useful for us to tabulate the various facts of gas behavior and the postulates of the kinetic-molecular theory derived from these facts. This we have done in Table 10. The facts as determined by laboratory experiments are placed in the left-hand column. Opposite each fact and in the column at the right is the postulate of the theory derived by logical reasoning from the fact. As this table is studied, each step in the logical reasoning which leads from fact to theory should be reviewed.

Table 10.—Derivation of the Kinetic-molecular Theory

Facts	Theory
1. A gas exerts the same pressure on every surface it bathes.	1. The pressure of a gas is caused by the bombardment of submicroscopic particles, called molecules. The movement of these molecules is so perfectly random that on the average the same number are moving in every direction. Hence the same number strike every unit area.
2. A gas diffuses into a space already occupied by another gas. Gases are compressed readily.	2. At other than high pressures, the average distance between molecules is relatively large as compared with their diameters Nothing fills the space between the molecules.
3. Boyle's law. If the temperature is constant, the volume of a given mass of gas varies *inversely* with the pressure. $[V]_T \propto \frac{1}{P}$	3. At a constant temperature, the pressure of a gas varies *directly* with its molecular concentration.
4. If the volume is kept constant, the pressure that a given mass of gas exerts is proportional to its absolute temperature. $[P]_V \propto T$	4. The kinetic energy of the molecules of a gas varies directly as the absolute temperature.
5. Charles' law. If the pressure is kept constant, the volume of a given mass of gas is directly proportional to the absolute temperature. $[V]_P \propto T$	5. The greater the volume, the greater the molecular kinetic energy required to exert the same pressure.
6. If the temperature and the volume of a given mass of gas are kept constant, its pressure remains the same indefinitely.	6. The molecules of a gas are perfectly elastic, losing none of their kinetic energy upon collision with other molecules at the same temperature.
7. Deviations from the gas laws occur at high pressures, low temperatures, and in the cases of easily liquefiable gases.	7. These deviations are due to van der Waals forces of intermolecular attraction.

EXERCISES

1. How does the kinetic-molecular theory explain the uniform pressure of a gas?

2. How does the theory explain Boyle's law?

3. According to the theory, of what is the absolute temperature a measure?

4. By what multiple must the absolute temperature be increased to double the average molecular velocity?

5. What is meant by the term perfectly elastic?

6. Why is it believed that the molecules are perfectly elastic?

7. Discuss the significance of absolute zero.

8. What are van der Waals forces?

9. Why does the behavior of carbon dioxide deviate under normal conditions from that predicted by the gas laws, whereas the behavior of helium is above reproach?

10. Why do deviations become more pronounced at low temperatures and high pressures?

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CHAPTER THIRTEEN

OXIDES AND THEIR REACTIONS

An oxide is a binary compound of oxygen. There are two classes: basic oxides, or those of metals, and acidic oxides, or those of nonmetals. Then there is water, an oxide, yet not a member of either class. This compound is such an essential part of the life of all creatures that it seems foolish to discuss its discovery. Yet in the sense of the understanding of its nature by science its discovery might well be dated. The Greeks classed it with air, earth, and fire as one of the elements. However, it was not until 1781 that Cavendish proved it to be an oxide of hydrogen by igniting mixtures of these elements with an electric spark and identifying the product. Its analysis by means of the electric current was first accomplished by Nicholson and Carlisle in 1800.

1. Occurrence.—Water is the most ubiquitous of all compounds. It covers three-quarters of the surface of the earth either as a liquid or as ice. Its vapor is always present in our atmosphere. Even the dry land, except in desert places, is wet with it. The earth's crust contains some 9 per cent of water by weight. The human body has been described by someone in a cynical mood as "twelve pounds of ashes and eight buckets of water." More accurately, it is composed of some 70 per cent of water by weight. We excrete 3 kg. of this compound daily. The body temperature is controlled by its evaporation from the skin. We can live only a relatively short time without it.

2. The Composition of Water.—The first accurate work on the composition of water was done in 1819 by Berzelius and Dulong. Later (1842), Dumas and Stas obtained more accurate results using the same method. Because of the relative difficulty in measuring gas volumes and densities accurately, they used an indirect method involving the reduction of cupric oxide by hydrogen:

$$CuO + H_2 \rightarrow H_2O + Cu$$

Dry hydrogen is passed over the heated oxide in the apparatus shown in Fig. 35, and the water formed is collected by absorption in a U tube filled with calcium chloride, an efficient drying agent (48-5). Since cupric oxide and copper are solids, their weights can be determined with great accuracy as can that of the water collected in the U tube. The cupric oxide is weighed in a porcelain boat before being placed in the apparatus. At the end of the experiment, the boat and its contents are again weighed. The loss in weight is the weight of oxygen from the oxide which has combined with hydrogen. The calcium chloride tube is weighed before and after the experiment, and the gain in weight is that of the water formed. The difference between this weight of water and the weight of the oxygen lost by the oxide in the boat is the weight of hydrogen involved in the reaction. Given the following data, calculate the weight of hydrogen that combines with 16.000 g. (1 gram-atom) of oxygen, using the logarithms in the Appendix.

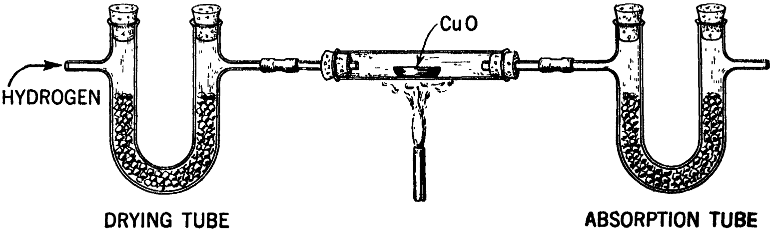


Fig. 35.—A determination of the composition of water.

Weight of boat before reduction = 15.2193 g.
Weight of boat after reduction = 10.6276 g.
Weight of calcium chloride tube before = 21.3251 g.
Weight of calcium chloride tube after = 26.4922 g.

These results were exceeded in accuracy by those of Morley at Western Reserve University. Using extraordinary precautions, he obtained the hydrogen-oxygen ratio directly by the synthesis of water. His results, representing an average of 12 experiments, were reported to the American Chemical Society in 1893. His ratio is 16.000:2.016. From these results, what is the atomic weight of hydrogen?

3. Properties of Water.—This compound is so available and so easily purified that many of its properties have been used to define the units of measurement. Thus the gram is the weight of

1 c.c. of water at 4°C. Its density at this temperature is, therefore, 1 g./1 c.c. The unit of heat energy, the calorie, is the amount of heat needed to raise the temperature of 1 g. of water 1°C. (strictly from 15 to 16°C.). The specific heat of water is, therefore, one calorie per degree. The fixed points on all thermometer scales are defined in terms of the freezing and boiling points of water (11-5).

Water is normally a liquid. However, if its molecules were as simple as H_2O in the liquid state, the forces of attraction between them would be so slight that its boiling point ought to be considerably below 0°C. instead of 100°C. The explanation of this anomaly seems to be that in the liquid simple water molecules are for the most part associated in pairs, in triplets, and even in larger groupings. Such groupings are continually breaking up as fast as they are forming. In the vapor, single molecules are the rule, but near the freezing point, the *average* degree of association corresponds to a triple molecule. Between such larger molecules, the forces of attraction are stronger. Hence the fact that water is normally a liquid. Fortunately, chemists are not so meticulous as to use any but the simple formula H_2O in their equations.

At 4°C., water is at its maximum density. Heated above this temperature, it expands as do other liquids. But the strange fact is that it *contracts* when heated from its melting point (0°C.) to 4°C.

Water is again almost unique in that it expands on freezing. Thus the density of ice is less than that of water; hence ice floats in water. This is fortunate for fish and ice skaters but is the cause of icebergs and burst water pipes. Briefly, the reason for this behavior is that the crystal structure of ice is an extraordinarily open one. With the breakdown of the orderly array of molecules when the crystals melt, molecules enter the free spaces which were in the crystal structure and a contraction in volume results.

Water is the best solvent for inorganic and for many organic substances. Its solvent action on salts is due to its high dielectric constant, as we shall see later.

4. The Role of Water in Nature.—In nature, water is constantly repeating a cycle that is of great importance in the economy of natural processes. The sun's rays, falling upon bodies of water, are absorbed partly as heat energy and partly by the molecules that evaporate from their surfaces. These molecules diffuse into all parts of the atmosphere. When meteorological conditions are such that any region of the atmosphere becomes supersaturated with water vapor, precipitation as liquid water occurs (15-3). We recognize this precipitation as rain, if the droplets are so large that they fall rapidly to the earth, or as a cloud or a mist, if they are small and remain suspended. The amount of water vapor in the atmosphere is sometimes enormous. A cubic mile of air, saturated with water vapor at 95°C., will precipitate 35,000,000 gal. of water when cooled to 32°C. Rain, as it falls to the earth, dissolves carbon dioxide, oxygen, and nitrogen from the air. Its solvent action continues after it strikes the earth's surface. Certain sparingly soluble sulfates, such as gypsum ($CaSO_4$), are leached out of the soil. Insoluble limestone formations ($CaCO_3$) are converted into the soluble bicarbonate of calcium by the carbon dioxide which natural waters contain:

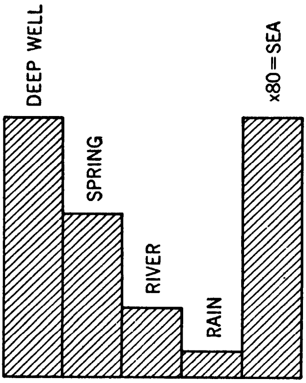
$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

Feldspar, $KAlSi_3O_8$, an important mineral found in all granites, is slowly converted into clay, $H_4Al_2Si_2O_9$,

$$2KAlSi_3O_8 + 2H_2O + CO_2 \rightarrow H_4Al_2Si_2O_9 + 4SiO_2 + K_2CO_3$$

In addition to its solvent and chemical action, water flowing under the influence of gravity exerts a mechanical action which disintegrates huge rocks into smaller and smaller particles. A small crack in a rock is widened when water freezes in it; small particles are rubbed off its surface when water flows over it; soluble minerals are leached out until eventually a barren rock is converted into fertile soil. Finely divided soil particles are carried in suspension as are also bacteria which are found wherever plant and animal life exists. Carrying all these substances in solution or suspension, water flows over and through the ground, collects in streams which mingle their waters into mighty rivers and flow to the sea. Suspended materials are dropped along the river beds and especially as deltas where the rivers meet the sea.

5. The Composition of Natural Waters.—The relative amounts of matter held in solution by natural waters of various types are shown in Fig. 36. Rain water contains some dust and a few bacteria in suspension and the gases carbon dioxide, sulfur dioxide, ammonia, nitrogen, and oxygen in solution. The composition of spring water is determined by the chemical nature of the soil and rocks with which it has come in contact. It usually contains carbonates and sulfates of calcium, magnesium, sodium, potassium, iron, and aluminum in solution; and oxides of silicon, iron, and aluminum in suspension. River and lake waters contain all these mineral substances and, in addition, are more liable to contain organic matter from the decay of vegetation and from sewage. Wherever organic matter is present, bacteria, some of which may be disease-producing, are usually found. Sea water contains an accumulation of the soluble materials that have been leached out of the land by water. The average salt content of all the oceans is about 3.5 per cent. These dissolved salts contain sodium, magnesium, potassium, chloride. sulfate, carbonate, and bromide ions.



RELATIVE AMOUNTS DISSOLVED IN NATURAL WATERS

Fig. 36.

6. Potable Water.—Man uses water in large quantities for three purposes: drinking, washing, and for the production of steam in boilers. Certain impurities render it unfit for use for these purposes. Drinking water obviously must be free from disease-producing bacteria and relatively free from organic compounds resulting from the decay of vegetal and animal matter. Water that contains a relatively high percentage of mineral matter, notably salts of calcium and magnesium, is called "hard". water and is unfit for use in laundering or as a boiler water. The methods by which such hard water may be softened will be discussed later (48-25).

Water that is clear and sparkling is not always fit to drink. The presence of disease-producing bacteria can never be detected without the aid of a microscope. The only safe way of testing the potability of a certain water supply is to resort to chemical and bacterial analysis. The most common water-borne diseases in this country are typhoid and paratyphoid fevers, cholera, and dysentery. These invariably get into the water supply with sewage. The presence of sewage in water, therefore, is sufficient evidence to condemn its use for drinking purposes. A class of nitrogenous organic substances, the albuminoids, is always present in fresh sewage. The nitrogen in these compounds can be determined by chemical analysis as "albuminoid ammonia." Pollution by fresh sewage is of the most dangerous type. These organic nitrogenous compounds are gradually converted into nitrites and later into nitrates by the action of certain nitrifying bacteria. The presence of nitrites or nitrates indicates that the pollution is of an older and of a less dangerous type. However, good drinking water should contain less than $\frac{1}{100}$ part of nitrite nitrogen per million parts of water. Fresh waters contain normally little if any salt. Since this gets into the water mainly from human excreta, its presence is an indication of dangerous pollution.

A bacterial analysis of water is more direct than a chemical one and is, therefore, perhaps more reliable. The bacteriologist, however, does not waste his time trying to find disease-producing bacteria under a microscope. He seeks another class of bacteria which are certain to be present in great abundance in the excreta of human beings and of higher animals—the *Escherichia coli*. These are harmless, but their presence is an indication of fresh sewage. They should not be present in greater concentration than 1 per 50 ml. of water.

7. The Purification of Drinking Water.—Absolutely pure water can be prepared by distillation only. Such a process, however, would be too expensive to carry out on a large scale, although ocean liners commonly distill sea water for their drinking-water supply. Boiling water for 10 min. will kill all the bacteria in it. Boiling, however, removes the dissolved gases from water and gives it a characteristic flat taste.

The purification of water for drinking purposes on a large scale is done by sand filtration and by chemical disinfection. Neither of these methods will remove dissolved impurities to any extent, but these are not the impurities that render water unsafe for drinking purposes. Disease-producing bacteria are in suspension and can be removed by filtration or killed by chemical disinfection.

The sand filters of municipal water-supply plants are of two types, slow and rapid. A cross section of a portion of a slow filter bed is shown in Fig. 37. Water seeps slowly through the bed, and, in so doing, the sand, mud, and most of the bacteria are held back by the filter. A growth of a certain class of aquatic plants, the algae, is encouraged on the surface of the filter and helps in removing the bacteria. The purified water runs off through a system of drain pipes of porous tile at the bottom of the filter. This method is efficient but is open to objection because of its slowness. Recently, more rapid methods of filtration have been installed in many cities. The filter beds are not as deep, and coarser gravel is used. The water is first allowed to stand in settling basins before going through the filter. A coagulant such as aluminum sulfate is added to accelerate the settling of the suspended matter. This forms a gelatinous solid in the water to which suspended matter adheres. It subsequently forms a film on the surface of the filter which assists in removing the bacteria. The rapid type is not so efficient as the slow filter in removing bacteria, but it does remove color and suspended matter almost completely. Its great advantage lies in the fact that it can be operated at the high filtration speed of 125,000,000 gal. per day per acre of filter surface. This is thirty to fifty times faster than slow filtration, which means that this type of filter needs less land and can, therefore, be located nearer the consumer.

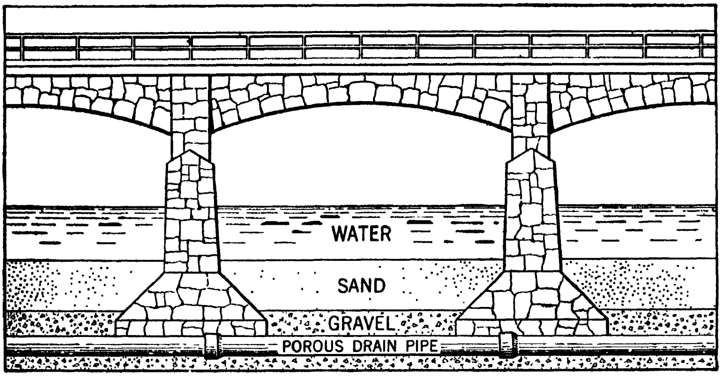


FIG. 37.—A water filter.

8. Chemical Methods of Water Purification.—Today, it is the almost universal practice in this country to chlorinate drinking water. The use of liquid chlorine for killing bacteria in drinking water was begun in 1913 in this country. This process is very simple and practically automatic. It represents the cheapest and, in certain respects, the most satisfactory method of killing bacteria in drinking water. Never more than 0.7 part of chlorine per million gallons of water is necessary to produce complete sterilization. It acts as a direct poison to the bacterial cells. The effect of filtration and of chlorination has been remarkable in reducing the death rate from typhoid fever. Filtration alone in the city of Lawrence, Mass., reduced the death rate from 114 to 25 per 100,000 population. Chlorination has resulted in a 75 per cent reduction in the death rate from this disease in many cities.

Many chemists are advocating a superchlorination of water that will be sufficient not only to kill all the bacteria, but also to destroy all organic matter that might prove a source of nutriment for the development of bacteria after an incomplete chlorination. The excess chlorine can then be removed by a process of dechlorination which has been developed for this purpose. They point to the serious epidemic of typhoid fever that broke out in Hanover, Germany, in 1926, in which 1,800 citizens lost their lives and over 60,000 became ill with the fever. This city draws its water supply from wells the water of which is filtered and chlorinated before use. A heavy rainfall caused a small creek to overflow its banks and to discharge some of its water into these wells. For 2½ hr. only this water which contained six times the normal amount of organic matter was pumped into the water mains. The amount of chlorine was insufficient, and the epidemic resulted.

9. Hydrates.—Many salts crystallize from an aqueous solution with water molecules included in their crystal structures. Such salts are called *hydrates* and the water they contain, *water of hydration*, or *water of crystallization*. The relative number of such water molecules to the ions of the salt is constant in a given hydrate so that formulas may be written for hydrates, *e.g.*, $CuSO_4.5H_2O$ and $Na_2CO_3.10H_2O$. The water of crystallization is either attached to the ions by electron-pair bonds, or it may simply fill regular spaces in the crystal lattice.

10. Reactions of Water.—We have studied the reactions of water with the active metals which result in the formation of hydrogen (10-3). Its reactions with nonmetals, such as the halogens, had best be considered later.

a. Water Reacts with Basic Oxides to Form Metal Hydroxides.—This type of reaction is limited in its usefulness to the oxides of the alkali metals (potassium and sodium), of the alkaline-earth metals (barium, strontium, and calcium), and to magnesium oxide. In other words, to the metals above aluminum in the electromotive series. Thus sodium oxide reacts with water to form sodium hydroxide:

$$Na_2O + H_2O \rightarrow 2NaOH$$

The slaking of lime, CaO, is the same type of reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The oxides of the metals below magnesium not only do not react with but are insoluble in water. Reactions such as

$$Al_2O_3 + 3H_2O = 2Al(OH)_3$$

do not occur. Nevertheless, it is well to keep in mind the relationship of a metal oxide to the corresponding hydroxide, as both classes of compounds enter into the same kinds of reactions.

b. Water Reacts with Acidic Oxides to Form Oxygen-containing Acids.—Equations for reactions of this type will seem difficult at the start. In the first place, nonmetals form more than one oxide. Thus two oxides of sulfur are known: the dioxide, SO_2, in which the valence number of sulfur is +4 and the trioxide, SO_3, in which its valence number is +6. There exist two oxygen-containing acids of sulfur, sulfurous acid, H_2SO_3, in which the valence number of sulfur is +4 (9-9) and sulfuric acid, H_2SO_4, in which sulfur has a valence number of +6. The rule to remember is that the valence of the nonmetal in its oxide and in the acid, formed when the oxide reacts with water, is the same. Thus sulfur dioxide forms sulfurous acid:

$$H_2O + SO_2 \rightarrow H_2SO_3$$

Similarly, sulfur trioxide forms sulfuric acid:

$$H_2O + SO_3 \rightarrow H_2SO_4$$

It may help to remember that the lower oxide, *i.e.*, the one in which the nonmetal is in its lower valence, forms the *-ous* acid. The higher oxide forms the *-ic* acid.

Phosphorus has two positive valences, +3 and +5. Hence it forms two oxides, P_2O_3 and P_2O_5. The lower oxide will react with water to form phosphorous acid:

$$3H_2O + P_2O_3 \rightarrow 2H_3PO_3$$

The higher oxide forms phosphoric acid:

$$3H_2O + P_2O_5 \rightarrow 2H_3PO_4$$

It may be well to remember that, in general, the reactions of oxides with water may be reversed if the corresponding metal hydroxides or acids are heated enough. All metal hydroxides, except those of sodium and potassium, decompose into the corresponding oxides and water on heating. Thus:

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

Similarly, sulfurous acid is readily decomposed:

$$H_2SO_3 \rightarrow SO_2 + H_2O$$

11. The reaction of a basic with an acidic oxide leads to the formation of an oxygen-containing salt. This reaction is similar in form to that of water on an acidic oxide:

$$\underset{\text{water}}{3H_2O} + \underset{\substack{\text{acidic}\\\text{oxide}}}{P_2O_5} \rightarrow \underset{\text{acid}}{2H_3PO_4}$$

$$\underset{\substack{\text{basic}\\\text{oxide}}}{3Na_2O} + \underset{\substack{\text{acidic}\\\text{oxide}}}{P_2O_5} \rightarrow \underset{\text{salt}}{2Na_3PO_4}$$

In both of these and all similar equations the higher oxide of phosphorus invariably forms phosphates. Had the lower oxide been used, phosphites would have been formed.

Problem.—Write a balanced equation for the reaction of a basic oxide with an acidic oxide to form ferric sulfate. We must use *ferric* oxide since *ferric* sulfate is to be formed. Our acidic oxide must be the higher oxide of sulfur, SO_3, since *higher oxides form -ate salts*. The equation is

$$Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3$$

12. The reaction of metal hydroxides with acidic oxides also results in the formation of oxygen salts, but water is formed at the same time. The rules given in the last paragraph may be applied to these reactions also. The following are typical examples:

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
$$2Al(OH)_3 + P_2O_5 \rightarrow 2AlPO_4 + 3H_2O$$

13. The reaction of a basic oxide and an acid results in the formation of a salt and water. Binary salts may be prepared by this method if a binary acid is used:

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
$$Al_2O_3 + 6HBr \rightarrow 2AlBr_3 + 3H_2O$$

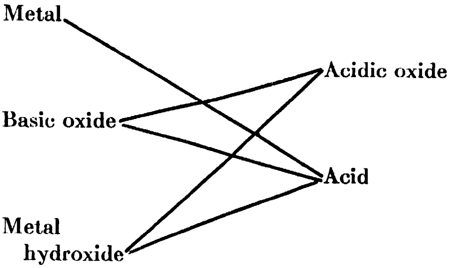
If an oxygen acid is used, -*ic* acids form -*ate* salts and -*ous* acids form -*ite* salts:

$$Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$$
$$Al_2O_3 + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2O$$
$$CaO + H_2SO_3 \rightarrow CaSO_3 + H_2O$$

14. Neutralization.—A neutralization reaction is one in which a metal hydroxide reacts with an acid to form a salt and water. The following examples are of this type:

$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$Fe(OH)_2 + 2HBr \rightarrow FeBr_2 + 2H_2O$$
$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$$

15. Formation of Salts.—To the types of reactions listed above, which result in the formation of salts, may be added that of a metal, above hydrogen in the electromotive series, with an acid (other than nitric) to form a salt and hydrogen. By grouping metals, basic oxides, and metal hydroxides in one column and acidic oxides and acids in another, we may readily summarize the reactions that lead to salt formation.



This illustration shows five methods by which salts may be prepared. One combination has been omitted, that of a metal with an acidic oxide. Any such reactions which do occur do not result in salt formation.

16. Peroxides.—In normal oxides, the oxygen atoms have valence numbers of −2 and are linked directly to other atoms by double valence bonds. Thus Na_2O, BaO, and H_2O are normal oxides. Peroxides are a class of binary compounds that contain the peroxide, or O_2, group. The valence of this group is −2; therefore the valence number of each oxygen atom is −1. Sodium peroxide, Na_2O_2, barium peroxide, BaO_2, and hydrogen peroxide, H_2O_2, are typical.

Hydrogen peroxide has become an industrial chemical of some importance. It is manufactured by two methods. The first of these involves heating the naturally occurring barium carbonate with coke:

$$BaCO_3 + C \rightarrow BaO + 2CO$$

The oxide is heated in oxygen and barium peroxide is formed:

$$2BaO + O_2 \rightarrow 2BaO_2$$

The latter is treated with sulfuric acid which results in the formation of hydrogen peroxide and the water-insoluble barium sulfate:

$$BaO_2 + H_2SO_4 \rightarrow H_2O_2 + BaSO_4 \downarrow$$

The second process involves the electrolysis of dilute sulfuric acid or acid sulfates (18-2) followed by blowing steam through the solution. The hydrogen peroxide thus formed is volatile in steam and can be condensed in a suitable receiver.

Pure hydrogen peroxide is a colorless, sirupy liquid which freezes at $-0.89°C.$ and boils at 151.4°C. Both the pure substance and its aqueous solutions are stable. However, sunlight and especially traces of metallic impurities hasten its decomposition:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Under such circumstances the pure substance is dangerous to handle. However, inhibitors, or stabilizers, have been developed which prevent sudden catalytic decomposition.

Dilute hydrogen peroxide solutions have long been used to treat wounds. Their value as an antiseptic is low, but the evolution of oxygen in contact with clotted blood helps to loosen dirt and assists in cleansing such wounds. More concentrated solutions containing 30 per cent hydrogen peroxide are used in large quantities commercially. A moderately active oxidizing agent, hydrogen peroxide is used extensively to bleach all kinds of textiles, straw in the manufacture of hats, fur, and wood, and even, 'tis rumored, to produce synthetic blondes.

EXERCISES

1. What does the fact that water is a liquid under normal conditions indicate as to the nature of water molecules?

2. Give at least two reasons why water is not a satisfactory liquid with which to fill thermometers.

3. Write equations for three reactions by which hydrogen may be prepared from water.

4. Write equations for the reactions of water with each of the following substances: SO_2, CaO, P_2O_5, K_2O, SO_3, P_2O_3.

5. Why does ice form on the surface of bodies of water?

6. Define the gram.

7. What is a calorie?

8. What is the density of water at 4°C.?

9. What is its specific heat?

10. Write equations for the following reactions:

a. Sodium oxide + sulfur trioxide →
b. Calcium oxide + phosphorus pentoxide →
c. Aluminum oxide + sulfuric acid →
d. Sodium hydroxide + hydrobromic acid →
e. Aluminum hydroxide + sulfur trioxide →
f. Sodium hydroxide + hydrosulfuric acid →
g. Aluminum + phosphoric acid →
h. Calcium hydroxide + phosphorus pentoxide →
i. Ferrous hydroxide + acetic acid →
j. Ferric oxide + nitric acid →

11. Write equations for five methods for preparing each of the following salts: ferrous sulfate and calcium phosphate.

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CHAPTER FOURTEEN

LIQUIDS

The kinetic-molecular theory was postulated originally to explain the behavior of gases. However, it may be extended with some modifications to the liquid state.

1. **Molecular Concentration in Liquids.**—When a gas condenses to the liquid state, a very large contraction in volume occurs. One mole of water vapor at 100°C. and atmospheric pressure occupies a volume of approximately 30,600 ml. When the mole of water is condensed to the liquid state at the same temperature, its volume is reduced to 18.7 ml. This represents a 1,600-fold contraction. Hence we must assume that the molecular concentration in the liquid state is several thousand times as great as in gases. It has been mentioned that the forces of intermolecular attraction increase rapidly as the average distance between the molecules is reduced. Actually, these van der Waals forces are approximately inversely proportional to the sixth power of the distance. Since a volume is proportional to the cube of one of its dimensions, a 1,600-fold decrease in volume corresponds roughly to a 12-fold reduction in the average distance between molecules. This reduction increases the van der Waals forces by a factor of over 10^6. We shall expect to find many of the properties that distinguish liquids from gases explainable in terms of these powerful forces.

2. **The Surface of a Liquid.**—Unlike a gas, a given mass of liquid does not expand to fill any container into which it is placed but occupies a definite volume. Hence a liquid is characterized by a *free surface*. In terms of theory, this fact may be explained by assuming that there exists a balance between the attraction forces and the stirring effect of molecular kinetic energy which determines the temperature of the liquid.

In the interior of a liquid, a molecule is surrounded uniformly by its fellow molecules. Hence the forces of attraction on it are the same from all directions and cancel out. Such a molecule is as free to move as if forces of attraction did not exist. However, a molecule in the surface should experience a pull to the interior which is not balanced by any outward pull (Fig. 38). The result should be that as few molecules should remain on the surface as possible. This is the prediction of the theory, and it is fully corroborated by the facts. The surface of a liquid acts as if it were under a tension that makes it shrink to as small an area as possible. Hence, drops of a liquid assume a spherical shape, since the surface of a sphere as compared with its volume is smaller than the surface of a volume of any other shape.

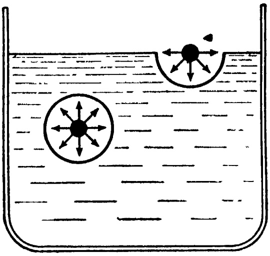

FIG. 38.—Surface tension.

3. Molecular Motion in Liquids. When a gas and a liquid at the same temperature are brought into contact, both remain at this temperature. If the molecules of a gas move with greater average kinetic energy than those of a liquid at the same temperature, molecular collisions at the surface would result in molecules of the liquid gaining kinetic energy from those of the gas and the temperature of the liquid would rise. Since this does not occur, the average kinetic energy of molecules of liquids and gases is the same at the same temperature.

Liquids expand when heated, although the relative expansion is less than that of gases. In the liquid as in the gaseous state, the theory postulates that molecular kinetic energy is proportional to the absolute temperature. As the temperature rises, the average distance between the molecules increases and the liquid expands.

4. Evaporation.—A liquid left in an open vessel will eventually evaporate completely. At a given temperature, however, the rates at which liquids evaporate vary widely. Thus ether evaporates more rapidly than water and water more rapidly than mercury. Evaporation must be an indication of the escape of molecules through the surface of the liquid and hence evidence of molecular motion. The escape of a molecule from its fellows must occur against their force of attraction. Since van der Waals forces are not the same between different kinds of molecules, the ease of escape and, hence, the rate of evaporation will vary with different liquids at the same temperature. Thus van der Waals forces between water molecules are greater than between those of ether but less than those between mercury molecules.

The rate of evaporation of a given liquid increases as the temperature is raised. This is additional evidence for the theory that molecular kinetic energy increases with the temperature.

5. Vapor Pressure.—If a liquid is placed in a closed vessel of greater volume, evaporation proceeds for a time and then seems to stop. The pressure of the vapor above the liquid increases until it reaches a maximum at a given temperature. These facts can also be explained by the theory: the rate of evaporation, *i.e.*, the rate of escape of molecules from the liquid state, depends upon the nature of the liquid, the temperature, and the total surface area. However, the rate of evaporation per unit surface area of a given liquid at a constant temperature is constant. As the liquid evaporates, the concentration of the molecules of the vapor increases. These molecules bombard the walls of the containing vessel with a pressure that increases as their concentration grows. They also strike the surface and return to the liquid. This process, the exact opposite of evaporation, is called condensation. The rate of condensation is determined by the concentration of the vapor molecules. As this concentration grows, due to the continued evaporation of the liquid, the rate of condensation increases until it becomes equal to the rate of evaporation. *A dynamic equilibrium* has then been established in which *two reactions, each the exact opposite of the other, are proceeding at equal rates.* Neither reaction has stopped; but one nullifies the effect of the other (Fig. 39).

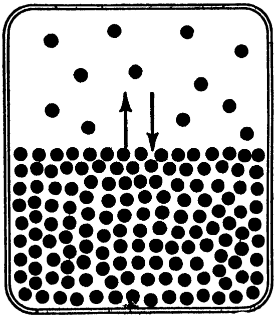

Fig. 39.—A liquid in equilibrium with its vapor.

Once the equilibrium has been established, the relative amounts of liquid and vapor remain fixed, since for every molecule evaporating a corresponding one condenses. The concentration of the vapor and the pressure that it exerts are also constant. *The pressure of the vapor in equilibrium with the liquid at a given temperature is called the vapor pressure of the liquid at that temperature.* At 20°C., the vapor pressures of ether, water, and mercury are 442.2, 17.5, and 0.001 mm., respectively.

The shape of the vessel which determines the total liquid surface and the relative volumes of liquid and vapor in the vessel have no effect on the value of the vapor pressure at equilibrium. The rate of evaporation *per unit area* is fixed for a given liquid at a constant temperature regardless of the total surface and of the depth of the liquid. The rate of condensation *per unit area*, which must equal this rate of evaporation, depends on the *concentration* and not on the total amount of vapor. In a stoppered bottle containing a relatively small amount of liquid, there will be a greater total amount of vapor than in one of equal size nearly filled with liquid. Nevertheless the concentration of the vapor and hence its pressure is the same in each bottle.

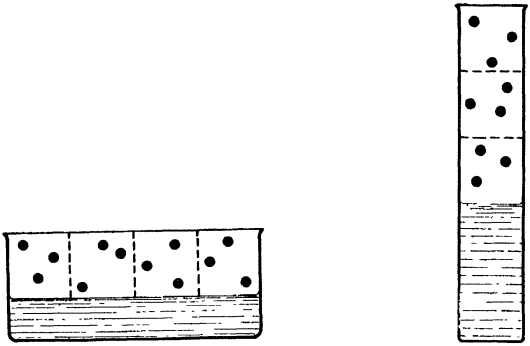

FIG. 40.—The concentration of the vapor and the vapor pressure of a liquid are the same at a given temperature regardless of the shape of the container.

6. Measurement of Vapor Pressure.—The vapor pressure of a liquid may be determined with the aid of a simple barometer tube. The space above the mercury is almost a perfect vacuum (Fig. 41). If a small amount of the liquid is introduced into this space with the aid of a medicine dropper held under the lower end of the tube, an equilibrium is soon established. The mercury will fall in the tube a distance equal to the vapor pressure of the liquid.

7. Kinetic and Potential Energy.—Evaporation is a cooling process as we are all aware when we wash our faces or get our feet wet. It is a process involving a separation of molecules against the force of mutual attraction. It requires energy to increase the distance between things that attract each other. To throw a baseball into the air requires energy because of the force of gravity acting between the ball and the earth. The act of throwing imparts to the ball a certain amount of kinetic energy. As the ball rises, the kinetic energy is expended in doing the work of increasing the distance between it and the earth against a force of mutual attraction. This energy is not destroyed, since energy like matter is conserved. But the kinetic energy with which the ball leaves the hand of the thrower changes gradually to potential energy as its distance from the earth increases. Potential energy is stored energy; and whenever energy is put in such storage, some other form of energy has been used to work against a force. If forces of attraction or of repulsion did not exist, it would be impossible to store energy.

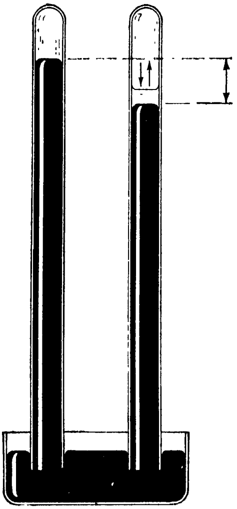

Fig. 41.—Measuring the vapor pressure of a liquid.

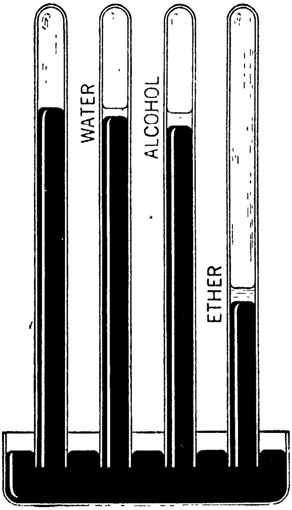

Fig. 42.—At the same temperature the vapor pressures of different liquids are not equal.

When the ball reaches the top of its flight, all its kinetic energy has been converted into potential energy. If at this point anyone suspects that energy has been destroyed, let him stand directly under the ball and await developments. As the ball falls, potential energy becomes kinetic again and the skeptic is appropriately convinced.

Let us apply this knowledge to the behavior of molecules. Any process that involves a separation of molecules converts kinetic into potential energy. Since molecular kinetic energy is heat, such a process must convert heat into potential energy and result in a fall in temperature. Such a process we say absorbs heat. This is an unfortunate choice of terms. Remember *a process that absorbs heat converts molecular kinetic energy into potential energy and produces a temperature fall.* Conversely, any process that involves molecules moving closer together converts potential energy into kinetic energy, thus producing a rise in temperature.

8. Heat of Vaporization.—Evaporation is a process that absorbs heat and hence produces a cooling effect because it involves a separation of molecules. Condensation, on the other hand, is exothermic. The heat of vaporization of water is 9,720 cal./mole. Thus when 18 g. of water evaporates, this quantity of heat is absorbed, and conversely, the condensation of one mole of water vapor liberates the same amount. Thus we may write

$$9{,}720 \text{ cal.} + H_2O \text{ (l.)} \rightleftarrows H_2O \text{ (g.)}$$

(l.) and (g.) indicating liquid and gas, respectively. Water has a disproportionally high heat of vaporization, since energy is used not only to separate the molecules, but also to break down the associated molecules (13-3) of the liquid into the simple H_2O molecules of the vapor. This high heat of vaporization is utilized in the steam radiators of domestic heating systems.

9. The Law of van't Hoff.—*If the temperature is raised on a system in equilibrium, the equilibrium will shift so that the reaction which absorbs the heat is more nearly complete.* This law, first stated by the great Dutch physical chemist van't Hoff, enables us to predict the effect of a rise in temperature on a liquid-vapor equilibrium. In general, we may write

$$\text{Heat} + \text{liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftarrows}} \text{vapor}$$

At some higher temperature a new equilibrium will be established in which the evaporation reaction will be more nearly complete. In other words, there will be less liquid and more vapor.

The explanation of this law as it applies to this equilibrium is as follows. Since an increase in temperature means an increase in molecular kinetic energy, it follows that the rates of all types of reaction, in which molecules take part, will be increased by a rise in temperature. In this case both evaporation and condensation take place at greater rates when the temperature is raised. If both were increased by the same amount, the system would remain in equilibrium and the relative amounts of liquid and vapor would not change. However, since evaporation absorbs heat, its rate is increased more than is the rate of condensation. During the period of readjustment which ensues, more liquid evaporates than vapor condenses and, therefore, the concentration of the vapor increases. But an increasing vapor concentration will increase the rate of condensation (Why?) until the two rates are once again equal and the new equilibrium is established. The vapor pressure at the higher temperature will be greater since the concentration of the vapor has increased. On the other hand, the concentration of the molecules in the liquid will be less. At the higher temperature, their increased kinetic energy demands a greater average separation so that there will be fewer molecules per unit volume.

EXERCISES

1. Explain the role that van der Waals forces play in the liquid state.
2. Why do drops of mercury assume a spherical shape?
3. At a given temperature, how does the average kinetic energy of the molecules of a liquid compare with that of the molecules of a gas?
4. What evidence indicates that the kinetic energy of molecules in liquids increases with a rise in temperature?
5. Describe the process by which an equilibrium is established between a liquid and its vapor in a closed vessel.
6. Define vapor pressure.
7. Does the presence of air above a liquid effect its vapor pressure?
8. How may energy be stored as potential energy?
9. Why is condensation an exothermic process?
10. Describe in detail the effect of a rise in temperature on the equilibrium between a liquid and its vapor.
11. Why are gases and liquids under standard conditions composed of molecules and not of ions?
12. Explain why the rate of evaporation per unit surface area does not depend upon the depth of a liquid.
13. Why is the vapor pressure of a liquid at a given temperature independent of the amount of the liquid and of its total surface?
14. Can you predict what would be the effect on the rate of evaporation of water if sugar were dissolved in the water? What would be the effect on the vapor pressure?

15. At the same temperature, alcohol has a greater vapor pressure than water. What fundamental difference in the properties of these substances accounts for this fact?

16. Why is the pressure above the mercury column in a barometer negligible?

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CHAPTER FIFTEEN

LIQUEFACTION OF GASES

The earliest recorded work on the liquefaction of gases was carried out by van Helmont in the early seventeenth century. To him we owe the terms "gas" and "vapor." The latter he applied to those gases which can be readily liquefied by cooling. This term will be defined more precisely later in this chapter. Not until the nineteenth century did this subject receive systematic attention. Then in 1823, Michael Faraday announced the liquefaction of nine gases. In one arm of an inverted V-shaped tube (Fig. 43) of heavy glass, a substance or mixture was heated which resulted in the evolution of the gas. The other arm of the tube was cooled in a freezing mixture of ice and salt. At this temperature (−21°C.), he was successful in liquefying each of the nine gases. Later, Thilorier succeeded in liquefying carbon dioxide in quantity and in obtaining the substance as a solid (Dry Ice). In 1835, he succeeded in attaining the low temperature of −110°C., using a mixture of solid carbon dioxide and ether. Using this mixture, Faraday (1845) liquefied four more gases. But he was

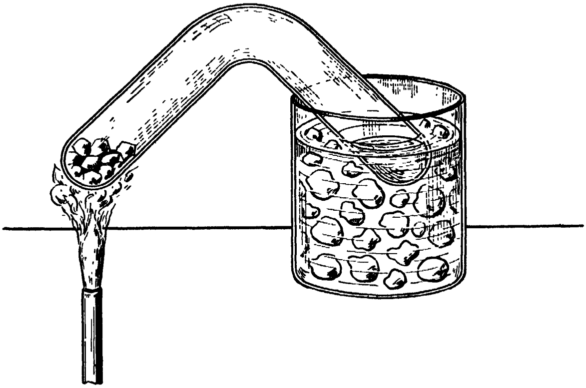

FIG. 43.—Faraday's simple apparatus for liquefying gases.

unsuccessful with hydrogen, nitrogen, oxygen, nitric oxide, carbon monoxide, and methane. As a result, the conviction grew that these were permanent gases, especially since Nalterer was equally unsuccessful after compressing the cooled gases to over 3,000 atm. This conception was recognized as incorrect when the fundamental condition that must be met before a gas can be liquefied was discovered by Andrews in 1869.

1. Critical Temperature.—To understand this essential condition, we must return to the effect of the temperature on liquid-vapor equilibrium. You will remember that as the temperature rises the concentration of the vapor molecules increases but that of the liquid molecules decreases. Eventually a temperature must be reached at which the two concentrations become equal. Then in both the vapor and the liquid the same molecules are the same average distance apart, and there ceases to be any difference between the two. The surface, which hitherto has marked a difference in properties, disappears, and the two phases become one. This is the *critical temperature at which the molecular concentration and all other properties of the liquid and the vapor become the same.* Since the surface has disappeared, the liquid state has gone. Above this temperature, the substance is a gas and no pressure, however great, will liquefy it.

Each substance, which is stable when heated, has its own characteristic critical temperature. By consulting Table 11, we may understand why Faraday was unsuccessful in the instances mentioned above. As −110°C., the temperature of his refrigerant, is above the critical temperature of these gases, he was unable to liquefy them.

The *critical pressure* is the vapor pressure at the critical temperature. It represents the limiting value that the vapor pressure of the liquid approaches as the temperature rises to the critical.

2. Vapor-pressure Curves.—If the vapor pressure of a liquid is plotted against the temperature, a curve similar to that shown in Fig. 44 is obtained. The curve is obviously not a straight line, so that it would be wrong to say that the vapor pressure is directly proportional to the temperature. The rate at which the vapor pressure changes with the temperature depends upon such factors as the heat of vaporization, the difference between the volumes of a mole of the substance as a liquid and as a vapor, and the temperature itself. Since these are not constant, the curve is not a straight line.

TABLE 11.—CRITICAL CONSTANTS OF COMMON SUBSTANCES

Substance	Formula	Critical temperature		Critical pressure, atm.	Boiling point, °A.	Ratio, T_B/T_C
		°C.	°A.			
Helium	He	−267.9	5.2	2.26	4.2	0.81
Hydrogen	H_2	−239.9	33.2	12.8	20.4	0.62
Neon	Ne	−228.7	44.4	25.9	27.2	0.61
Nitrogen	N_2	−147.1	126.0	33.5	77.3	0.61
Carbon monoxide	CO	−139.5	133.6	35	81	0.60
Oxygen	O_2	−118.8	154.3	49.7	90.1	0.58
Nitric oxide	NO	−91	179	65	122	0.68
Carbon dioxide	CO_2	31.1	304.2	73		
Nitrous oxide	N_2O	36.5	309.6	71.7	183.6	0.59
Hydrochloric acid	HCl	51.4	324.5	81.6	188	0.58
Hydrogen sulfide	H_2S	100.4	373.5	88.9	213.5	0.57
Ammonia	NH_3	132.4	405.5	111.5	239.7	0.59
Chlorine	Cl_2	144.0	417.1	76.1	238.5	0.57
Sulfur dioxide	SO_2	157.2	430.3	77.7	263.1	0.61
Ethyl alcohol	C_2H_5OH	243.1	516.2	63.1	351.5	0.68
Water	H_2O	374.0	647.1	217.7	373.1	0.58

The curve starts at the freezing point T_f and ends at the critical temperature T_c. Every point on the curve represents a pressure and a corresponding temperature at which the liquid is in equilibrium with its vapor. Thus the equilibrium conditions corresponding to point 1 are pictured at the lower left of Fig. 44. This is an imaginary submicroscopic cylinder with a piston upon which a weight is placed which exerts a pressure over the area of the piston equal to the vapor pressure P_1. Since the vapor is exerting the same pressure underneath, the piston is at rest. Note that the concentration of the vapor molecules is small and that of the molecules in the liquid large at this relatively low temperature.

If the temperature is raised to T_2, the picture changes (Fig. 44-2). The vapor pressure has increased to P_2 owing to the larger molecular concentration of the vapor. However, that of the liquid is less. At the critical temperature T_c, the two concentrations are equal and the surface (see arrow at right of cylinder) has disappeared. Above the critical temperature, the substance is a gas.

3. Condensation of Vapors.—Let us return to the temperature T_1 and to the conditions represented by point 4. Here the vapor has been compressed to a pressure that is above the vapor pressure at T_1. This is represented by the weight, greater than that corresponding to P_1, on the piston pictured at the right. The concentration of the vapor is increased because the piston is descending and the rate of condensation is greater than the rate of evaporation. The descent of the piston is finally checked when all the vapor has condensed. Thus *if the pressure of the vapor is maintained at a value above the vapor pressure at a given temperature, complete condensation results.* Every point above the curve represents conditions under which the liquid is the only stable phase.

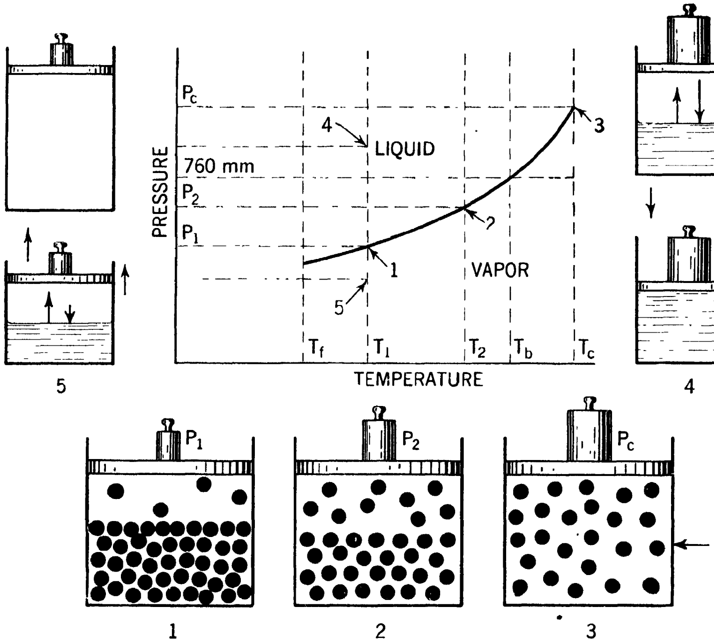

Fig. 14.—The vapor-pressure curve of a liquid.

Below the curve, any point represents a pressure of vapor less than the vapor pressure. Conditions represented by point 5 are illustrated at the left. Under these, the piston rises because the pressure due to the weight is less than the pressure of the vapor underneath and the molecular concentration of the vapor diminishes. This results in a rate of condensation less than that of evaporation, and the liquid evaporates completely. Hence any point below the curve represents conditions under which the vapor alone is stable.

4. Liquefaction of Gases.—*To liquefy a gas, its temperature must first be lowered to below its critical temperature. Then its pressure must be raised to above its vapor pressure at this lower temperature.*

The problem of producing the low temperatures needed to liquefy such gases as nitrogen, oxygen, hydrogen, and helium is an interesting one. Any process that absorbs heat will result in a lowering of the temperature (14-7). Thus the rapid evaporation of a liquid and the sudden expansion of a highly compressed gas produce a cooling effect, since they involve a separation of molecules.

In 1878, Cailletet and Pictet working independently, the former at Paris and the latter at Geneva, reported the liquefaction of oxygen. Cailletet compressed oxygen to 300 atm., cooling it at the same time with either boiling sulfur dioxide or solid carbon dioxide under diminished pressure. The gaseous oxygen was then allowed to expand suddenly, whereupon it so cooled itself that liquefaction took place. In this way, he was also successful in liquefying air, nitrogen, and carbon monoxide.

In 1908, the Dutch physicist Kamerlingh Onnes, working in the Leyden cryogenic laboratory, succeeded in liquefying helium. Its critical temperature is but 5°C. above absolute zero. With liquid helium, Onnes succeeded in reaching a temperature of -272.18°C., less than a degree above absolute zero. In 1926, Prof. W. H. Keesom, working in Onnes' laboratory, succeeded in solidifying helium at -271.6°C. under a pressure of 26 atm.

In these experiments for the production of low temperatures, a reversible compression-expansion process is employed. Compression involves a liberation of heat and hence a rise in temperature. This heat of compression is removed and the temperature lowered by means of a suitable refrigerant. Expansion follows with an accompanying absorption of heat and the attainment of a yet lower temperature. Within recent years, another type of reversible process has been used successfully to attain temperatures a few thousandths of a degree above absolute zero. Some crystalline substances give out heat when acted upon by a powerful magnet and absorb heat when the influence of the magnet is removed. The initial heat of magnetization is removed by liquid helium boiling under reduced pressure, thus lowering the temperature of the substance to about 1.5°A. Then the magnet is turned off, and the resulting demagnetization further reduces the temperature. By this means, Giauque at the University of California reached a temperature of 0.097°A. and de Hass and Wiersma at Leyden, one of 0.0044°A.

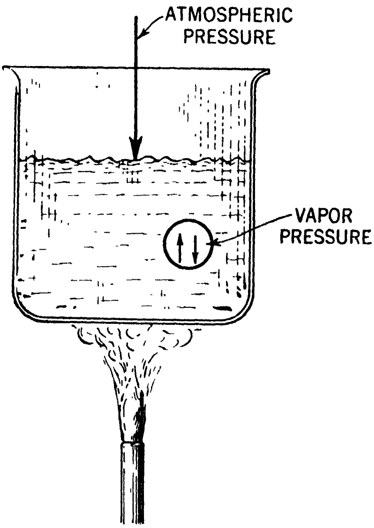

FIG. 45.—A liquid boiling in an open vessel.

5. Boiling Point.—Thus far we have not mentioned the fact that a liquid boils. The reason has been that liquids do not boil when heated in the closed vessels we have been considering. Liquids boil usually in open vessels in which their surfaces are exposed to atmospheric pressure. We recognize boiling by the formation of vapor bubbles beneath the surface. We shall understand this process better by first considering under what conditions these bubbles may form. Obviously, a bubble cannot be stable unless the pressure inside is at least equal to the external pressure. Bubbles of vapor must be in equilibrium with the surrounding liquid; and the internal pressure must be equal to the vapor pressure (Fig. 45). The external pressure is that of the atmosphere. A liquid boils in an open vessel, therefore, at that temperature at which its vapor pressure becomes equal to atmospheric pressure. Since the latter may vary, the temperature at which boiling occurs may vary also. More exactly, the *boiling point of a liquid is the temperature at which its vapor pressure becomes equal to* 760 *mm.* (Fig. 46).

Since the barometric pressure falls with increasing altitude, cooking of food on a mountaintop becomes a problem. The temperature and not the boiling cooks the potatoes. For every mile above sea level, the boiling point of water is decreased approximately 5°C. At an altitude of 11,000 ft., it takes twice as long to cook a meal.

Under such conditions, a pressure cooker is indicated. Above the water in such a closed vessel, the pressure is equal to the vapor pressure of the liquid and, in addition, that of the air enclosed. Under such conditions, the water cannot boil (Why?) and temperatures greater than 100°C. are easily attained. The rough approximation that the speed of a chemical reaction is doubled when the temperature rises 10°C. may be applied to the reactions involved in cooking foods. Hence an appreciable saving in time results from the use of a pressure cooker.

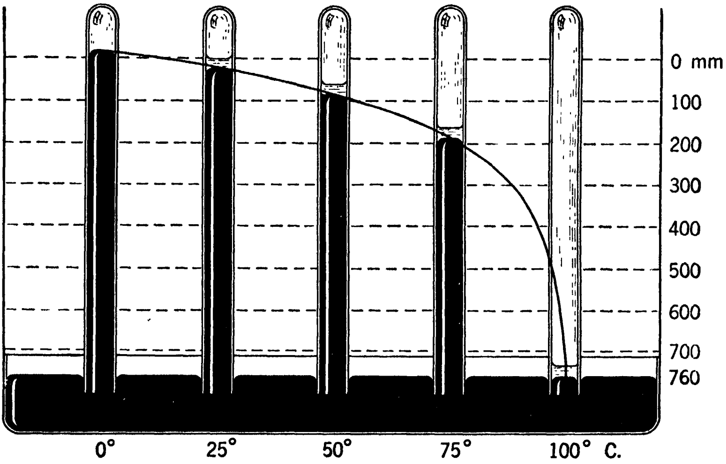

FIG. 16.—The vapor pressure of water increases with the temperature and becomes equal to 760 mm. at its boiling point.

6. Distillation under Diminished Pressure.—Distillation is a process frequently used to purify a liquid. If a given liquid decomposes before its boiling point is reached, its purification by distillation at atmospheric pressure is impossible. However, if the pressure above the liquid is kept low by means of a pump, the boiling point may be lowered to a temperature below that at which decomposition takes place and purification by distillation becomes possible.

7. Liquid Air.—Thirty years ago, liquid air was a curiosity whose intriguing properties were the feature of the Sunday magazine sections of the newspapers. In 1932, the 156 plants in this country produced over 2,086,301,000 cu. ft. of oxygen valued at $24,000,000 by a process that involves the liquefaction of air. About 1907, a demand for compressed oxygen was created by the infant oxyhydrogen-welding industry; and liquid air offered one of the most economical means by which pure compressed oxygen could be prepared. Liquid air consists of a mutual solution of two liquids, oxygen and nitrogen, which can be readily separated because of the difference of their boiling points.

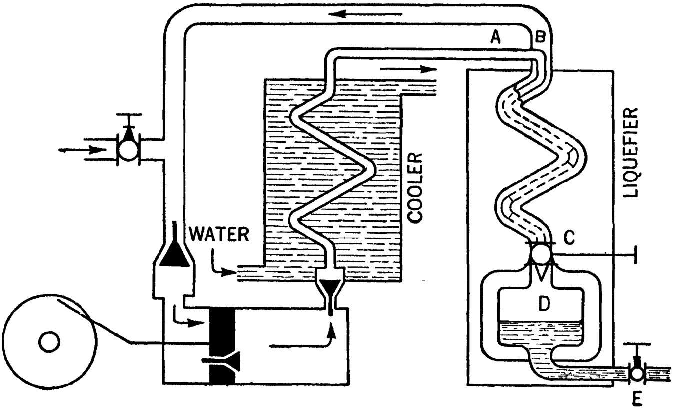

Fig. 47.—An air liquefier.

Nitrogen with the lower boiling point distills away first, and a separation is accomplished. At first, nitrogen was a by-product of this separation which was of little use. Now there is a demand for this by-product by the nitrogen-fixation industry (38-5) and by the electric-light-bulb manufacturers who have discovered the superiority of the nitrogen-filled bulb.

Liquid air is an almost colorless liquid that gradually turns to a delicate blue tint, the color of liquid oxygen, as the nitrogen boils away. Nitrogen boils at atmospheric pressure at $-195.5°C.$, and the boiling point of oxygen is $-182.93°C.$ Liquid air can be kept for several days in vacuum-jacketed flasks. At its low temperature, flowers, eggs, meat, rubber, and many other more or less elastic objects become as brittle as glass.

8. Liquid-air machines make use of the fact that when a gas expands it becomes cooler. In a liquid-air machine, successive expansions produce successively lower temperatures until the critical temperatures of oxygen and nitrogen are reached below which air liquefies at the pressure in the machine. Figure 47 represents a diagram of a laboratory liquefier. Air, which has been carefully freed from carbon dioxide and water vapor, is raised by the compressor to a pressure of 200 atm. which heats the gas. The heat of compression is removed in the cooler in which the compressed gas passes through a spiral pipe, jacketed by cold running water or by solid carbon dioxide. The cooled gas then passes into the liquefier in which it flows through the inner of two concentric spiral tubes *A*. In so doing, it is further cooled by gases that are flowing in the opposite direction through the outer spiral tube *B*. It is then allowed to expand to a much lower pressure through the expansion valve *C* into the chamber *D* cooling itself in the process. The cold gas passes out of the liquefier through the outer spiral, thus cooling the compressed gases in the inner tube, which are about to enter the chamber through the expansion valve. In this way, each successive portion of gas that expands into the chamber does so at an initially lower temperature and is cooled to a correspondingly lower temperature. Eventually, temperatures that are lower than the critical temperatures of oxygen and nitrogen are reached, and some of the gas will condense to a liquid in the chamber *D* from which it can be drawn off through the valve *E* as needed.

9. Artificial Refrigeration.—The principles that have been applied to liquid-air machine design have been extensively employed in the designing of the various types of household refrigerators. These are in general of two types, compression machines and absorption machines.

Compression machines employ some readily liquefiable vapor, such as ammonia, sulfur dioxide, ethyl chloride, or dichlorodifluoromethane (Freon). The critical temperatures of these substances are all above room temperature so that they can be liquefied by pressure alone. Figure 48 represents a somewhat simplified machine of this type, consisting of a compressor, run by an electric motor, a condenser, an expansion valve, and an evaporator which is surrounded by the space to be refrigerated. The vapor is compressed by the right-to-left stroke of the compressor piston. The heat of compression is removed in the condenser by a stream of air which is blown over the cooling coils by means of a fan, when the unit is located beneath the refrigerated space, or by the natural circulation of air, when the cooling coils are on top. This cooling is sufficient to liquefy the greater part of the compressed vapor, and the liquid collects in the reservoir tank. It is then allowed to vaporize and expand into the coils of the evaporator and in so doing absorbs heat from the space surrounding it. The vapor is then drawn back into the compressor to repeat the cycle.

Absorption machines, paradoxically enough, produce cold by means of heat. These machines usually make use of the fact that ammonia gas is exceedingly soluble in water. At standard temperature and pressure, 1 g. of water will dissolve an equal weight, or some 1.2 liters, of ammonia. Since 1 g. of water occupies a volume of 1 ml., it absorbs about 1,200 times its own volume of ammonia. The solubility of the gas, however, diminishes rapidly as the temperature is raised. Based upon these facts, a clever substitute for a motor-driven compressor has been devised. An absorption refrigeration machine (Fig. 49) consists of a generator absorber, condenser, reservoir, expansion valve, and evaporator. During the first phase of the cycle, cold water is circulated through coils inside the generator. At the temperature of the cooling water, ammonia is dissolved by the water and drawn through the valve *A*. At the completion of the absorption, the cold water is shut off and steam substituted for it. At the temper-

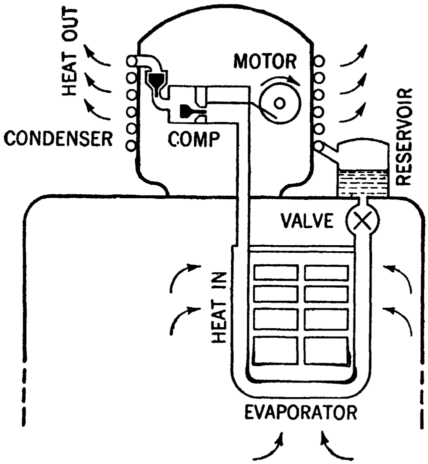

FIG. 48.—A compression type of artificial refrigerator.

ature of steam, the ammonia is driven out of solution, and the pressure of the ammonia gas above the water in the generator increases rapidly, closing valve *A* and opening valve *B*. The compressed gas is cooled and liquefied in the condenser. The liquid ammonia collects in the reservoir and finally vaporizes and expands through the expansion valve into the coils of the space to be refrigerated. The steam is then shut off, cold water substituted, and a new cycle started.

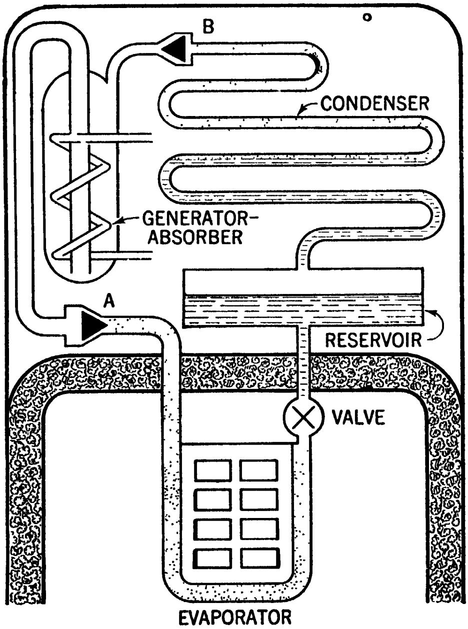

Fig. 49.—An absorption refrigerator.

One of the difficulties encountered in designing such machines is that water also is volatile and yet must not be permitted to enter the condenser as a vapor. In practice, this difficulty is met by introducing between the generator and the condenser what is called a rectifier and analyzer in which any water vapor is condensed. Another method of meeting this difficulty is the use of a nonvolatile absorbent in place of water. Such solids as calcium chloride will absorb considerable quantities of ammonia. A refrigerator of this type is on the market.

EXERCISES

1. Define critical temperature in two ways.

2. Why is the critical temperature of mercury higher than that of oxygen?

3. Why has helium the lowest critical temperature of any known substance?

4. When oxygen is drawn off from the steel cylinder, in which it is stored, the pressure falls. This is not the case with chlorine since the pressure in cylinders of this element remains at 6.6 atm. until nearly all the chlorine has been removed. Explain.

5. At room temperature, which substance would you predict has the greater vapor pressure, sulfur dioxide or ammonia?

6. The vapor pressure of carbon dioxide at 20°C. is 56.5 atm. In a steel cylinder of this substance at room temperature, the pressure is 300 lb./sq. in. Is carbon dioxide a vapor or a liquid under these conditions?

7. What changes in conditions are necessary to liquefy a gas completely?

8. What conditions determine the boiling point of a liquid?

9. Why is boiling prevented when a liquid is heated in a closed vessel?

10. A certain liquid decomposes at a temperature 10°C. above its boiling point under atmospheric pressure. How would it be possible to decompose this liquid by heat?

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CHAPTER SIXTEEN

SOLIDS

True solids are composed of crystals, *i.e.*, particles of regular shape bounded by plane surfaces. Each of the crystals of a given substance are not only of the same characteristic form, but even the angles between corresponding surfaces are the same. Such regularity of form must indicate a regular arrangement in space of the molecules, ions, or atoms which are the structure units of crystals. Even in liquids at temperatures near their freezing points, evidence is beginning to accumulate which indicates that some regularity in the arrangement of molecules exists. But the forces that are responsible for this rudimentary structure are too slight to prevent liquid flow.

1. Sublimation.—There is much evidence of the theory that the molecules, ions, or atoms, of which crystals are composed, are in motion. That their motion is restricted to a vibration about fixed points in the crystal is clearly indicated by the rigidity and regular form of the crystal itself. Solids expand when they are heated, a fact that must be taken into account when railroad rails are laid. Spaces are left between the ends of the rails, lest the expansion that takes place on a hot summer day cause a buckling of the tracks. Here, as in liquids, an increase in temperature means an increased kinetic energy of the structure units which creates a demand for increased elbowroom.

Solids, in whose crystals molecules are the structure units, evaporate as do liquids, but the process is called *sublimation*. Solids like menthol, camphor, and naphthalene (moth balls) are readily recognized by their odor, evidence that some of their molecules have escaped from crystal surfaces and found their ways into our noses. Snow, at temperatures consistently below the melting point of ice, sublimes gradually into the air.

The rates at which different solids sublime vary widely at the same temperature. This is an indication that the forces which bind the structure units together in crystals must also vary for different substances. If the forces are small, the ease of escape and hence the rate of sublimation are great. Significantly, we may divide solids into two classes. Salts, which are invariably solids of high melting point, show no tendency to sublime. Consequently they have no odor—smelling salts to the contrary notwithstanding (38-16). On the other hand, solids like ice, camphor, menthol, and naphthalene have relatively low melting points and sublime readily at ordinary temperatures. As we have mentioned before, these solids are molecular with comparatively weak van der Waals forces binding their molecules together. On the other hand, salt crystals are made up of oppositely charged ions between which strong Coulomb forces operate.

As we might suspect, the rate of sublimation of a given solid increases with a rise in temperature, an indication of an increase in the kinetic energy of vibration of the structure units.

Finally if a solid, a liquid, and a gas all at the same temperature are brought into mutual contact, the temperature of each will remain the same. This leads, by the same reasoning we have applied before (14-3), to the hypothesis that at the same temperature molecules in any of the three states of matter have the same average kinetic energy (the law of equipartition of energy).

2. Vapor Pressure of a Solid.—If a solid is placed in a closed vessel, an equilibrium is established between the solid and its vapor when the rate of sublimation is equaled by the rate at which molecules of the vapor crystallize on the solid surface. The mechanism of the establishment of this equilibrium is analogous to that considered in the case of a liquid and its vapor (14-5). Similarly, the vapor pressure of a solid is that pressure which its vapor exerts when in equilibrium with the solid at a given temperature. Since sublimation absorbs heat, a temperature increase favors this reaction and, accordingly, the vapor pressure rises.

If the vapor pressures of both the solid and the liquid forms of a given substance are plotted against the temperature, curves similar to those in Fig. 50 are obtained. Since the solid form exists at lower temperatures and at lower vapor pressures, the curve for the solid-vapor equilibria is to the left and lower than for the corresponding liquid-vapor equilibria. Any point on this curve, *e.g.*, 6, represents a pressure of vapor and a corresponding temperature at which solid and vapor are in equilibrium. At the pressure and temperature corresponding to point 7, the vapor crystallizes faster than the solid sublimes and the solid phase only is stable. Under conditions represented by 8, the solid sublimes faster than the vapor crystallizes; and the vapor only is stable.

3. Freezing, or Melting, Point.—When ice and liquid water are brought together, the temperature changes to 0°C. and remains there as long as both phases are present. If heat is supplied to this system, a certain amount of ice melts but the temperature does not rise above 0°C. until all the ice has melted. If heat is withdrawn, an equivalent amount of water freezes, thus liberating enough heat to keep the temperature constant. If heat is neither supplied nor withdrawn, the two phases remain in equilibrium indefinitely at 0°C. This temperature is both the freezing point of water and the melting point of ice.

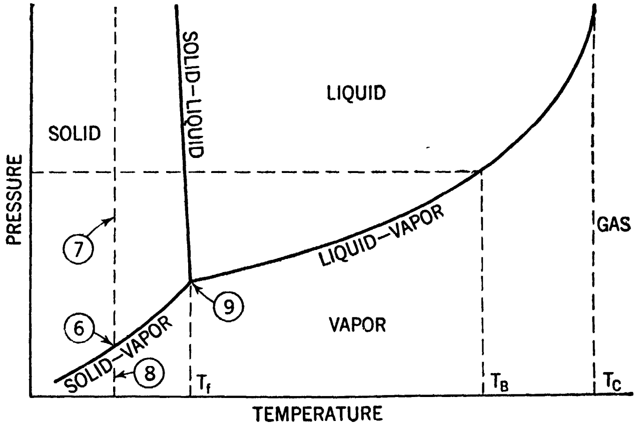

FIG. 50.—Equilibria between phases of water.

In general, *the freezing point of the liquid phase and the melting point of the solid phase of a substance is that temperature at which the liquid and solid are in equilibrium.* At this temperature, the rates of freezing and of melting are equal. *This is* also *the temperature at which the vapor pressures of the liquid and solid forms are the same.* In Fig. 50, these conditions are satisfied at point 9, where the vapor-pressure curves cross. The corresponding temperature T_f is the freezing-melting point. If at this temperature the two vapor pressures are equal, then both the solid and the liquid are in equilibrium with a vapor of the same concentration.

The vapor pressure of ice and of water at 0°C. is 4.579 mm., so that both phases are in equilibrium with water vapor of the concentration corresponding to this pressure (Fig. 51*a*). Since two phases in equilibrium with a third must be in equilibrium with each other, ice and water are in equilibrium at the temperature at which their vapor pressures are equal (Fig. 51*b*). At 0°C. and when the partial pressure of the vapor is 4.579 mm., all three phases of water are in equilibrium and the rates of evaporation and condensation, of sublimation and crystallization, and of melting and freezing are equal.

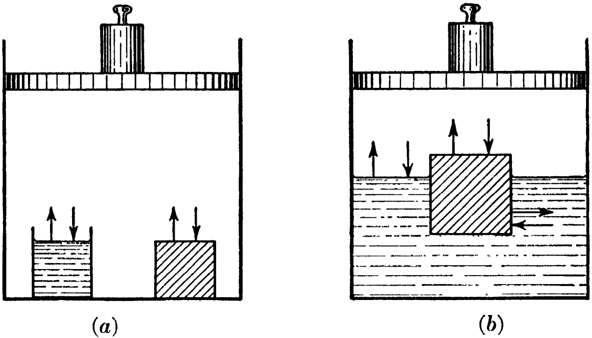
(*a*) (*b*)

Fig. 51.—The solid, liquid, and vapor phases of a substance in equilibrium at the temperature at which the solid and the liquid have the same vapor pressure.

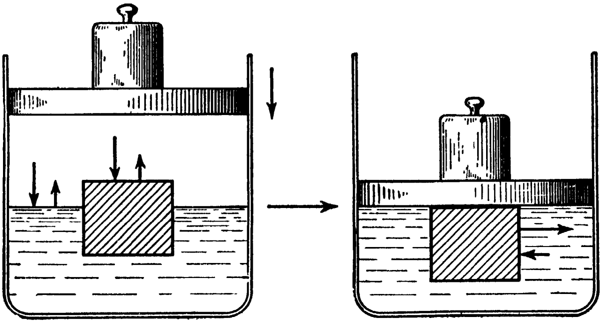
Fig. 52.—The effect of pressure on the melting point.

4. The Effect of Pressure on the Freezing Point.—The effect of compressing the vapor (Fig. 52) will be to increase the rates of condensation and crystallization until only the liquid and solid phases remain. An increase in pressure on a system in equilibrium favors the reaction that tends to reduce the volume.

Since the melting of ice is accompanied by a contraction in volume, a pressure increase at 0°C. maintains a greater rate of melting than of freezing and the liquid is the only stable phase. To keep the solid and liquid forms of water in equilibrium at an increased pressure, the temperature must be simultaneously lowered. This is shown by the slope of the solid-liquid curve in Fig. 50. However, since water is practically the only substance that contracts when it melts, an increase in pressure raises the freezing point of most substances. In any case, the effect is small. At a pressure of 1,000 atm., water freezes at −7.1°C.

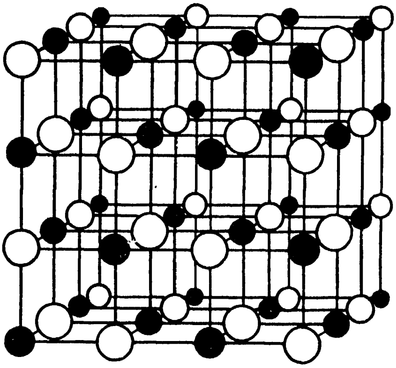

FIG. 53.—Ions are the structure units in the crystals of a salt like sodium chloride.

The melting point of a solid is so characteristic and so easily determined that it is used frequently as an aid in identification.

5. Crystal Structure.—Since 1912, methods have been developed by which not only the spacing but also the fundamental character of the structure units in crystals may be investigated. These methods are alike in that they make use of the diffraction or reflection of *x*-rays of known wave-lengths by crystals. For our present purposes, it will be sufficient to give a general idea of the nature of the results and of how they agree with the known facts.

We have mentioned the theory that ions are the structure units in salt crystals. *X*-ray analysis of a sodium chloride crystal indicates that sodium and chloride ions are arranged alternately at the corners of a cubical space pattern, or crystal lattice, shown in Fig. 53. *X*-ray evidence and even a relatively simple calculation based on the geometry of the crystal indicate that the distance between planes of ions in the sodium chloride crystal structure is 2.814 Å. The angstrom unit Å. is equal to a length of 10^{-8} cm. Further, the actual radii of various ions in salt crystals may be calculated from x-ray evidence. The radius of the sodium ion, 0.98 Å. (Table 12), and that of the chloride ion, 1.81 Å., show that there is little space in the crystal if the centers of these ions are 2.814 Å. apart. Actually, ions behave as if they are spheres packed closely together in the crystal lattice (Fig. 54). The relative sizes of the radii of the ions of a salt determine the most

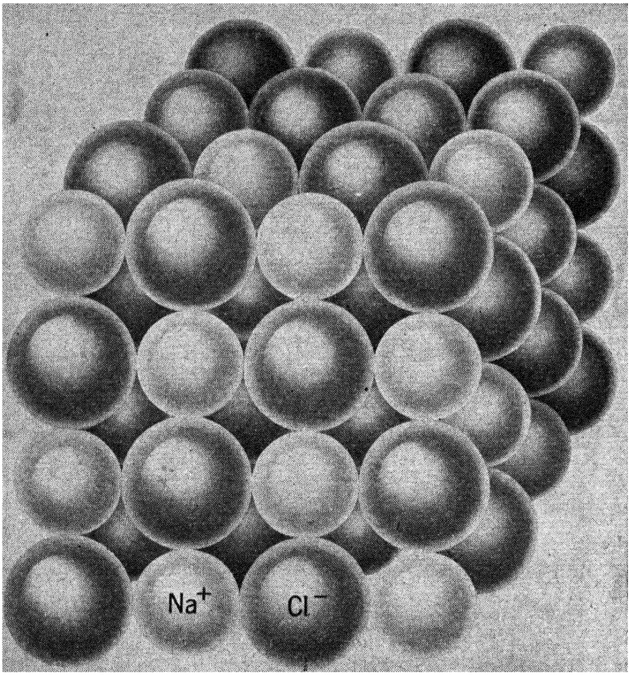

Fig. 54.—Sodium and chloride ions packed closely together in the salt crystal structure.

Table 12.—Typical Ionic Radii in Angstrom Units

Ion	Radius	Ion	Radius	Ion	Radius	Ion	Radius
Li^+	0.68	Be^{++}	0.34	$O^{=}$	1.32	F^-	1.33
Na^+	0.98	Mg^{++}	0.78	$S^{=}$	1.74	Cl^-	1.81
K^+	1.33	Ca^{++}	0.98	$Se^{=}$	1.96	Br^-	1.96
Rb^+	1.48	Sr^{++}	1.15	$Te^{=}$	2.18	I^-	2.19
Ca^+	1.65	Ba^{++}	1.37				

efficient way in which they may be packed and, therefore, in large measure the crystal form of the salt. Each ion in sodium chloride is surrounded by six equidistant ions of opposite charge. Hence no pairing of ions into molecules can be detected. *Salts,* in general, *are composed not of molecules but of ions.*

When we write NaCl for salt, we mean that in its crystals there are equal numbers of sodium and chloride ions. Since the *x*-ray evidence for the ionic character of salt crystals is relatively recent as compared with the length of time during which chemists have been using the term "salt molecule," we shall probably be talking and writing of "molecules" of a salt instead of "ion pairs" and of "molecular" weights in place of "formula" weights for some time to come.

6. Coulomb Forces in Ionic Crystals.—Salt crystals sublime exceedingly slowly and melt at rather high temperatures. Both of these facts indicate the existence of strong forces of attraction between the ions. Since the ions are oppositely charged, comparatively strong Coulomb forces of attraction bind the ions together, hence the low rates of sublimation, the low vapor pressures, and high melting points of all true salts.

7. Molecular Crystals.—Atoms may also combine by sharing a pair of electrons. This type of combination, called covalence, does not result in ion formation, as charged atoms result only when electrons are completely transferred. Instead, neutral molecules are formed. *Within* such molecules the atoms are held together more or less strongly by sharing electron pairs. *Between* such neutral molecules, relatively weak van der Waals forces operate. Such forces of intermolecular attraction are very small between molecules of low molecular weight and between those whose atoms are arranged symmetrically. As the molecular weight increases and especially as molecular symmetry decreases, van der Waals forces grow in strength.

We have seen that molecules of the halogens are diatomic. Each pair of atoms is held together by a covalent bond, *i.e.*, by a shared pair of electrons. As the molecular weight increases from fluorine to iodine (F_2 = 38, Cl_2 = 71, Br_2 = 106, I_2 = 254), the van der Waals forces between molecules increase. Thus at ordinary temperatures fluorine and chlorine are vapors; bromine is a volatile liquid; and iodine is a solid. The structure units in iodine crystals are neutral I_2 molecules (Fig. 55). Between such molecules van der Waals forces are much smaller than the Coulomb forces between ions in the crystals of a salt. Hence iodine sublimes readily and has a low melting point. Dry-ice, or solid carbon dioxide (Fig. 56), sublimes so rapidly that its crystals cannot be melted at atmospheric pressure. Camphor, menthol, and naphthalene are also molecular crystals.

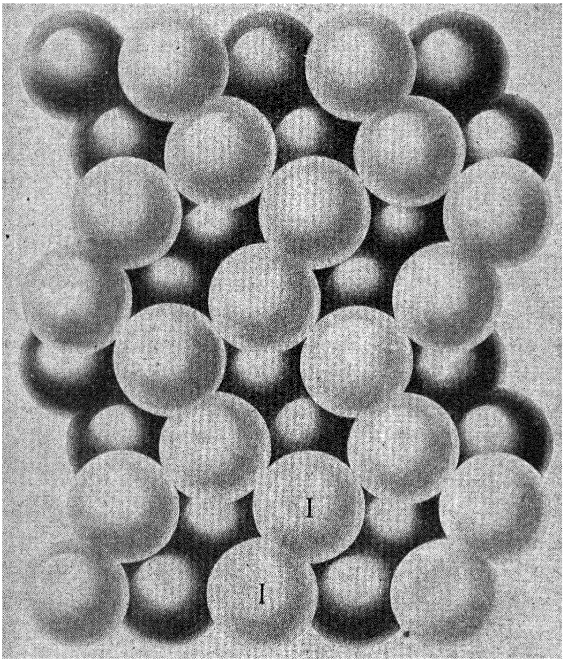

Fig. 55.—Diatomic molecules of iodine in the crystals of the solid. Weak van der Waals forces between molecules permit sublimation.

8. Giant Molecules in Crystal Structure.—A third type of crystal is made up of giant molecules, or macromolecules. Here atoms, linked together by covalent bonds, build up single molecules of giant size in one, two, or all three dimensions. Crystals, in which molecules are long chains of atoms linked by strong covalent bonds but with weak van der Waals forces holding the chainlike molecules together, are fibrous like asbestos. Macromolecules developed in two directions are found in layer lattices like graphite (Fig. 57). A crystalline form of carbon, graphite consists of macromolecules which are sheets of carbon atoms linked by shared pairs of electrons. Between adjacent sheets, the

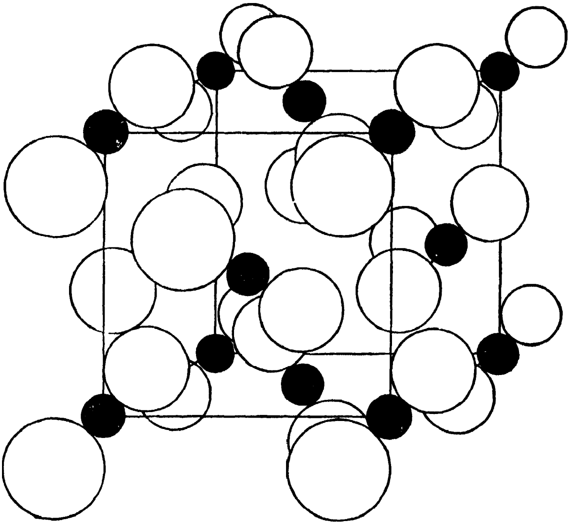

FIG. 56.—Crystal structure of carbon dioxide.

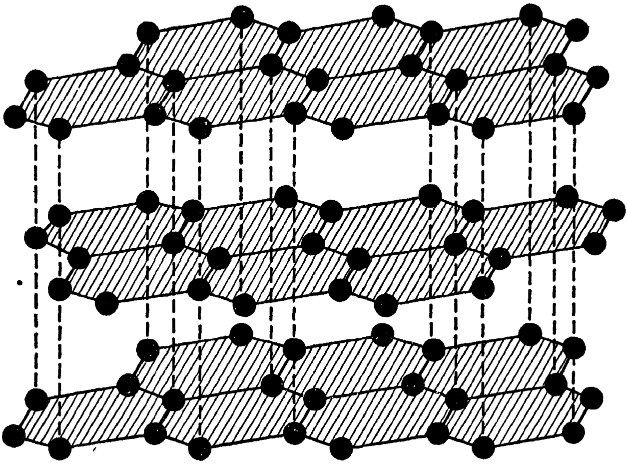

FIG. 57.—Two-dimensional giant molecules in graphite crystals.

relatively weak van der Waals forces permit slipping of one sheet over another, which makes graphite a lubricant.

Finally in the case of three-dimensional macromolecules, the entire crystal is a single molecule. Thus in the diamond, a second crystalline form of carbon, atoms are linked by covalent bonds in three directions as shown in Fig. 58. Crystals of this type are extremely hard and have very high melting points.

9. Preparation of Crystals.—Crystals of a given substance may be prepared in various ways, two of which only will be mentioned at this time. The substance in its liquid state may be allowed to cool to its freezing point. At this temperature, molecular motion has been decreased to such an extent that the attractive forces between the molecules get the upper hand and the molecules fit themselves into the crystal structure of the solid state peculiar to the substance. This method usually results in a mass of small crystals closely intertwined.

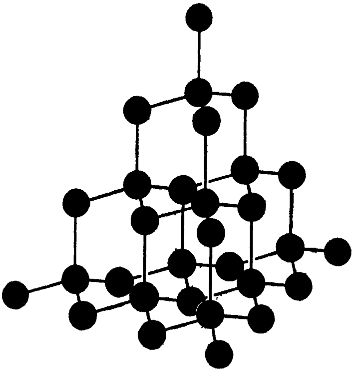

Fig. 58.—Diamond.

A second method, by the aid of which larger and more perfectly formed crystals may be obtained, consists in allowing a solid to crystallize out of a solution. The solid is dissolved in some suitable solvent at an elevated temperature, enough solid being dissolved in a given volume of the solvent to saturate it. Any excess solid or foreign suspended matter is then filtered off quickly without allowing the solution to cool appreciably in the process. A single seed crystal of the solid may then be suspended in the solution to act as a nucleus upon which the molecules of the substance in solution can crystallize. The solution is then allowed to cool slowly. The amount of a dissolved solid that a certain volume of a liquid can dissolve decreases, in general, with a decrease in temperature. Hence as the solution, which was saturated at the original temperature, cools it becomes supersaturated. The excess of the dissolved substance crystallizes out, usually building up the seed crystal to a larger size. The slower the rate of cooling, the larger and more perfect will be the crystals formed; for time is then given to the molecules to find places on the surface of crystals that have already formed, instead of forming new crystals.

10. Crystal Size.—If the rate of crystallization is very rapid, very small crystals are formed. Thus when salts which are practically insoluble in water are formed as products of a rapid chemical reaction, crystallization of the product is so rapid as to be precipitous. Indeed the term *precipitation* is used to denote an almost instantaneous crystallization of the product of a rapid chemical reaction which is nearly insoluble in the medium in which it is formed. Thus when aqueous solutions of silver nitrate and of sodium chloride are mixed, silver and chloride ions rapidly build up countless microscopic crystals of the insoluble salt silver chloride. These appear as a white cloud as soon as the clear solutions of the reactants are mixed. Sometimes a freshly formed precipitate is hard to filter from the liquid, as its crystals are small enough to go through pores in the filter paper. However, since small crystals are less stable than larger ones, the grain size of the precipitate will increase on standing.

Crystallization from liquids that are very viscous also tends to produce small crystals. Since diffusion is slow in such liquids, countless small crystals rather than a few large ones are formed. The candymaker takes advantage of this knowledge by adding substances to sugar solutions which increase their viscosity. The resulting candy is smoother because the sugar crystals are finer grained.

Crystallization may sometimes be prevented by sudden cooling. Thus when melted sulfur is suddenly cooled by pouring into cold water, a plastic mass of *amorphous* sulfur results—amorphous (without form) because the cooling caused such a rapid increase in viscosity as to prevent crystallization. A supercooled liquid is the result. On standing, however, this plastic material crystallizes.

11. Glasses.—We have mentioned the fact that the molecules in liquids near their freezing points are associated to a certain extent in groupings that are to be considered as incipient crystals. If the crystals to be formed are giant molecules and if the liquids from which they form are viscous, supercooling may occur to temperatures below the true freezing point. The crystals to be formed in such cases are so complex and the viscous liquid so sluggish that the complex molecules of the liquid remain as such as the temperature falls until the viscosity becomes so high that a glass results.

12. Hydrates.—Many salts crystallize from aqueous solutions with water molecules included in their crystal structures. Such salts are called *hydrates* and the water they contain, *water of hydration* or *water of crystallization.* The proportion of water molecules to the ions of the salt is constant in a given hydrate so that formulas may be written for them, *e.g.*, $CuSO_4 \cdot 5H_2O$, $Na_2SO_4 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$. The water of crystallization is frequently attached to the ions of the crystal by covalent bonds, or it may simply be used to fill regular spaces in the crystal lattice.

Water molecules evaporate from the crystals of hydrates and also return to the crystals from the water vapor in the surrounding air. Hydrated crystals in a stoppered tube come to an equilibrium with water vapor much as does liquid water under the same circumstances. Hydrates, therefore, have a definite vapor pressure at a given temperature.

13. Efflorescence.—When crystals of a hydrate are exposed to the open air, water will evaporate faster from their structure than it returns from the water vapor in the air if the partial pressure of water vapor in the atmosphere is less than the vapor pressure of the hydrate. Such a loss of water from the crystals of a hydrate is called *efflorescence.* The loss of water causes a disintegration of the crystal structure. Thus transparent crystals of washing, or sal, soda ($Na_2CO_3 \cdot 10H_2O$) crumble to a white powder at their surfaces. Deliquescence, or the absorption of water vapor from the air by a solid, will be discussed later (20-2).

14. Crystal Forms of a Substance.—The solid state of a given substance is characterized by one or at most a few crystalline forms. Such substances as sulfur, calcium carbonate, and water may exist in more than one form; for this reason they are called *polymorphous.* This polymorphism indicates that there is more than one stable arrangement that the molecules or ions of such substances can assume in the solid state. However, each of the several crystalline forms of a polymorphic substance is stable over a certain temperature range only, so that at any one temperature one form is more stable than any of the others. If an element is polymorphous, its various crystal modifications are known as *allotropic forms.* For example, the element carbon may exist in either of the two allotropic forms, the diamond or graphite.

EXERCISES

1. What forces bind the structure units in ionic, micromolecular (small molecules), and macromolecular (giant molecules) crystals?

2. What properties are characteristic of each of these three types of crystals?

3. In organic chemistry, solids are often identified by their melting points, whereas this procedure is useless in inorganic chemistry. Why?

4. Why do such solids as iodine and camphor have an odor, whereas salt is odorless?

5. Define the vapor pressure of a solid. How does this vary with the temperature?

6. Define the melting point of a solid in two ways.

7. What is the effect of an increase in pressure on the melting point of most solids? Why is the behavior of ice exceptional?

8. What factors determine crystal size?

9. Explain the phenomenon of efflorescence.

10. If an element is polymorphous, what are its different crystalline forms called?

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CHAPTER SEVENTEEN

CHLORINE

Chlorine together with fluorine, bromine, and iodine are a group of closely related nonmetals called the halogens (salt formers). These are the most active nonmetals known. Too active to occur free in nature, chlorine was first prepared by Scheele (7-1) in 1774 by the reaction of manganese dioxide on hydrochloric acid. However, it was not until 1810 that Sir Humphry Davy recognized it as an element.

1. Occurrence.—Since nearly all chlorine compounds are soluble in water, we are not surprised to find the greatest amount of the element in the sea. Crystals of its most abundant compound, common salt, you will remember are composed of equal numbers of sodium, (Na^+), and chloride, (Cl^-), ions. In aqueous solution, salts do not exist as molecules but as individual ions. Hence sea water cannot be regarded as containing individual salts but rather ions of metals with positive charges and of nonmetals and groups of nonmetals bearing negative charges. Table 13 will give you information as to the relative proportions of the various ions to be found in the sea. Since the figures given are weights and not mole percentages, we should not expect to find an equal percentage of positive and negative ions. Suffice it to say that the total positive charge on all the metal ions is exactly equal to and balanced by the total negative charge of the nonmetal ions.

TABLE 13.—ANALYSIS OF IONS IN SEA WATER

Ion	Per cent	Ion	Per cent
Sodium (Na^+)............	30.59	Chloride (Cl^-)..........	55.29
Magnesium (Mg^{++}).......	3.73	Sulfate ($SO_4^{=}$)..........	7.69
Calcium (Ca^{++})..........	1.20	Carbonate ($CO_3^{=}$).......	0.21
Potassium (K^+)..........	1.11	Bromide (Br^-)..........	0.19

When a body of sea water is cut off from the ocean by an upheaval of the ocean bottom, an inland salt lake is the result. If this lake receives less water by drainage from the surrounding terrain than it loses by evaporation, the salts become more concentrated until eventually they begin to crystallize out of solution. In view of the abundance of the sodium and chloride ions, it is not surprising that common salt makes up the greater part of such deposits. Magnesium and potassium chlorides are also found in them. One of the few insoluble chlorides, that of silver, occurs in nature and is used to a certain extent as a source of silver.

2. **Preparation.**—Since chlorine is such an active nonmetal, its compounds are very stable. Each chloride ion represents a chlorine atom that has gained an electron from a metal atom with which it is combined. To this electron, the chloride ion holds tenaciously. The problem of preparing free chlorine from sodium chloride involves the removal of these electrons from chloride ions:

$$Cl^- \rightarrow Cl^0 + 1e^-$$

or, better, since free chlorine molecules are diatomic,

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

This is an oxidation and must be accompanied by the reduction of some other element which gains the electrons lost by the chlorine.

a. **Electrolysis of Fused Salt.**—The electrolysis of melted sodium chloride is used commercially primarily to prepare metallic sodium; and the chlorine, formed at the same time, is considered a by-product. However, the process illustrates very simply the use of the electric current to accomplish oxidation-reduction. Melted sodium chloride (m.p. 804°C.) is made up of sodium and chloride ions that have gained mobility with the melting of the crystals in which they were bound. Two graphite rods may be used as electrodes. The current generator connected to these electrodes acts as an electron pump which draws electrons from the positive pole, the anode, thus making it more positive, and forces electrons into the negative pole, the cathode. Since opposite charges attract, sodium ions will move to the cathode and chloride ions to the anode. At the cathode, each sodium ion gains an electron and becomes metallic sodium.

$$Na^+ + 1e^- \rightarrow Na$$

At the anode, each chloride ion loses its electron, becomes a neutral atom, and finds a partner to form a molecule of free chlorine.

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Thus we see that *reduction takes place at the cathode and oxidation at the anode in electrolysis reactions.* The complete oxidation-reduction reaction is the sum of the two electrode reactions:

$$\text{Energy} + 2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$$

Note that the electrons lost by the chloride ions at the anode are pumped by the current source to the cathode where they are gained by the sodium ions. Further note that the above reaction can be balanced by making sure that the number of electrons lost by the atoms of the element oxidized is equal to those gained by the element reduced. Thus the cathode reaction must be multiplied by two to show a gain of the two electrons lost in the anode reaction:

$$\begin{array}{l} 2Na^+ + 2e^- \rightarrow 2Na \\ \underline{2Cl^- \qquad\quad \rightarrow Cl_2 + 2e^-} \\ 2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2 \end{array}$$

When one mole of sodium chloride is formed from metallic sodium and chlorine gas, 98,000 cal. of heat are liberated. We have been considering the reverse of this reaction. Hence when one mole of salt is decomposed by electrolysis, an amount of electrical energy equal to 98,000 cal. is required. Since the joule, the unit of electrical energy, is equal to 0.239 cal. and hence 1 cal. equals 4.18 joules, 98,000 cal. are equal to 410,000 joules (98,000 × 4.18).

The commercial electrolysis cell must be so designed as to keep the products apart. Otherwise the active, free elements would recombine.

b. Electrolysis of Aqueous Sodium Chloride.—The most important commercial source of chlorine is the production of this element by the electrolysis of *water solutions* of sodium chloride. The anode reaction produces free chlorine as before:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

However, since hydrogen is lower in the electromotive series than sodium, it is formed with the expenditure of less energy than is required for the liberation of sodium metal. Since water is a molecular compound, the liberation of hydrogen at the cathode is more complicated:

$$HOH + 1e^- \rightarrow OH^- + H$$

Since hydrogen molecules are diatomic, the equation should be doubled:

$$2HOH + 2e^- \rightarrow 2OH^- + H_2$$

Hydroxyl ions, OH^-, are formed at the same time. Since sodium ions remain in solution and chloride ions are moving toward the anode, the solution around the cathode gradually becomes one of sodium hydroxide. By evaporating this solution, sodium hydroxide may be obtained as a white solid. It is known commercially as caustic soda, or lye. The cell reaction is

$$\text{Energy} + 2Na^+ + 2Cl^- + 2HOH \rightarrow 2Na^+ + 2OH^- + H_2 + Cl_2$$

or, more simply using formulas in place of ions,

$$\text{Energy} + 2NaCl + 2HOH \rightarrow 2NaOH + H_2 + Cl_2$$

Chlorine and caustic soda were first manufactured electrolytically in 1892 by a process developed by Castner. Today there are over fifty such plants in this country alone, which consume $10,000,000 worth of electricity and produce over 500,000 tons of chlorine annually.

In the commercial process, chlorine is discharged on graphite anodes. The cathodes are of iron. Since chlorine reacts with sodium hydroxide in aqueous solution (17-4d), asbestos diaphragms are used to keep the solutions apart.

c. Laboratory Preparation.—The oxidation of the chloride ion is most readily accomplished in the laboratory by the use of oxidizing agents such as manganese dioxide or potassium permanganate. Since the element reduced oxidizes the element oxidized, *the oxidizing agent must be the substance containing the element that is reduced.* Although this last sentence might win a prize as a tongue twister, it will pay to study it carefully and to return to it from time to time as we study the following example.

In manganese dioxide, MnO_2, and in potassium permanganate, $KMnO_4$, the valence numbers of manganese are +4 and +7

(9-9), respectively. (Why?) Manganese atoms are readily reduced to a valence number of +2 which they possess in the manganous ion (Mn^{++}) and, therefore, in all manganous salts. Hence the dioxide and the permanganate are oxidizing agents. On the other hand, chlorine in hydrochloric acid has a valence number of −1 and can be oxidized to free chlorine. Hence manganese dioxide and hydrochloric acid will enter into an oxidation-reduction reaction in which free chlorine and a compound of divalent manganese will be among the products. This compound must be manganous chloride, $MnCl_2$, as the only other possibilities, MnO and $Mn(OH)_2$, would react with hydrochloric acid to form $MnCl_2$ (13-12). Further, the hydrogen and the oxygen involved must appear as water, their most stable compound, in the products. Hence we may write the unbalanced equation:

$$\overset{+4}{Mn}O_2 + H\overset{-1}{Cl} \rightarrow \overset{+2}{Mn}\overset{-1}{Cl_2} + \overset{0}{Cl_2} + H_2O$$

Before balancing this equation, we must keep in mind that only part of the chlorine is oxidized. The part that appears in manganous chloride retains its valence number of −1. To balance, we analyze the valence changes:

$$Mn^{+4} + 2e^- \rightarrow Mn^{+2}$$
$$Cl^{-1} \rightarrow Cl^0 + 1e^-$$

Hence one manganese atom will oxidize two chlorine atoms:

$$Mn^{+4} + 2e^- \rightarrow Mn^{+2}$$
$$2Cl^- \rightarrow Cl_2 + 2e^-$$

and the atoms involved in the oxidation-reduction may be balanced:

$$MnO_2 + 2HCl \rightarrow MnCl_2 + Cl_2 + H_2O$$

However, two more molecules of hydrochloric acid will be needed to furnish the chlorine atoms, which are not oxidized, for the manganous chloride. Hence the final equation is:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

The equation for the reaction of potassium permanganate with hydrochloric acid is slightly more complicated. The metals will be found as chlorides for reasons discussed above. To balance the skeleton equation

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + Cl_2 + H_2O$$

we proceed as above.

$$2\mathrm{Mn}^{+7} + 10e^- \rightarrow 2\mathrm{Mn}^{+2}$$
$$10\mathrm{Cl}^{-1} \rightarrow 5\mathrm{Cl}_2 + 10e^-$$

Balancing the elements oxidized and reduced,

$$2\mathrm{KMnO}_4 + 10\mathrm{HCl} \rightarrow \mathrm{KCl} + 2\mathrm{MnCl}_2 + 5\mathrm{Cl}_2 + \mathrm{H}_2\mathrm{O}$$

and noting that 2KCl must be written on the right, we find that six additional hydrochloric acid molecules are needed. Hence the final equation is

$$2\mathrm{KMnO}_4 + 16\mathrm{HCl} \rightarrow 2\mathrm{KCl} + 2\mathrm{MnCl}_2 + 5\mathrm{Cl}_2 + 8\mathrm{H}_2\mathrm{O}$$

The apparatus used in the laboratory is shown in Fig. 59. Because of its solubility in water, chlorine cannot be collected conveniently by the displacement of water. Because it is more than twice as dense as air under the same conditions, it is collected by the displacement of air.

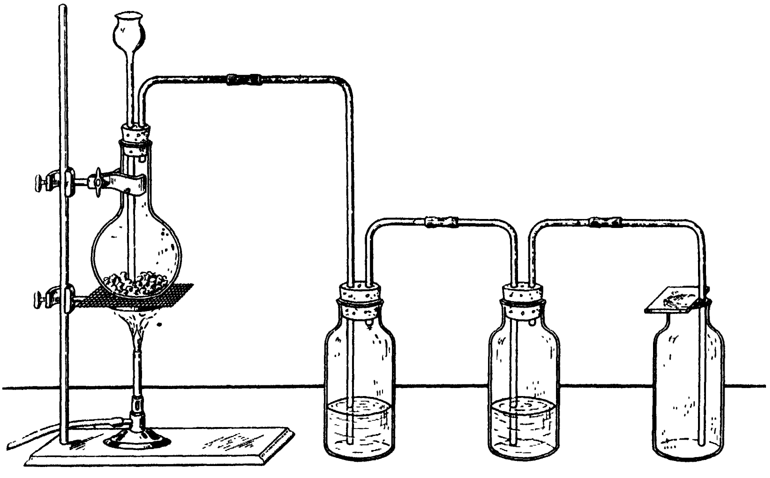

FIG. 59.—Laboratory preparation of chlorine.

3. Properties.—Chlorine is a greenish-yellow vapor under normal conditions. Its critical temperature is 146°C., and its vapor pressure is 6.62 atm. at 20°C. Hence it may be liquefied by increasing its partial pressure to above this value. In the steel cylinders in which the element is shipped, it exists as a liquid in equilibrium with its vapor. Hence the pressure in such cylinders remains at 6.62 atm. at 20°C. as long as any liquid is left in them. At standard pressure, liquid chlorine boils at −34.6°C. and freezes at −101.6°C. At 20°C., 2.3 ml., or 0.73 g., dissolve in 100 g. of water. At the same temperature and pressure, its vapor is about 2.5 times as dense as air.

Chlorine is very toxic so that laboratory experiments with this gas should be carried out under a hood. Inhaled, it is extremely irritating to the mucous membranes of the nose and throat. In concentration as small as 100 parts of chlorine per million, breathing becomes almost impossible and death results if the victim is not removed to fresh air.

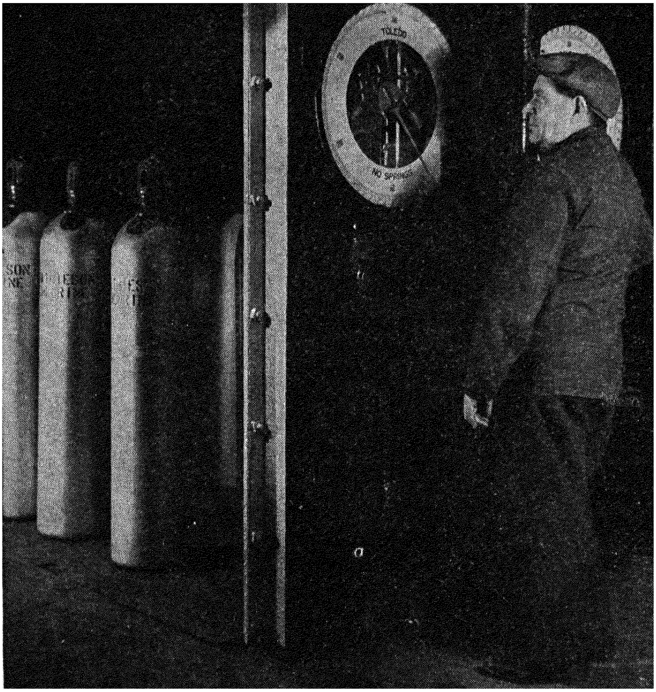

FIG. 60.—Filling cylinders with chlorine. (*Courtesy of Mathieson Alkali Works, Inc.*)

4. Chemical Reactions.—Since chlorine is a very active nonmetal, it enters into many reactions.

a. With Metals.—Chlorine combines directly with all metals except gold and platinum. In the presence of minute traces of moisture, such reactions proceed vigorously. Oddly enough when the gas has been carefully dried, such reactions take place with extreme slowness if at all. Taking advantage of this fact, dry liquid chlorine may be safely stored in steel cylinders. It is even shipped in tank cars holding 30 tons. Powdered metals take fire spontaneously when sprinkled into chlorine, and hot metal foils burn vigorously. In every case, a chloride of the metal is formed as the following typical equations show:

$$2Na + Cl_2 \rightarrow 2NaCl$$
$$Mg + Cl_2 \rightarrow MgCl_2$$
$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

b. With Hydrogen.—A jet of hydrogen continues to burn when lowered into an atmosphere of chlorine. Hydrochloric acid, a gas, is formed:

$$H_2 + Cl_2 \rightarrow 2HCl$$

Mixtures of the two gases explode violently when exposed to the sunlight or to the light of burning magnesium. The reaction is the same.

c. With Nonmetals.—In spite of the fact that chlorine itself is a nonmetal, it combines directly with many other nonmetals. Carbon, nitrogen, oxygen, and the inert gases are exceptions, although chlorides of the first three may be prepared indirectly.

With phosphorus, the trichloride is formed first followed by the pentachloride if chlorine is in excess:

$$2P + 3Cl_2 \rightarrow 2PCl_3$$
$$PCl_3 + Cl_2 \rightarrow PCl_5$$

Such nonmetal chlorides are not salts but are molecular not ionic in character. However, since chlorine is the more active nonmetal its valence number is -1, whereas the valence numbers of phosphorus are $+3$ and $+5$ in the trichloride and the pentachloride, respectively.

d. With Water.—Chlorine not only is moderately soluble in water but actually reacts with water molecules:

$$Cl_2 + H_2O \rightleftarrows HCl + HClO$$

Two acids are formed, hydrochloric and hypochlorous. The reaction is reversible, however, and hence does not go to completion but to an equilibrium when the rate of the reverse reaction (right to left) becomes equal to that of the direct reaction (left to right). This dynamic equilibrium is analogous to that established between a liquid and its vapor in a closed vessel (14-5).

In the sunlight, hypochlorous acid, in which the valence number of chlorine is +1 (Why?), is gradually reduced to hydrochloric acid and oxygen is liberated:

$$2HClO \rightarrow 2HCl + O_2$$

This disturbs the equilibrium by slowing up the reverse reaction. Just as the escape of vapor from an open vessel lowers the rate of condensation and permits water to evaporate completely, so the decomposition of hypochlorous acid permits the reaction of chlorine with water to go to completion.

Since the chlorine in hypochlorous acid is so readily reduced, this acid is an oxidizing agent. The color of organic dyestuffs is destroyed when their molecules are oxidized by this acid. Organic substances, which discolor paper pulp or cotton and linen textiles, are easily oxidized by the hypochlorous acid in chlorine water. Hence the extensive use of chlorine in bleaching. Woolens and silk, however, are attacked by chlorine.

The use of chlorine as a disinfectant depends on a similar action. Hypochlorous acid and its salts, *e.g.*, sodium hypochlorite, NaClO, destroy bacteria by oxidation. Indeed chlorine itself acts as a direct poison by attacking their tissues. Thus 2 parts of chlorine per 10,000,000 of water protects our water supply from bacterial contamination.

If chlorine is passed into an aqueous solution of sodium hydroxide, the two acids formed by the chlorine-water reaction are neutralized (13-12) and sodium hypochlorite is formed:

$$Cl_2 + H_2O \rightarrow HCl + HClO$$
$$HCl + NaOH \rightarrow NaCl + H_2O$$
$$HClO + NaOH \rightarrow NaClO + H_2O$$

or by adding the above reactions

$$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$$

The same result can be achieved by allowing the products of the electrolysis of aqueous salt solutions to mix. The use of such hypochlorite solutions in disinfecting wounds was introduced by Carrel and Dakin during the First World War. Such solutions must contain over 0.4 per cent sodium hypochlorite to be effective but not above 0.5 per cent lest they be too irritating.

If slaked lime, $Ca(OH)_2$, is substituted for sodium hydroxide, bleaching powder is the product:

$$Cl_2 + Ca(OH)_2 \rightarrow Ca(ClO)Cl + H_2O$$

This calcium salt is both a chloride and a hypochlorite. As might be expected, it is an active bleach and disinfectant.

e. Displacement Reactions.—Since chlorine is more active than bromine, iodine, and sulfur, it will displace these nonmetals from their salts:

$$Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$$
$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$
$$Cl_2 + Na_2S \rightarrow 2NaCl + S$$

In each case the more active nonmetal is reduced and the less active one oxidized. When we considered displacement reactions involving metals (10-9), the reverse was found to be true. Since metals tend to lose electrons, they are oxidized when they form compounds. On the other hand, nonmetals tend to gain electrons and be reduced. The more active the metal, the more readily it loses electrons and is oxidized. The more active the nonmetal, the more readily it gains electrons and is reduced.

f. With Organic Compounds.—Chlorine reacts with many organic compounds. A few of these reactions will be considered later, but many others are beyond the scope of this text.

5. Uses.—Within the past decade, the use of chlorine in the manufacture of organic chemicals has grown by leaps and bounds. Today over half is used in this field. We have mentioned its uses as a bleach and as a disinfectant to sterilize drinking water and sewage. It is used in the preparation of certain types of synthetic rubber and in petroleum refining. Finally, it is used in the preparation of bromine from sea water and in the manufacture of pure hydrochloric acid.

EXERCISES

1. During an electrolysis, at which electrode does oxidation take place?

2. How could you predict from the electromotive series of metals that hydrogen is more readily reduced than sodium?

3. What would be the final product if an aqueous solution of sodium chloride were subjected to electrolysis and the products permitted to mix?

4. Balance the following oxidation-reduction reactions using the method outlined in paragraph 2*c*:

$$Al + Cl_2 \rightarrow AlCl_3$$
$$FeCl_2 + Cl_2 \rightarrow FeCl_3$$
$$MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$$
$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$$
$$HCl + K_2Cr_2O_7 \rightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

5. What physical properties of chlorine indicate that it is composed of relatively small molecules?

6. Prepare a list of the nonmetals sulfur, bromine, chlorine, and iodine arranged in the order of their activity.

7. Mention two uses of chlorine which protect our health.

8. Write equations for the reactions of chlorine, with zinc, iron, copper, silver, and phosphorus.

9. When chlorine is dissolved in water, what reaction takes place?

10. Write the equation for the formation of bleaching powder from slaked lime.

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CHAPTER EIGHTEEN

HYDROCHLORIC ACID

Since hydrochloric acid is a simple binary acid and its properties are typical of acids in general, this chapter will serve as an introduction to the properties of acids.

1. History and Occurrence.—Aqueous solutions of hydrochloric acid, HCl, were well-known to the alchemists who prepared it by the action of sulfuric acid on salt. However, the pure, dry, gaseous acid was first prepared by Priestley in 1772. Commercially it is called muriatic acid. Its only occurrence is in very dilute solution in gastric juice.

2. Preparation.—Hydrochloric acid may be prepared by the following methods:

a. Dry Salt Heated with Concentrated Sulfuric Acid.—This is the most important *laboratory* and *commercial* method. Dry sodium chloride is heated with concentrated sulfuric acid at temperatures that must be kept below the boiling point of sulfuric acid (338°C.). Under these conditions, hydrochloric acid escapes as a gas. The reaction takes place in two steps

$$H_2SO_4 + NaCl \rightarrow NaHSO_4 + HCl\uparrow$$
$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl\uparrow$$

Sodium acid sulfate, or sodium bisulfate, $NaHSO_4$, is the first example we have met of an acid salt. It may be regarded as half sodium sulfate and half sulfuric acid and may be prepared by a reaction that indicates this relationship:

$$Na_2SO_4 + H_2SO_4 \rightarrow 2NaHSO_4$$

A salt as its ionic crystal structure composed of sodium (Na^+) and bisulfate (HSO_4^-) ions indicates, it nevertheless is an acid in aqueous solution, turning blue litmus paper red.

A chloride of any other metal may be substituted for the salt. Any stable acid, which is not too volatile and does not react with hydrochloric acid, may be used instead of sulfuric acid. Thus:

$$2FeCl_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 6HCl\uparrow$$
$$3CaCl_2 + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6HCl\uparrow$$

b. Direct Union of Hydrogen and Chlorine.—It will be remembered that both hydrogen and chlorine are products of the electrolysis of aqueous salt solutions. At times when the demand for chlorine is low, synthetic hydrochloric acid of high purity is manufactured:

$$H_2 + Cl_2 \rightarrow 2HCl$$

c. Hydrolysis of Phosphorus Trichloride.—Phosphorus trichloride (41-7) will react with water and form hydrochloric acid:

$$PCl_3 + 3HOH \rightarrow P(OH)_3 + 3HCl$$

The substance $P(OH)_3$ is a nonmetal hydroxide and, therefore, as we shall see later (41-10) an acid. If we write its formula "H_3PO_3" you will recognize it as phosphorous acid. The above reaction is an example of *hydrolysis*, a double-decomposition reaction in which water is one of the reactants.

3. Properties.—Hydrochloric acid is a colorless gas under normal conditions with a choking odor. Below its critical temperature (51.4°C.) at room temperature, it may be liquefied by pressure alone. It is exceedingly soluble in water. At 20°C., 442 ml. of the gas dissolves in 1 ml. of water. This may be demonstrated by the apparatus shown in the Fig. 61. As soon as a small amount of water from the medicine dropper is forced into the upper flask, gaseous hydrochloric acid dissolves thus lowering the pressure. The atmospheric pressure forces water from the flask below into the upper flask, and a fountain is the result.

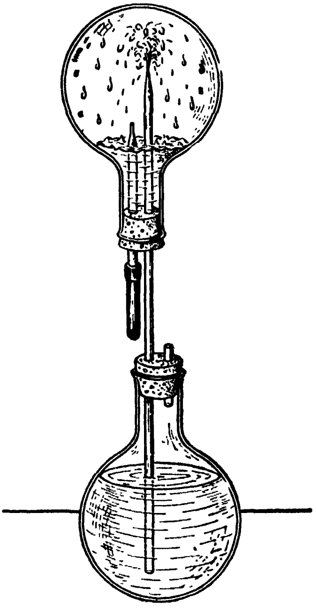

Fig. 61.

The gas is almost invariably used in aqueous solution. The concentrated acid is essentially a saturated solution containing 37 per cent by weight of HCl. Its density is 1.19 g./ml. If the concentrated acid is heated, the gas is forced out of solution until its concentration in the liquid falls to 20.24 per cent. Then the solution boils at a constant temperature of 110°C., losing water and hydrochloric acid in the same proportions as they are found in the solution. More dilute solutions lose water faster than hydrochloric acid until the composition of the constant-boiling mixture is reached.

4. Physical Properties of Acids in General.—We have learned that hydrochloric acid is a gas, a clear indication that it is composed of neutral molecules and not ions. The hydrogen and the chlorine atoms in its molecule must be linked by a covalent linkage, *i.e.*, a shared pair of electrons. Between such neutral molecules, the weak van der Waals forces are insufficient to hold the molecules together as a liquid at concentrations that correspond to normal pressures at normal temperature. Similarly, hydrobromic (HBr) and hydriodic (HI) acids are gases. However, these are simple molecules. As the molecular complexity of acids increases, so do the van der Waals forces between their molecules; and we find such acids liquids. For example, nitric (HNO_3), sulfuric (H_2SO_4), and phosphoric (H_3PO_4) acids are liquids. Only when the molecular complexity is still greater, do we find solid acids. And even in these cases, the melting point is low unless the acid is made up of giant molecules.

We have seen that salts are solids of high melting points between whose ions strong Coulomb forces operate. Further, when salts are melted, their ions endow them with high electrical conductivity. On the other hand, pure acids in the liquid state show little if any conductivity. This is again an indication of their molecular composition.

It is surprising to learn, therefore, that aqueous solutions not only of salts *but also of acids* conduct electricity. Despite the theory that pure acids are molecular, *their aqueous solutions must contain ions*. We shall not present the explanation of this anomaly here but shall return to it later (32-3).

5. Reactions of Hydrochloric Acid.—This acid enters into reactions common to all acids that have been discussed before. However, as a review, study the following equations.

a. With metals above hydrogen in the electromotive series

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$
$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

but $Ag + HCl \rightarrow$ no reaction

b. With basic oxides

$$\begin{aligned} & ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \\ & Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \\ \textit{and} \quad & Ag_2O + 2HCl \rightarrow 2AgCl + H_2O \end{aligned}$$

c. With metal hydroxides (neutralization)

$$\begin{aligned} & Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O \\ & Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O \end{aligned}$$

d. With Metal Carbonates and Sulfites.—This is a new type of reaction. Metal carbonates and sulfites are able to neutralize the characteristic properties of acids and form salts in an analogous manner to metal hydroxides. Instead of water, however, the unstable carbonic or sulfurous acid is formed. These decompose on formation as follows:

$$\begin{aligned} & H_2CO_3 \rightarrow H_2O + CO_2\uparrow \\ & H_2SO_3 \rightarrow H_2O + SO_2\uparrow \end{aligned}$$

and the gases CO_2 or SO_2 are evolved, causing pronounced effervescence. Reactions of this type are illustrated by the following equations:

$$\begin{aligned} & Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2CO_3 \\ & H_2CO_3 \rightarrow H_2O + CO_2 \\ \text{or} \quad & Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2 \\ & K_2SO_3 + 2HCl \rightarrow 2KCl + H_2O + SO_2 \\ & CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \end{aligned}$$

e. With Ammonia.—The gas ammonia, NH_3, is not an acid despite the fact that it is a hydride of a nonmetal. On the other hand, it is able to neutralize acids whether pure or in aqueous solution. Under such circumstances, ammonium salts of the corresponding acids are formed. Thus when ammonia and hydrochloric acid, both as gases, are mixed, a dense white smoke of tiny crystals of the salt ammonium chloride is formed.

$$NH_3 + HCl \rightarrow NH_4Cl$$

The same reaction takes place when aqueous solutions of these substances are mixed.

f. With Strong Oxidizing Agents.—As we have learned (17-2c), when hydrochloric acid is treated with a strong oxidizing agent chlorine is liberated, *e.g.*,

$$4HCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$$
$$16HCl + 2KMnO_4 \rightarrow 2MnCl_2 + 2KCl + 5Cl_2 + 8H_2O$$

Although hot concentrated sulfuric acid is an oxidizing agent, it is not strong enough to oxidize the chlorine in hydrochloric acid.

g. With Soluble Silver Salts.—When an aqueous solution of any metal chloride or of hydrochloric acid is mixed with one of a silver salt, *e.g.*, silver nitrate or silver sulfate, a white precipitate of silver chloride is formed.

$$AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$$

This precipitate is insoluble in nitric acid but dissolves in ammonia water. Since lead and mercurous chlorides are also insoluble, they will precipitate when hydrochloric acid is added to solutions of soluble lead or mercurous salts:

$$Pb(NO_3)_2 + 2HCl \rightarrow PbCl_2\downarrow + 2HNO_3$$
$$HgNO_3 + HCl \rightarrow HgCl\downarrow + HNO_3$$

6. Bases.—Although we shall have to postpone giving an exact definition of the term "base," it will be helpful to define *a base* for the time being as *a substance that will neutralize an acid.* Thus metal oxides, hydroxides, carbonates, and sulfites and the substance ammonia possess basic properties.

7. Uses of Hydrochloric Acid.—The annual production of hydrochloric acid in the United States is about 90,000 tons. Its uses are so varied that its distribution is hard to obtain.

EXERCISES

1. What properties of acids, in general, indicate that they are molecular compounds?
2. Why does hydrogen invariably form covalent bonds with other atoms?
3. Write equations for three reactions by which hydrochloric acid may be prepared.
4. Write equations for five methods by which zinc chloride may be prepared.
5. Write equations for the reactions of ammonia with each of the following acids: hydrochloric, sulfuric, nitric, and phosphoric.
6. Define precipitation.
7. What chlorides are insoluble?
8. Write equations showing the precipitation of each of the insoluble chlorides.

9. How may chlorine be prepared from hydrochloric acid?

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CHAPTER NINETEEN

SOLUTIONS

Solutions have played many an important role since the earth cooled enough for water to condense. Indeed before this happened, minerals were crystallizing from the molten drop of solution in space that was our earth. Every diamond crystallized from solution under intense pressure when the earth was young. As soon as water cooled enough to become a liquid, its solvent action went to work, modifying the earth's surface and finally producing a solution on a truly grand scale—the oceans. The atmosphere itself is a solution of gaseous components. All living organisms depend upon solutions for their food. The roots of a plant cannot absorb food from the soil unless it is in solution. Our own food must be broken down into water-soluble materials by the process of digestion before it can be carried by the blood stream to the various tissues of the body. Many of the materials with which we come in daily contact are solutions—glass, gasoline, tincture of iodine, 18-carat gold, vinegar, lubricating oils, the air we breathe and the water we drink to mention only a few.

1. Characteristics.—*A solution may be defined as a homogeneous mixture of two or more substances whose composition may be varied.* Like a compound, a solution is homogeneous; but unlike a compound, the proportions by weight of its component substances may be varied. When elements combine to form a compound, they do so in fixed proportions by weight. Further, each element loses the properties that characterize it in the free state; and those of the compound are in no sense a composite of the properties of the free elements before combination. The synthesis of a compound is a chemical change. On the other hand, the process of dissolving one substance in another is a physical change. Each substance retains its fundamental properties because its molecules or ions retain their identity. True, certain properties like crystalline form, which are due to molecular or ionic aggregates, are lost. When sugar crystals dissolve in water, this form is lost but the essential properties, which single molecules of sugar possess, are retained.

At 20°C., about 200 g. of sugar will dissolve in 100 g. of water. This is the limit to the solubility of sugar in water at this temperature. But within this limit, solutions of sugar in water of any desired composition may be prepared.

2. Particle Size.—The distinction between heterogeneous mixtures and solutions is not a sharp one. A solution is homogeneous only in the sense that we cannot distinguish particles with different properties in it with the aid of instruments at our disposal. After coarse sand has been stirred up in water, its particles settle quickly. More finely divided sand grains settle more slowly. It is possible to grind a solid so thoroughly that its particles will remain in suspension for some time in a medium in which it is insoluble. Indeed such suspensions may even appear homogeneous to the naked eye. However, a bright beam of light passed through them will be reflected by the suspended particles as dust reflects a beam of light in a dark room. By this means, their heterogeneous character is revealed.

Very finely divided material, whose particles are below the limit of microscopic visibility but are larger than single molecules, remains suspended indefinitely in media in which it is insoluble. Such a dispersion is called a *colloidal suspension* (Chap. 44). Colloidal particles are of diameters less than 0.00005 cm., or 5000 Å., and greater than about 5 Å., which latter dimension corresponds to that of moderately large molecules.

The suspended particles in a true solution show no more tendency to settle than do the molecules of a gas and for the same reason. Each particle is a single molecule or an ion. Their average kinetic energy, corresponding to the temperature, keeps them uniformly distributed throughout the solution.

Giant molecules, like those of proteins, have dimensions of the order of 1000 Å. and are not much below the limit of microscopic visibility. Indeed, some of these macromolecules have been photographed by means of the electron microscope. When such molecules are suspended in a medium, we must consider the suspension colloidal. A substance composed of macromolecules can never be truly dissolved.

3. Solute and Solvent.—In true solutions, it is customary to call the dissolved substance the *solute* and the medium, in which it is dissolved, the *solvent*. The choice is usually but not always an easy one. In the case of a solution of sugar in water, sugar is obviously the solute and water, the solvent. In general, the solvent is the component which, when pure, exists in the same state as the solution. Water is a liquid and so is a solution of sugar in water. Hence water is the solvent. In those cases in which the pure components are in the same state before solution, the choice is purely an arbitrary one. Alcohol and water are both liquids which dissolve in each other in any proportions. In such cases, the component present in the greater quantity is usually considered the solvent.

4. Types of Solutions.—By far the commonest type of solution is that of a solid dissolved in a liquid. But there are eight other types. The solute may be a gas, a liquid, or a solid and so may the solvent. Thus there are nine possible combinations as shown in Table 14. Some of these types we may discuss briefly in this paragraph. Others will receive more attention in the paragraphs that follow.

TABLE 14.—TYPES OF SOLUTION

Solute	Solvent	Example
Gas	Gas	Air
Gas	Liquid	Soda water
Gas	Solid	Hydrogen in palladium
Liquid	Gas	Water vapor in air
Liquid	Liquid	Alcohol and water
Liquid	Solid	Mercury in gold
Solid	Gas	Iodine vapor in air
Solid	Liquid	Sugar in water
Solid	Solid	Silver in lead

Since gases are composed of single molecules with plenty of space between, any gas will diffuse readily into any other. The result is a homogeneous mixture and, therefore, a solution. Gases dissolve in one another in all proportions. When a liquid evaporates or a solid sublimes into a space occupied by a gas, the process may be considered as the solution of a liquid or of a solid in a gas.

Solutions of a gas in a solid are rare. The case of hydrogen in palladium has been the most thoroughly studied. It appears that the gas goes in solution in the metal crystals as single atoms which fill "holes" in the crystal structure. There seems to be one such space, large enough for a hydrogen atom, for every pair of palladium atoms. When the crystal dissolves half as many hydrogen atoms as the number of palladium atoms in its structure, no more hydrogen will dissolve.

Solid solutions of one solid in another are more common. Compounds of similar composition, such as lead chloride and lead bromide, and closely related elements, like silver and gold, cobalt and nickel, are apt to form such solutions. Many copper-nickel alloys of the solid-solution type are of importance; among these may be mentioned nickel coins, caps of rifle bullets (20 per cent nickel) and a wire whose high electrical resistance varies little with the temperature and finds use in various electrical instruments. Certain Canadian ores are mixtures of the sulfides of copper and nickel. From such ores, the two metals are obtained as a solid-solution alloy containing 67 per cent nickel and 28 per cent copper with the remaining 5 per cent iron and manganese. This is called Monel metal, has a high tensile strength and ductility, and is remarkably resistant to corrosion. It is used extensively for kitchen sinks and countertops.

5. Solutions of Solids in Liquids.—When a solid dissolves in a liquid, particles escape from its surface and enter the solvent. The nature of these particles is determined in large measure by the crystal-structure units of the solid. If these are ions, as in the case of salts, they will dissolve separately and the resulting solution will conduct electricity. *Substances whose aqueous solutions conduct electricity are called electrolytes.* If the crystals are made up of molecules, these are the particles that dissolve. [illegible] the resulting solution does not conduct the electric current. Acids are exceptions to this rule. Undissolved they are molecular; but their aqueous solutions conduct electricity. This is the result of a chemical reaction (32-3) between their molecules and water which results in the formation of ions. Acids are classed, therefore, as electrolytes. *Substances whose aqueous solutions do not conduct electricity are called nonelectrolytes.*

In some respects, the behavior of solutions of nonelectrolytes is more regular than that of electrolytes, and for this reason will be studied first.

6. Rate of Solution.—The rate at which a solid dissolves in a liquid depends upon the nature of the solid and that of the liquid. In general, the more nearly alike the solute and solvent are in the structure of their molecules, the more readily will solution take place. Those substances whose molecules contain hydroxyl groups (OH), like sugar, $C_{12}H_{22}O_{11} = C_{12}H_{14}O_3(OH)_8$, and ethyl alcohol, C_2H_5OH, are soluble in water, HOH. Hydrocarbons are soluble in one another.

The rate of solution also depends upon the total surface of the solid, for obvious reasons. Breaking up a solid by grinding exposes new surfaces. Hence a finely divided solid will dissolve more rapidly than one of coarse crystals. Finally, the rate of solution increases as the temperature is raised, since any change that involves molecular activity is accelerated by a rise in temperature.

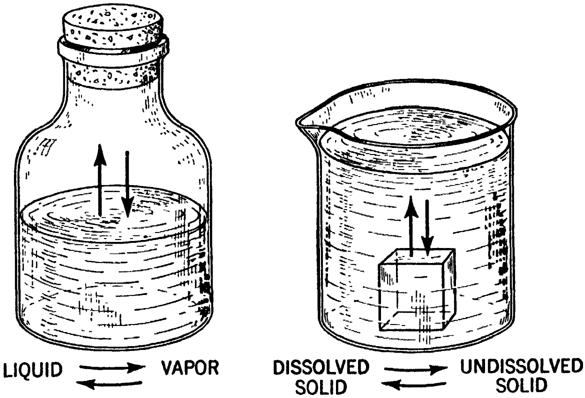

Fig. 62.

7. Saturated Solutions.—We have learned that evaporation is a reversible process and that an equilibrium is established between a vapor and a liquid when the rate of condensation becomes equal to the rate of evaporation (14-5). The solution of a solid in a liquid is also reversible. Not only do solid particles escape into the liquid, but also dissolved solid molecules, striking the surface of some undissolved crystal, will fit themselves into its structure and so crystallize. The rate at which a given solid dissolves in a given liquid at a given temperature per unit area of surface is fixed. The rate of crystallization, however, under the same circumstances depends upon the concentration of the solute molecules. As this increases, owing to the solution of more and more of the solid, the rate of crystallization also increases. When the two rates are equal, an equilibrium is the result

Undissolved solid ⇄ dissolved solid

The solution is then said to be saturated. *A saturated solution is one in which dissolved and undissolved molecules of the solute are in equilibrium.* Figure 62 illustrates the similarity between evaporation and solution, condensation and crystallization, and between a gas saturated with vapor and a saturated solution of a solid in a liquid.

8. Methods Used in Expressing Concentrations.—The best way to be certain that a solution is saturated is to add so much of the solute that some will remain undissolved. The excess can then be filtered off if necessary. Many times, however, it may neither be necessary nor desirable to use a saturated solution. In any case, some method of expressing the concentration of a solution is necessary. It may often suffice to state qualitatively that a solution is concentrated or dilute. Odd though it may seem at first, a saturated solution may not be concentrated. At 18°C., only 0.0023 g. of barium sulfate will dissolve in a liter of water. Such a saturated solution is scarcely concentrated.

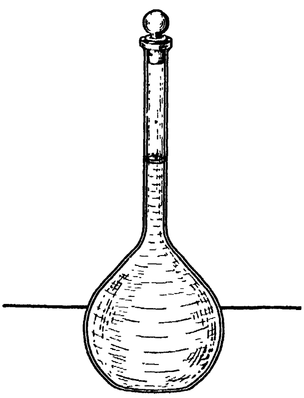

FIG. 63.—A volumetric flask.

The concentration may be expressed quantitatively by stating the weight or volume of the solute in a given weight or volume of solvent. Grams of solute per 100 g. of solvent is used frequently. Concentrations may be expressed in weight percentages. A 10 per cent sugar solution is made up in the proportions of 1 g. of sugar to 9 g. of water. The method of expressing concentrations which has certain very definite advantages from the point of view of a chemist is in terms of the number of moles of solute per liter of solution. *A molar solution contains one mole of solute per liter of solution.* In the case of salts, which are not molecular, a gram-formula weight is always considered as a mole. A molar solution of sugar in water would be made up as follows. One mole of sugar, 342 g. ($C_{12}H_{22}O_{11}$, molecular weight = 342), is placed in a 1-liter volumetric flask (Fig. 63) on the neck of which a line has been etched to mark off a volume of exactly 1 liter. Enough water is added to dissolve the sugar and finally to bring the surface of the solution to the etched line. By this method, one mole of solute can be dissolved in a total solution volume of 1 liter of water. The *molarity* of a solution is the number of moles of solute per liter of the solution. Thus a 0.1M sugar-water solution contains 34.2 g. of sugar per liter. Since moles of all substances contain the same number of molecules, *solutions of the same molarity are of the same molecular concentration.*

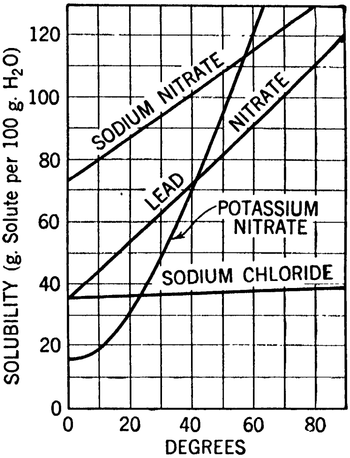

FIG. 64.—Influence of temperature changes on solubility.

A slightly different way of expressing concentrations is in terms of molality. *A molal solution* contains one mole of solute per 1,000 *grams of solvent.* The molality of a solution is the number of moles of solute per 1,000 g. of solvent. Concentrations expressed in molarity are more convenient when volumes of the solution are to be measured, whereas the molality is preferred when portions are to be weighed. We shall use a capital M for molarity and a small m for molality.

9. Solubility.—*The solubility of a solute in a given solvent is the concentration of their saturated solution at a given temperature.* Hence solubility depends upon equilibrium conditions between dissolved and undissolved solute. The way such equilibria shift, when the temperature changes, will determine how the temperature affects the solubility of a substance. We have applied van't Hoff's law to vapor-liquid equilibria (14-9). It applies equally well to our present problem. Since the solution of a solid in a liquid absorbs heat in the vast majority of cases, a rise in temperature favors this change. Hence the solubility of a solid in a liquid usually increases as the temperature is raised, as can be seen in Fig. 64.

10. Supersaturation.—When a solution, saturated at an elevated temperature, is allowed to cool, the excess solute usually but not always crystallizes since its solubility is decreased by cooling. If some undissolved crystals or even dust particles are present in the solution, these act as nuclei upon which crystallization takes place. If, however, all undissolved solid particles are carefully filtered from the hot saturated solution, the excess solute usually does not crystallize out on cooling. Such solutions are supersaturated. If a dust particle or a crystal of the solute is dropped into such solutions, crystallization of the excess solute starts instantly. Many pure liquids may be cooled below their freezing points under similar circumstances.

11. Solutions of Gases in Liquids.—Solutions of gases in liquids, though less common than the type that we have been discussing, are nevertheless of some importance. If oxygen did not dissolve in water to some extent, fish could not live. Carbon dioxide in natural waters plays an important part in soil formation and refreshes us in soda water.

The molecules of a gas confined in a closed vessel above the surface of a liquid will bombard the surface of the liquid and dissolve in it at a rate that is proportional to their concentration and to the temperature. The dissolved gas molecules will diffuse throughout the volume of the liquid and escape again into the gas phase. As their concentration in the liquid grows due to continued solution, their rate of escape from solution will increase until it equals the rate of solution. An equilibrium is then established and the liquid is saturated with the gas

$$\text{Gas (undissolved)} \rightleftarrows \text{gas (dissolved)}$$

The weight of a gas dissolved by a given volume of a liquid is directly proportional to the pressure of the gas (Henry's law). The volume of gas dissolved, however, is independent of its pressure. Let us see why this must be so. The pressure of a gas is determined by its concentration at a given temperature. This in turn determines the rate at which gas molecules strike the surface of the liquid and dissolve in it. At equilibrium, the higher the pressure of the gas above the liquid, the greater the number of gas molecules dissolved in a given volume of it. Since the weight of gas dissolved is proportional to the number of dissolved molecules, Henry's law follows very simply. If we double the pressure, we double the number of molecules dissolved in a given volume of the liquid. However, at twice their former pressure, the same volume of a gas will contain twice as many molecules. Therefore, twice as many molecules occupying the same volume will dissolve at twice the pressure. Henry's law is obeyed by sparingly soluble gases like oxygen or nitrogen but not by very soluble gases like ammonia.

Solutions of gases in liquids must be kept in tightly stoppered bottles. Otherwise the gas pressure cannot be maintained above the surface of the liquid. As the gas diffuses out of the mouth of an open bottle, its pressure becomes less, and consequently dissolved gas molecules will come out of solution. Soda water contains carbon dioxide dissolved in water under high pressure. To keep this high concentration of gas in solution, the bottles must be tightly capped. When the cap is removed, the pressure is released, and the excess carbon dioxide fizzes out of solution.

When a gas is dissolved in a liquid, heat is evolved; for its molecules are brought nearer together. Hence an increase in temperature lowers the solubility of a gas in a liquid

$$\text{Gas (undissolved)} \rightleftarrows \text{gas (dissolved)} + \text{heat}$$

12. Solutions of Liquids in Liquids.—Some liquids are mutually soluble in each other in all proportions as are, for example, alcohol and water. Others are partially miscible as in the case of ether and water. After being shaken together, ether and water form two liquid layers, one of which, the upper layer, is a saturated solution of water in ether and the lower, a saturated solution of ether in water. In the majority of such cases, when the temperature rises the solubility of each in the other becomes greater until a temperature is reached above which they are soluble in all proportions.

EXERCISES

1. What is a solution?
2. How finely divided are the solute particles in a true solution?
3. What is a saturated solution?
4. How is solubility defined?
5. Why does the solubility of most solids in water increase with the temperature?
6. Why should boiling remove all dissolved gases from a liquid?
7. Calculate the weight of glycerine, $C_3H_5(OH)_3$, needed to prepare 100 ml. of a molar solution.
8. How many grams of sugar are contained in 500 ml. of a 0.75*M* solution?

9. What weight of water must be added to 68.4 g. of sugar to prepare a 0.1*m* solution?

10. How can a supersaturated solution be prepared?

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CHAPTER TWENTY

THE SOLUTION LAWS

The laws that are to be discussed in this chapter have the same limitations as the gas laws. These, you will remember, are obeyed to the last letter of the law only by a hypothetical perfect gas. Real gases become more perfectly behaved the lower their pressure, and hence the lower their molecular concentration. Further, the greater the van der Waals forces between gas molecules, the less well-behaved the gas. Similarly, *the solution laws are obeyed closely only in dilute solutions*, in which the concentration of the solute is low, and *by solutions of nonelectrolytes* between whose neutral molecules the forces of attraction are characteristically low.

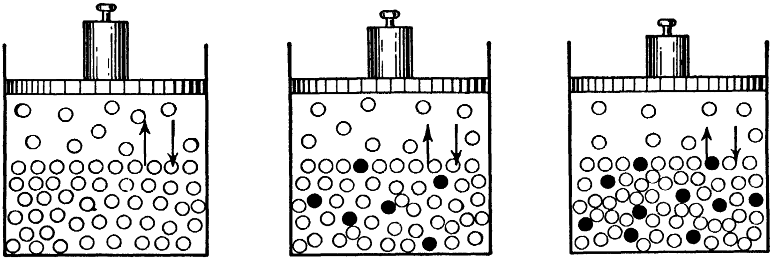

FIG. 65.—The vapor pressure lowering is proportional to the molecular concentration of the solute.

1. The Depression of the Vapor Pressure.—The vapor pressure of a pure liquid is greater than that of any solution in which it is the solvent. The effect of dissolving some substance in a solvent is to dilute the solvent. Water molecules are less concentrated in a sugar-in-water solution than in pure water. Hence the rate of evaporation from the solution is less than from pure water at the same temperature. At equilibrium in a closed vessel, the vapor pressure of the solution is also less than that of pure water (Fig. 65). The lower rate of evaporation of the solution requires a lower rate of condensation to equal it and, hence, a lesser concentration of vapor molecules.

The law, governing the extent to which the vapor pressure is depressed, we owe mainly to the work of Raoult done in 1887–1888. *In dilute solutions of nonelectrolytes, the lowering of the vapor pressure of the solvent is proportional to the molecular concentration of the solute.* Further, this depression is the same for solutions of the same molecular concentration of different solutes in the same solvent. Thus the kind of dissolved molecule makes no difference. Any molecule of whatever kind has the same effect. If we plot the vapor pressures of pure water and of two aqueous solutions, in which the concentrations of solute are 0.01 and 0.02 mole per 1,000 g. of water, respectively, against the temperature, we obtain the curves shown in Fig. 66. At any one temperature *t*, the vapor pressure of water p_0 is greater than that of the 0.01*m* solution $p_{.01}$ which in turn is greater than that

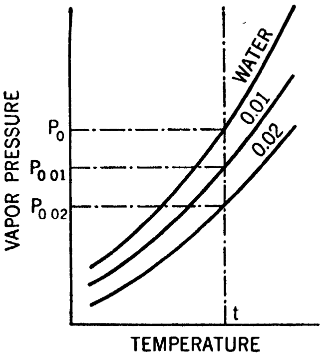

FIG. 66.—The vapor pressure curves of water and of two aqueous solutions.

TABLE 15.—VAPOR-PRESSURE LOWERING OF SOLUTIONS OF MANNITE
(In water at 20°C., p_0 = 17.51 mm.)[1]

Concentration (molality)	Vapor-pressure lowering		Percentage deviation
	Observed	Calculated from Raoult's law	
0.0984	0.0370	0.0311	+1.3
0.1977	0.0614	0.0622	+1.3
0.2962	0.0922	0.0931	+1.0
0.3945	0.1227	0.1239	+1.0
0.4938	0.1536	0.1547	+0.7
0.5944	0.1860	0.1858	−0.1
0.6934	0.2162	0.2164	+0.1
0.7927	0.2478	0.2469	−0.3
0.8922	0.2792	0.2775	−0.7
0.9908	0.3096	0.3076	−0.6

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[1] FRAZER, LOVELACE, and ROGERS, *J. Am. Chem. Soc.*, 42, 1793 (1920).

of the 0.02m $p_{.02}$. That the vapor-pressure depression is proportional to the molecular concentration of the solute is shown by the fact that

$$\frac{p_0 - p_{.01}}{p_0 - p_{.02}} = \frac{0.01}{0.02} \qquad (1)$$

That actual experimental results of vapor pressures of nonelectrolytes are in agreement with Raoult's law is illustrated by a typical example in Table 15.

2. Deliquescence.—Very soluble salts show a tendency to extract water vapor from the air in which to dissolve themselves. Vapor molecules condensing on the surface of such a salt form microscopic droplets each of which is a saturated solution. The rate of evaporation of water from such a concentrated solution is very low. Usually it is less than the rate of condensation of water vapor into the droplets. This would be the case if the partial pressure of the water vapor in the atmosphere is greater than the vapor pressure of the saturated solution of the salt. (Why?) In all such cases, water continues to condense faster than it evaporates; more salt dissolves until finally all has gone into solution. This process is called *deliquescence.*

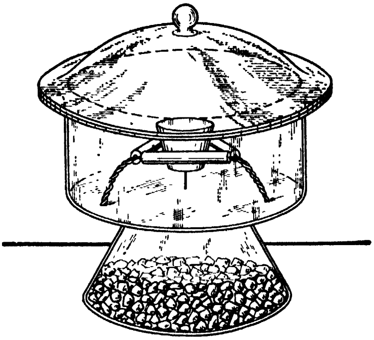

Fig. 67.—A desiccator.

Deliquescent substances, like calcium chloride and magnesium perchlorate, are used as drying agents. Placed in a closed vessel, called a desiccator (Fig. 67), they keep the partial pressure of the water vapor in the enclosed space down to the extremely low vapor pressure of their saturated solutions. Any material placed in the desiccator will be dried. Calcium chloride is used to keep the surface of dirt roads moist.

3. The Freezing Point of a Solution.—You will remember that the freezing point of a pure liquid is the temperature at which its vapor pressure is equal to that of the solid into which it freezes. The freezing point of a liquid is, therefore, intimately connected with its vapor pressure. What affects one will affect the other. You are all familiar with the fact that bodies of salt water remain unfrozen at temperatures at which skating is being enjoyed on fresh-water ponds. The owner who forgets to add an "antifreeze" to his car's cooling water goes to work on a cold morning in an animated teakettle. A solution evidently freezes at a lower temperature than the pure solvent.

Crystals of pure solvent freeze from a solution in which the solute is sufficiently dilute. Hence a dilute solution will start to freeze at the temperature at which its vapor pressure is equal to that of the pure solid solvent. In Fig. 68, the vapor pressures of water and of the two solutions, 0.01 and 0.02m, respectively, are plotted against the temperature as in Fig. 66 and in addition the vapor-pressure curve for ice. The temperatures at which the three vapor-pressure curves cross that of ice are their respective freezing points. Here again

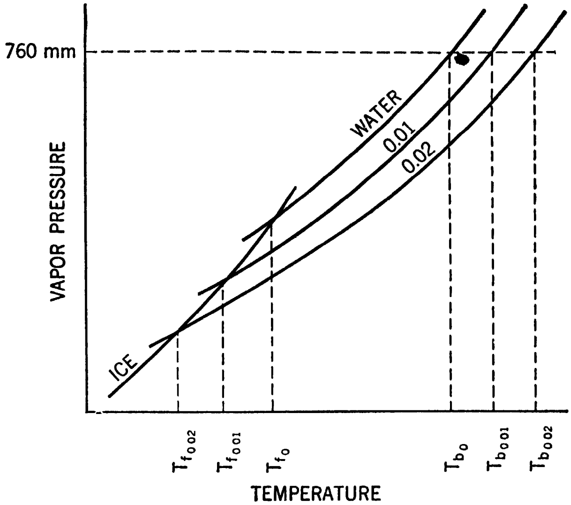

Fig. 68.—The freezing and boiling points of water and of two aqueous solutions.

$$\frac{T_{f_0} - T_{f_{.01}}}{T_{f_0} - T_{f_{.02}}} = \frac{0.01}{0.02} \qquad (2)$$

or, in words, *the lowering of the freezing point is proportional to the molecular concentration of the solute.* This may be expressed in a slightly different form:

$$\Delta T_f = Fm \qquad (3)$$

where ΔT_f is the freezing-point depression, m the molality of the solution, and F the freezing-point constant. This constant relates the depression to the molality of the solution and has a characteristic value for each solvent. Since $1m$ solutions contain one mole of solute per 1,000 g. of solvent, their molecular concentrations are equal and the freezing-point depression is the same in each case. This depression of the freezing point of water is 1.86°C. It is called the *molal freezing-point depression.* In equation (3) it is easily seen that when the molality is one the depression is equal to the freezing-point constant F. For water F is equal to 1.86°. Other solvents have their own values of F some of which may be found in Table 16.

TABLE 16.—MOLAL DEPRESSION OF THE FREEZING POINT

Solvent	T_f, °C.	F	Solvent	T_f, °C.	F
Benzene	5.5	5.1	Phenol	42.0	7.27
Camphor	178.4	37.7	p-Toluidine	44.5	5.2
Diphenyl	70.0	8.0	Water	0	1.86

Let us calculate the number of grams of sugar that must be added to 100 g. of water to lower the freezing point 3.00°C. Substituting in equation (3),

$$3.00° = 1.86°m$$

$$m = \frac{3.00°}{1.86°} = 1.61$$

we find that the molality of such a solution is 1.61 moles per 1,000 g. A mole of sugar is 342 g. ($C_{12}H_{22}O_{11}$). Hence

$$\frac{1.61 \text{ moles}}{1{,}000 \text{ g.}} = \frac{342 \times 1.61 \text{ g.}}{1{,}000 \text{ g.}} = \frac{551 \text{ g.}}{1{,}000 \text{ g.}} = \frac{55.1 \text{ g.}}{100 \text{ g.}}$$

We should, therefore, dissolve 55.1 g. of sugar in 100 g. of water to obtain a solution that freezes at −3.00°C.

4. A Practical Problem.—The next problem is more practical. Ethylene glycol, $C_2H_6O_2$, is an organic liquid used extensively as an "antifreeze" in automobile radiators. How many quarts of this compound must be added to a cooling system of 19-qt. capacity to lower the freezing point to −20°F.? First of all, we have to take care that we convert to the proper units to solve such a problem correctly. A temperature of −20°F. corresponds to what centigrade temperature?

$$C = \tfrac{5}{9}(F - 32)$$
$$C = \tfrac{5}{9}(-20 - 32) = -28.9°C.$$

Hence the molality of such a solution is

$$28.9° = 1.86°m$$
$$m = \frac{28.9}{1.86} = 15.5$$

Such a solution is rather concentrated. Under these circumstances, the freezing-point depression law will not hold exactly and we should be justified in considering our solution 16 *m*.

The molecular weight of ethylene glycol can be calculated from its formula $C_2H_6O_2$:

$$\begin{aligned} 2 \times 12(C) &= 24 \\ 6 \times 1(H) &= 6 \\ 2 \times 16(O) &= \underline{32} \\ & \ 62 \end{aligned}$$

Again we should not use exact atomic weights. (Why?) Thus a solution of 62 g. of ethylene glycol in 1,000 g. of water will start to freeze at −1.86°C. Sixteen moles corresponds to 992 g.

We shall next have to look up the density of the glycol to convert its weight to a volume, since our problem requires a volume of this substance in quarts. Its density is 1.1 g./ml. Hence

$$\frac{992 \text{ g.}}{1.1 \text{ g./ml.}} = 900 \text{ ml.}$$

Therefore, a solution of 900 ml. of ethylene glycol in 1,000 ml. of water will start to freeze at −20°F. This means, of course, 9 qt. of glycol to 10 qt. of water. Luckily the radiator capacity is 19 qt., and so we have our answer.

5. Freezing Mixtures.—The younger generation has not had the experience of turning the crank of an old-fashioned ice-cream freezer to prepare the dessert for Sunday dinners. In these freezers, a mixture of rock salt and ice produced a lower temperature than ice alone. However, you may have noticed that in the winter rock salt is spread on car-rail switches to prevent ice from freezing in them. From dilute solutions, pure solvent freezes at first and the solute in the remaining solution becomes more concentrated. Hence the freezing temperature falls. Finally the remaining solution becomes saturated with solute. Then both solute and solvent crystallize in the same proportion as that of the solution. Since the concentration of the solution does not change under these conditions, the temperature of freezing remains constant. If a solution of this concentration is cooled, both solute and solvent crystallize simultaneously at a constant temperature which is the lowest freezing point of any solution of this solute and solvent. A 23.3 per cent salt solution is of this type and freezes at −21.13°C. Thus the equilibrium mixture of solid salt, ice, and a solution of this composition will be at this temperature. In general, a solution that becomes saturated simultaneously with both solute and solvent is called a *eutectic mixture.*

6. Boiling-point Elevation.—The boiling point of a liquid is the temperature at which its vapor pressure becomes equal to atmospheric pressure. So it is also with solutions. Referring back to Fig. 68, the temperatures, corresponding to the intersections of the vapor-pressure curves and the 760-mm. coordinate, are the respective boiling points. It will be seen that the boiling point of a solution is higher than that of the pure solvent. This is true in general, provided the solute is not volatile as, for example, in the case of alcohol-water solutions. We shall limit our consideration to solid solutes that do not evaporate. Here again

$$\frac{T_{b_{.01}} - T_{b_0}}{T_{b_{.02}} - T_{b_0}} = \frac{0.01}{0.02}$$

The boiling-point elevation is proportional to the molecular concentration of the solute in dilute solutions of nonvolatile nonelectrolytes.

$$\Delta T_b = Bm$$

where B is the molal boiling-point elevation and has a characteristic value for each solvent. For water B is equal to 0.51°C., *i.e.*, a molal solution of a nonelectrolyte in water boils at 100.51°C.

7. An Experiment.—If one beaker containing pure water and another containing a sugar-in-water solution are placed beneath a bell jar (Fig. 69), a change takes place slowly the understanding of which will be of great help in the discussion of osmosis in the next paragraph. In such an arrangement, water will evaporate more rapidly from the pure water than from the solution. If pure water were alone, the enclosed space would become saturated with water vapor when the rates of evaporation and condensation become equal. But such a concentration of vapor will produce a rate of condensation into the solution greater than its lower rate of evaporation. Hence the system is not in equilibrium. From the pure water, evaporation exceeds condensation; from the solution, condensation exceeds evaporation. The net result will be that the water molecules are transferred from the pure water into the solution. If the solute had been alcohol instead of sugar, it would have evaporated from the solution and found its way into the pure water. In this case, an equilibrium would have been established when the concentrations of alcohol and water in each beaker became equal. In the first case the space above the liquids is permeable to water but not to sugar. Hence diffusion of water from the pure water through the intervening space into the solution persists.

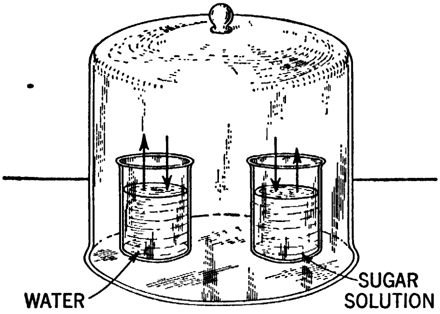

FIG. 69.

8. Osmosis.—Living cells are bounded by membranes which serve the same purpose as a wall surrounding a medieval city—a protection against harmful influences from without and yet a valve through which friendly foods may pass and harmful wastes be eliminated. Diffusion through such membranes is of great interest in the study of physiology. Osmosis is one type of such diffusion.

If pure water is separated from an aqueous solution by a membrane through which water molecules alone can pass, water diffuses faster from the pure solvent into the solution than vice versa. Such a membrane is called a *semipermeable membrane*, and the transfer of solvent through it is *osmosis*. Such membranes may be made of a section of an animal bladder or of substances like copper ferrocyanide deposited in the pores of an earthenware cup. Such a cup, filled with a sugar solution and closed with a rubber stopper through the hole of which a long glass tube has been passed, is immersed in pure water (Fig. 70*a*). Consider the conditions on each side of the membrane in one of the pores of the cup (Fig. 70*b*). The rate of diffusion from one side of the membrane depends on the concentration of the water molecules on that side. Since the molecules are more concentrated in pure water, the rate of diffusion from the water into the solution will be greater. The water level in the tube will rise and finally run over the top.

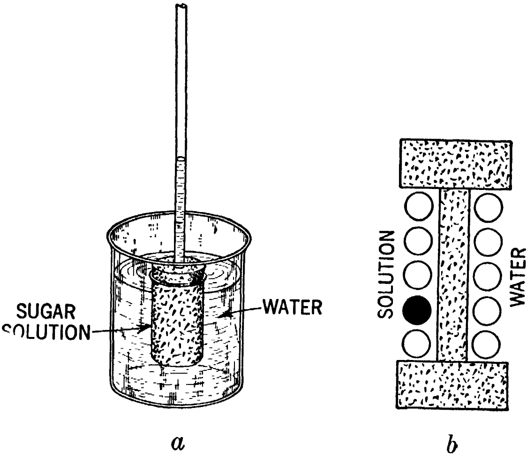

Fig. 70.—Osmosis.

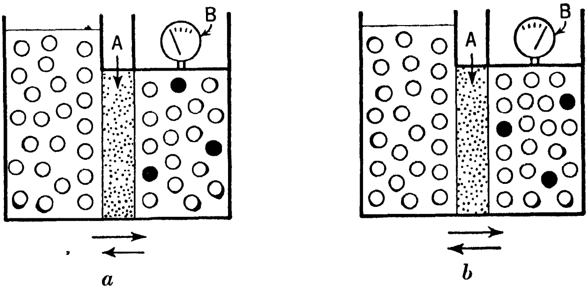

Fig. 71.—Osmotic pressure.

9. Osmotic Pressure.—If the solution is confined in a constant volume and thus prevented from expanding, the pressure instead of the volume will increase. Imagine a submicroscopic apparatus such as that shown in the diagram of Fig. 71*a*. The solution fills a closed vessel equipped with a pressure gauge *B*.

Its volume remains constant. Nevertheless, as long as the concentration of the water molecules is greater in the pure water, osmosis will take place through the semipermeable membrane A. The concentration of water molecules in the solution will increase since the volume is fixed, and the pressure rises accordingly. When the concentrations of water molecules on each side are equal (Fig. 71*b*), the diffusion rates are equal and osmosis stops. The pointer of the gauge shows the osmotic pressure of the solution. If, instead of this arrangement, the fixed top of the solution were replaced by a piston, then by applying a pressure equal to the osmotic pressure to the piston the solution will be compressed until equal diffusion rates are attained. *The osmotic pressure of a solution*, therefore, *is that excess of pressure which must be applied to the solution to prevent diffusion of pure water into it through a semipermeable membrane.*

10. The Magnitude of Osmotic Pressure.—If we consider this theory of the origin of osmotic pressure further, we note that for every solute molecule an additional water molecule must find its way into the solution. Therefore, the gain in the concentration of the water molecules is equal to the concentration of the solute molecules. It is this increase in the concentration of the water that exerts the osmotic pressure. This theory is substantiated by the fact *that the osmotic pressure of a solution is equal to the pressure that the molecules of the solute would exert if their concentration as a gas were equal to their concentration in the solution.* We shall learn in the next chapter that a mole of any gas in a volume of 1 liter exerts a pressure of 22.4 atm. at 0°C. Similarly, the osmotic pressure of a molar solution (1 mole/liter) at 0°C. is 22.4 atm.

If we return to the rise of the solution in the tube of the apparatus of Fig. 70, we realize that this column of solution will exert a hydrostatic pressure on the solution in the cup. Remember that a column of water 34 ft. high (11-2) exerts a pressure of 1 atm. If a molar sugar were in the cup, its osmotic pressure of 22.4 atm. would support a column of water over 760 ft. high. With a perfect semipermeable membrane that would not break under this enormous pressure, the solution would rise in the tube to this height.

If two solutions of different concentrations but in which the solvent is the same are separated by a semipermeable membrane, osmosis of the solvent will take place from the more dilute into the more concentrated solution. Osmosis will not take place if the osmotic pressures of the two solutions are equal. Such solutions are called *isotonic.*

11. Importance of Osmosis in Physiology.—A living cell is covered by a semipermeable membrane. Through this membrane, water and simple molecules and ions may pass freely. However, more complex molecules built up within the cell from these materials cannot escape. If a cell is immersed in a solution of slightly lower osmotic pressure (hypotonic) than that of the cell contents, water diffuses into and distends the cell. If the osmotic-pressure difference is too great, the cell wall will burst. On the other hand, in a solution of greater osmotic pressure (hypertonic), water diffuses out of the cell and its contents shrink away from the cell walls. This phenomenon is called *plasmolysis.*

Saline solutions injected into the blood stream must be isotonic with the solution inside the red blood cells. If such solutions are hypotonic, water will diffuse into the cells and cause them to burst. If they are hypertonic, plasmolysis takes place. In either event, death of the organism follows. Therefore, all materials injected into the blood stream are in physiological saline solution which contains 0.9 per cent of salt and is isotonic with the blood.

EXERCISES

1. Combine the laws of vapor-pressure and freezing-point lowering and boiling-point rise in one general statement.

2. Explain why these laws do not apply to concentrated solutions and to those of electrolytes.

3. Explain Raoult's law in terms of theory.

4. Calculate the lowering of the freezing point produced by dissolving 10 g. of glycerine, $C_3H_5(OH)_3$, in 100 g. of water.

5. How many grams of naphthalene, $C_{10}H_8$, must be dissolved in 100 g. of benzene to lower its freezing point to 5.0°C.?

6. Explain deliquescence.

7. What is a eutectic mixture?

8. At what temperature does a $0.25m$ solution of sugar in water boil?

9. A $0.1m$ aqueous glycerine solution freezes at $-0.186°C$. At what temperature will an aqueous glucose, $C_6H_{12}O_6$, solution of the same molality freeze?

10. Calculate the lowering of the freezing point of phenol produced by dissolving 0.5 g. of resorcinol, $C_6H_6O_2$, in 100 g. of the solvent.

11. Explain why the osmotic pressure of a solution is proportional to its molecular concentration.

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CHAPTER TWENTY-ONE

DETERMINATION OF MOLECULAR AND ATOMIC WEIGHTS

Up to this point we have accepted molecular and atomic weights on faith. Now the time has come to consider how they may be determined. Dalton stated his atomic theory in 1803, but he had no real conception of the relationship between atoms and molecules or of atomic to molecular weights. It was not until the great Italian physicist Amadeo Avogadro stated his hypothesis in 1811 that this conception was first clearly pointed out.

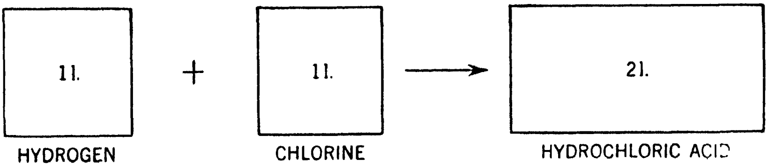
Fig. 72.—Amadeo Avogadro.

1. Gay-Lussac's Law of Combining Volumes.—In 1805, Gay-Lussac published the results of a series of experiments on the proportions by volume in which gases combine and are formed in chemical reactions. These results he summarized in the law that bears his name. *Measured at the same temperature and pressure, the volume ratios in which gases combine and are formed are those of small whole numbers.* Thus 2 liters of hydrogen combines with every 1 liter of oxygen and forms 2 liters of water vapor. One liter of hydrogen combines with 1 liter of chlorine to form 2 liters of hydrochloric acid gas; and 1 liter of nitrogen combines with 3 liters of hydrogen to form 2 liters of the gas, ammonia. Upon these and many other similar results, Gay-Lussac's law of combining volumes is based.

2. Avogadro's Hypothesis.—This famous hypothesis is the basis of all chemical theory. Without it, the science of chemistry would still be in its infancy, content merely to describe isolated facts. It was based mainly upon the law of combining volumes, although it must be admitted that this evidence was meager indeed. Avogadro's hypothesis was little more than a thoughtful guess when first it was proposed. Today the mass of evidence supporting his guess is truly impressive. Nevertheless this hypothesis is still theory as it is stated in terms of molecules whose existence is theoretical.

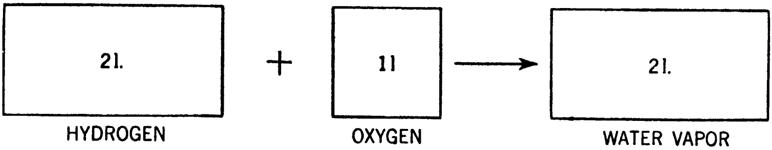
The hypothesis states: AT THE SAME TEMPERATURE AND PRESSURE, EQUAL VOLUMES OF ALL GASES CONTAIN THE SAME NUMBER OF MOLECULES. This should have been printed in red ink to emphasize its importance. The reasoning that led Avogadro to this conclusion may have been the following. The chemical reactions that Gay-Lussac studied must have been reactions between the molecules of which the gases were composed. When we consider the fact that 1 liter of hydrogen combines with exactly 1 liter of chlorine, we find the simplest explanation in Avogadro's hypothesis. The equal volumes of hydrogen and chlorine, which combine to form hydrochloric acid gas, contain equal numbers of molecules. Therefore, it is clear that every molecule of hydrogen is combining with a corresponding molecule of chlorine. In general, if we accept Avogadro's hypothesis, the simple volume ratios, in which gases combine and are formed, are identical with those of the molecules involved in the change.

3. Diatomic Molecules.—An immediate consequence of this hypothesis is that the molecules of oxygen, hydrogen, nitrogen, and chlorine are diatomic. If 1 liter of hydrogen and 1 liter of chlorine combine to form 2 liters of the gas hydrochloric acid, then one molecule of hydrogen must furnish hydrogen atoms for two molecules of hydrochloric acid, each of which must contain a hydrogen atom. Similar reasoning leads to the conclusion that the chlorine molecule is also diatomic.



$$H_2 + Cl_2 \rightarrow 2HCl$$

The reaction of hydrogen with oxygen to form water vapor may be used to prove that the oxygen molecule is diatomic.



$$2H_2 + O_2 \rightarrow 2H_2O$$

At the time when Avogadro first stated his hypothesis, the great Berzelius (5-1) had developed a theory that unlike atoms are held together in molecules by electrical forces due to opposite charges, to explain his pioneer work on electrolysis. It seemed inconceivable to him that like atoms could join in pairs. His influence was so great that Avogadro's hypothesis was generally rejected. Hence this idea, which would have clearly fixed the relationship between atoms and molecules, was promptly forgotten until it was revived by Cannizzaro, a student of Avogadro, in 1860 after his teacher's death. In the meanwhile, chemistry theory was in such a muddle that Cannizzaro's clear and forceful presentation of the usefulness of Avogadro's hypothesis led to its acceptance. This marks the start of a rapid development of chemistry as a science. For the first time, molecular and atomic weights could be determined with certainty and correct formulas for molecules established. This chapter will show how it was done.

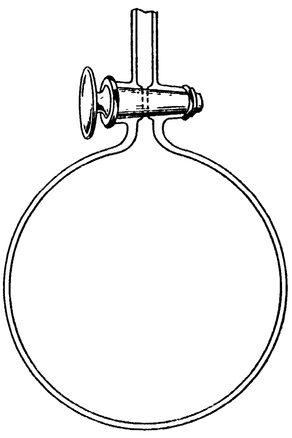


Fig. 73.

4. Determination of Molecular Weights.—It follows from Avogadro's hypothesis that the weights of equal volumes of two gases at the same temperature and pressure are the weights of equal numbers of molecules. These weights must be in the same ratio as their molecular weights. Thus if the weights of equal volumes at the same temperature and pressure of two gases, one of known and the other of unknown molecular weight, are determined, it is possible by a simple proportion to calculate the unknown molecular weight; since

$$\frac{\text{Weight of a certain volume of } A}{\text{Weight of the same volume of } X} = \frac{\text{molecular weight of } A}{\text{molecular weight of } X}$$

A glass bulb, provided with a stopcock (Fig. 73), of about 250 ml. capacity is used in such a determination. The solution of a typical problem will help you understand the method.

5. Problem.—An evacuated glass bulb weighs 15.3952 g. Filled with oxygen, the bulb weighs 16.0094 g., and with X at the same temperature and pressure, 16.2312 g. What is the molecular weight of X?

Weight of the bulb + oxygen = 16.0094 g.
Weight of empty bulb = 15.3952 g.
Weight of oxygen in bulb = 0.6142 g.

Weight of bulb + X = 16.2312 g.
Weight of empty bulb = 15.3952 g.
Weight of X in bulb = 0.8360 g.

Then

$$\frac{0.6142 \text{ g.}}{0.8360 \text{ g.}} = \frac{32}{x}$$

$$x = 43.6, \text{ molecular weight of } x$$

6. Method Based on the Molar Volume.—Since moles of all substances, including gases, contain the same number of molecules and since, according to Avogadro, the same number of molecules of all gases occupy the same volume at the same temperature and pressure, it follows *that moles of all gases will occupy the same volume at any given temperature and pressure.* At 0°C. and 760 mm. this volume is 22.4 liters and is known as the *gram-molecular,* or *molar, volume.* It may be defined as *the volume that will be occupied by a mole of any gas, under standard conditions.* This volume filled under standard conditions with oxygen weighs 32 g. (a mole of oxygen); with ammonia, 17 g. (a mole of ammonia); with carbon dioxide, 44 g.; etc.

This suggests a method of determining the molecular weights of gaseous substances. A glass bulb might be blown of 22.4 liters capacity (somewhat larger than a basketball) and be provided with a stopcock through which the bulb could be filled with gas. The air within the bulb could then be as completely removed as possible by means of a vacuum pump and the empty bulb weighed. The gas, of which the molecular weight was to be determined, could then be admitted into the bulb at a pressure of 760 mm. and at 0°C. and the combined weight of the gas and bulb obtained. The difference between the weight of the gas and bulb filled with the gas and its weight evacuated would be the weight of 22.4 liters of the gas and would be, therefore, the gram-molecular weight of the gas. However, a bulb of this size would be too large to weigh on a sensitive balance, and the experiment would also have to be carried out in a room the temperature of which would have to be accurately controlled at 0°C. and the pressure maintained at 760 mm.

Fortunately it is merely necessary to obtain the weight of a known volume of a gas at a known temperature and pressure in order to calculate its molecular weight. The solution of a typical molecular weight problem will illustrate the method.

7. **Problem.**—A glass bulb of 231 ml. capacity weighs evacuated 15.3952 g. Filled with a gas of unknown molecular weight at a temperature of 20°C. and a pressure of 753 mm., it weighs 16.6329 g. From these data, calculate the molecular weight of the gas.

$$\begin{aligned}\text{Weight of bulb + gas} &= 16.6329\text{ g.}\\ \text{Weight of empty bulb} &= \underline{15.3952\text{ g.}}\\ \text{Weight of gas} &= 1.2377\text{ g.}\end{aligned}$$

If this weight of gas occupies a volume of 231 ml. at 20°C. and 753 mm., what would be its volume under standard conditions?

$$\begin{array}{lll} V_1 = 231\text{ ml.} & t_1 = 20°\text{C. }(293°\text{A.}) & P_1 = 753\text{ mm.}\\ V_2 = ? & t_2 = 0°\text{C. }(273°\text{A.}) & P_2 = 760\text{ mm.}\end{array}$$

$$\frac{231\text{ ml.}}{V_2} = \frac{293°}{273°} \times \frac{760\text{ mm.}}{753\text{ mm.}} \qquad V_2 = 213\text{ ml.} = 0.213\text{ l.}$$

This step had to be taken in order that the volume of the 1.2377 g. of gas could be compared with the 22.4 liters which is at standard temperature and pressure.

We now have to solve the problem: if 0.213 liter of gas weighs 1.2377 g., what is the weight of 22.4 liters?

$$\begin{aligned}\frac{0.213\text{ l.}}{1.2377\text{ g.}} &= \frac{22.4\text{ l.}}{x\text{ g.}}\\ x\text{ g.} &= 130\text{ g.}\\ x &= 130,\text{ molecular weight}\end{aligned}$$

8. **Molecular Weight of Substances in Solution.**—Avogadro's hypothesis provides methods by which the molecular weights of gases or volatile liquids may be determined. Fortunately, the solution laws provide means for determining those

of soluble solids and liquids. The effect, which a solute in dilute solution has on the vapor pressure, freezing point, and boiling point of the solvent, depends only on its molecular concentration and not on its chemical composition. In the same solvent, solutes of equal molecular concentration cause the same vapor-pressure and freezing-point depressions and the same rise in boiling point. A mole of sugar or of glycerine, for example, in 1,000 g. of water lowers the vapor pressure 0.31 mm. and the freezing point 1.86°C. and raises the boiling point 0.51°C. So do moles of all nonelectrolytes in the same amount of water. Knowing this we have a method by which the molecular weight of a substance in solution can be calculated. For an example, let us consider the freezing-point method which is the one most frequently used.

We know that a mole of any nonelectrolyte in 1,000 g. of water will lower its freezing point 1.86°C. A known weight of the substance is dissolved in a known weight of water and the freezing point of this solution is measured. From these data it is simple to calculate what weight of this substance must be dissolved in 1,000 g. of water to lower the freezing point 1.86°C. This weight will be a mole of the substance. For example, 8.55 g. of cane sugar in 100 g. of water causes a freezing-point depression of 0.465°C.

$$\frac{8.55\text{ g.}}{100\text{ g.}} = \frac{85.5\text{ g.}}{1{,}000\text{ g.}}$$

$$\frac{85.5\text{ g.}}{0.465^\circ} = \frac{x\text{ g.}}{1.86^\circ}$$

$$x = 342,\ \text{molecular weight of sugar}$$

In general:

$$\frac{\text{Weight of solute in 1,000 g. water}}{\text{Observed } \Delta T_f} = \frac{\text{molecular weight of solute}}{1.86^\circ}$$

The calculations for the boiling-point method are similar except that the molal boiling-point elevation of water is 0.51°C. Solvents other than water may be used, but their characteristic molal freezing-point depression and boiling-point rise constants should be substituted for those of water.

The accuracy with which molecular weights may be determined by the methods we have been discussing depends upon how exactly gases or vapors obey the gas laws and upon how exactly solutes obey the solution laws. The results are rarely trustworthy beyond 1 per cent. The molecular weight of sugar as determined above was given as 342, but we are not certain of the accuracy of the 2. It might be 341 or 343 or even 340 or 344.

9. The Determination of Atomic Weights.—The determination of an accurate atomic weight of an element is no easy task. A table of the atomic weights of the elements will be used with far greater respect when the painstaking effort that has been expended in the determination of each of these weights is realized. The reasoning involved in the general method seems so very simple, once it is understood; but it gives trouble at first.

The molecule of any compound of an element must contain at least one atom of that element. Therefore, *there can be never less than one atom of an element in one molecule of any of its compounds.* In any compounds whose molecules contain only one atom of the element, there will be one atomic weight of the element in one molecular weight of the compound. Thus *there can never be less than one atomic weight of an element in one molecular weight of any of its compounds.* THE ATOMIC WEIGHT OF AN ELEMENT IS THE SMALLEST WEIGHT OF THE ELEMENT TO BE FOUND IN A MOLECULAR WEIGHT OF ANY OF ITS COMPOUNDS.

Table 17.—The Atomic Weight of Sulfur

Compound of sulfur	Molecular weight (± 1 %)	Per cent sulfur (± 0.01 %)	Weight of sulfur per molecular weight (± 1 %)
Free sulfur	250	100.00	250
With oxygen (1)	64	50.05	32
With oxygen (2)	80	40.04	32
With hydrogen	34	94.08	32
With chlorine	135	47.49	64
With carbon	76	84.22	64

Let us suppose that we are the proud discoverers of the element sulfur and that we are to determine its atomic weight. Since this element may be vaporized, we determine its molecular weight with some difficulty by a method based on Avogadro's hypothesis. The value of 250 which is obtained for the molecular weight we admit is only approximately correct since we were compelled to work at 450°C. This is some multiple of the atomic weight, but since we have just discovered the element, no textbook will tell us how many atoms there are in a molecule of sulfur vapor. We next prepare pure samples of as many molecular compounds of sulfur as our patience will allow and determine their molecular weights. These values are accurate to the nearest per cent only. Next we devise a method of analysis by which the percentage by weight of sulfur in each of these compounds may be determined accurately. Since analytical methods are far more precise than those used for molecular-weight determinations, our method should be accurate to the nearest hundredth of a per cent. The results are summarized in Table 17. Now if we multiply each molecular weight by the percentage of sulfur, the weight of sulfur in a molecular weight of each compound is obtained. The smallest of these weights is the atomic weight of sulfur; and this seems to be 32. Evidently each molecule of the two oxides and of hydrogen sulfide contains one atom of sulfur. Those of sulfur chloride and of carbon disulfide must each contain two sulfur atoms; and the molecules of free sulfur, eight. Of course the atomic weight of 32 is no more accurate than the molecular weights from which it has been obtained.

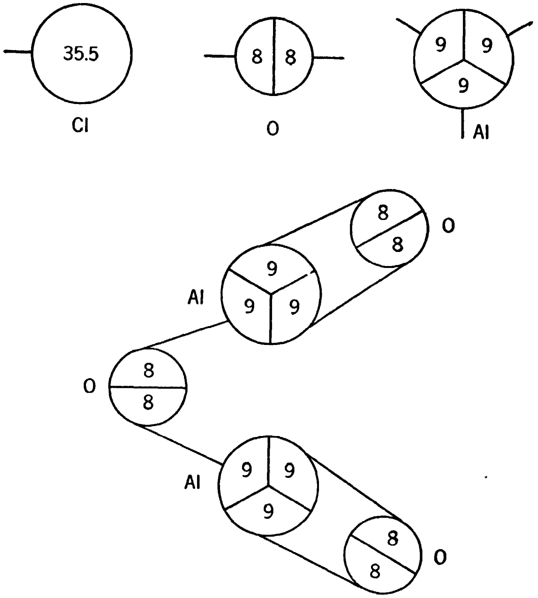


Fig. 74.—Equivalent weights.

10. Equivalent Weights.—Before the accurate atomic weight of an element can be determined, *its equivalent weight* must be calculated. This *is equal to its atomic weight divided by its valence* and, hence, may be regarded as the weight associated with each valence bond. Thus the equivalent weight of chlorine is equal to its atomic weight; that of oxygen is one-half of its atomic weight; and that of aluminum is one-third of its atomic weight as shown in Fig. 74. Since these are the weights at the ends of each valence bond, they represent the relative weights in which elements combine. The structure of the molecule of aluminum oxide, shown in Fig. 74, will help in understanding why this is so. Since the valence of oxygen is 2 and its atomic weight, 16.0000, by definition, its equivalent weight is exactly 8.0000, again by definition. We may define *the equivalent weight of an element as that weight which combines with* 8.0000 *weights of oxygen.* As this weight is based on analytical data alone, it may be determined very accurately.

11. Accurate Atomic Weights.—By comparing the equivalent weight of sulfur with its approximate atomic weight of 32, we may determine its valence. We know that the composition of the first oxide of sulfur is 50.05 per cent sulfur and, therefore, 49.95 per cent oxygen. If 50.05 g. of sulfur combines with 49.95 g. of oxygen, how many grams will combine with 8.0000 of oxygen?

$$\frac{50.05\text{ g.}}{49.95\text{ g.}} = \frac{x}{8.0000\text{ g.}}$$

$$x = 8.015\text{ g.}$$

Hence 8.015 is the equivalent weight of sulfur. The approximate atomic weight of 32 is four times the equivalent weight, hence the valence of sulfur in this oxide is 4. Upon multiplying the accurate equivalent weight 8.015 by 4, the valence, the accurate atomic weight of sulfur 32.06 is finally obtained.

If we had chosen the second oxide, the valence of sulfur and, therefore, its equivalent weight would have been different. In this oxide, 40.04 g. of sulfur is combined with 59.96 g. of oxygen. Hence the proportion

$$\frac{40.04\text{ g.}}{59.96\text{ g.}} = \frac{x}{8.0000\text{ g.}}$$

gives the equivalent weight

$$x = 5.343$$

Hence the valence of sulfur is 6 and again its accurate atomic weight

$$5.343 \times 6 = 32.06$$

EXERCISES

1. Equal volumes of a gas of unknown molecular weight and of oxygen weigh 0.528 and 0.352 g., respectively. Calculate the molecular weight of the gas.

2. What is the molecular weight of ethylene if 0.625 g. occupies a volume of 518 ml. at a temperature of 17°C. and a pressure of 780 mm.?

3. Calculate the density of acetylene, C_2H_2, under standard conditions.

4. Prove that the oxygen molecule is diatomic.

5. Does the following statement follow from Avogadro's hypothesis? All gases are of the same molecular concentration at the same temperature and pressure.

6. Calculate the pressure exerted by 34 g. of ammonia, NH_3, in a vessel of 10 l. at standard temperature.

7. Calculate the molecular weight of a substance 10 g. of which in 100 g. of water lowers the freezing point of water 0.31°C.

8. A solution containing 4.65 g. of aniline in 100 g. of benzene lowers the freezing point of the latter 2.6°C. Calculate the molecular weight of aniline.

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CHAPTER TWENTY-TWO

PROBLEMS BASED ON EQUATIONS

More frequently than not in our lives the useful things we have to do seem the least interesting. Johnny likes to play baseball far more than to mow the lawn. Mary prefers the "movies" to writing a theme. Father would rather play golf than weed; and mother plays bridge with more zest than she peels potatoes. This is a very useful chapter!

1. What Information May Be Derived from an Equation? One of the first equations we studied was that for the laboratory preparation of oxygen:

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

In words, the equation signifies that two molecules of potassium chlorate, each of which is made up of one atom of potassium, one of chlorine, and three of oxygen, decompose into two molecules of potassium chloride, each containing one atom of potassium and one of chlorine, and three diatomic molecules of oxygen. Since moles of all substances contain the same number of molecules, it follows that two moles of potassium chlorate form two moles of potassium chloride and three moles of oxygen. Since the mole of any substance can be readily calculated from its formula and the atomic weights, we have a means of calculating the weight relationships between the substances in the reaction

$$\begin{array}{rcrcr}
2KClO_3 & \rightarrow & 2KCl & + & 3O_2 \\
2 \times 39\ (K) = 78 & & & & \\
2 \times 35.5\ (Cl) = 71 & & 2 \times 39\ (K) = 78 & & \\
6 \times 16\ (O) = \underline{96} & & \underline{2 \times 35.5\ (Cl) = 71} & & \underline{6 \times 16\ (O)} = 96 \\
(2\ \text{moles} = 245\ \text{g.}) & \rightarrow & (2\ \text{moles} = 149\ \text{g.}) & + & (3\ \text{moles} = 96\ \text{g.})
\end{array}$$

Hence 245 g. of potassium chlorate will form 149 g. of potassium chloride and 96 g. of oxygen. Of course 245 lb. of the chlorate decomposes into 149 lb. of the chloride and 96 lb. of oxygen.

2. Problems Involving Weights Only.—Such knowledge makes it possible to solve problems of which the following is typical:

Problem.—How many grams of aluminum sulfate will be formed when 6 g. of aluminum metal is treated with an excess of sulfuric acid?

First: The correctly balanced equation for the reaction should be written.

Second: The problem should be summarized above the equation.

Third: The weight relationships should be calculated beneath the formulas of the substances involved in the problem. Thus:

$$\begin{array}{lllll}
\text{Problem:} & 6\text{ g.} & \dashrightarrow & x\text{ g.} & \\
\text{Equation:} & 2\,\text{Al} & +\ 3H_2SO_4 \longrightarrow & Al_2(SO_4)_3 & +\ 3H_2 \\
 & & & 2 \times 27\ (\text{Al}) = 54 & \\
 & & & 3 \times 32\ (\text{S}) = 96 & \\
 & 2 \times 27\ (\text{Al}) = 54 & & 12 \times 16\ (\text{O}) = \underline{192} & \\
\text{Relationship:} & 54\text{ g.} & \dashrightarrow & 342\text{ g.} &
\end{array}$$

If 54 g. of aluminum yields 342 g. of aluminum sulfate, 6 g. of aluminum will form how many grams of the sulfate? The data are arranged above and below the equation to give the correct proportion:

$$\frac{6\text{ g.}}{54\text{ g.}} = \frac{x\text{ g.}}{342\text{ g.}}$$

$$x = 38\text{ g. } Al_2(SO_4)_3$$

Problem.—What weight of phosphorus will be required to form 71 g. of phosphorus pentoxide?

$$\begin{array}{llll}
x\text{ g.} & \dashrightarrow & & 71\text{ g.} \\
4P & +\ 5O_2 & \longrightarrow & 2P_2O_5 \\
 & & & 4 \times 31\ (\text{P}) = 124 \\
\underline{4 \times 31\ (\text{P}) = 124} & & & \underline{10 \times 16\ (\text{O}) = 160} \\
124\text{ g.} & \dashrightarrow & & 284\text{ g.}
\end{array}$$

$$\frac{x}{124\text{ g.}} = \frac{71\text{ g.}}{284\text{ g.}}$$

$$x = 31\text{ g. P}$$

In problems involving weights only, pressure and temperature changes need never be considered. (Why?)

3. Problems Involving Gas Volumes Only.—Avogadro's hypothesis tells us that at the same temperature and pressure equal numbers of molecules of all gases occupy the same volume. Hence the volume ratios, in which gases react and are formed, are the same as the molecule ratios as given by the equation. The equation for the synthesis of ammonia

$$N_2 + 3H_2 \rightarrow 2NH_3$$

tells us that 1 liter of nitrogen reacts with 3 liters of hydrogen to form 2 liters of ammonia, since these are the number of molecules of each substance in the equation. The same proportions would hold no matter what volume unit is used.

Problem.—How many cubic feet of carbon dioxide is formed from the combustion of 7 cu. ft. of carbon monoxide, provided both gas volumes are measured under the same conditions?

$$\begin{array}{lcl}
7\text{ cu. ft.} & \xrightarrow{\hspace{6em}} & x\text{ cu. ft.} \\
2CO \;+ O_2 & \xrightarrow{\hspace{6em}} & 2CO_2 \\
2\text{ cu. ft.} & \xrightarrow{\hspace{6em}} & 2\text{ cu. ft.}
\end{array}$$

$$\frac{7\text{ cu. ft.}}{2\text{ cu. ft.}} = \frac{x}{2\text{ cu. ft.}}$$

$$x = 7\text{ cu. ft.}$$

The answer is obvious by inspection.

4. Problems Involving Weights and Gas Volumes.—One mole of any gas under standard conditions occupies approximately 22.4 liters.

Problem.—What volume of oxygen under standard conditions will be formed by decomposing 98 g. of potassium chlorate?

$$\begin{array}{rcl}
98\text{ g.} & \xrightarrow{\hspace{8em}} & x\text{ l.} \\
2KClO_3 & \xrightarrow{\hspace{8em}} & 2KCl + 3O_2 \\
2 \times 39\ (K) = 78 & & \\
2 \times 35.5\ (Cl) = 71 & & \\
6 \times 16\ (O) = \underline{96} & & \underline{22.4\text{ l.} \times 3} \\
245\text{ g.} & \xrightarrow{\hspace{8em}} & 67.2\text{ l.}
\end{array}$$

$$\frac{98\text{ g.}}{245\text{ g.}} = \frac{x\text{ l.}}{67.2\text{ l.}}$$

$$x = 26.9\text{ l. } O_2 \text{ at } 0°\text{C. and } 760\text{ mm.}$$

Problem.—How many liters of oxygen at 20°C. and a pressure of 750 mm. will be formed by the electrolysis of 4.5 g. of water? This is a combination of a gas-law problem with the type we have been considering. We may first calculate the volume of oxygen formed under standard conditions;

$$\begin{array}{lcl}
4.5\text{ g.} & \xrightarrow{\hspace{8em}} & x\text{ l.} \\
2H_2O & \xrightarrow{\hspace{8em}} & 2H_2 + O_2 \\
36\text{ g.} & \xrightarrow{\hspace{8em}} & 22.4\text{ l. at S.T.P.}
\end{array}$$

$$\frac{4.5\text{ g.}}{36\text{ g.}} = \frac{x}{22.4\text{ l.}}$$

$$x = 2.8\text{ l. at } 0°\text{C. and } 760\text{ mm.}$$

and then convert this volume to the conditions given in the problem:

$$\begin{array}{lll}
V_1 = 2.8\text{ l.} & T_1 = 273°\text{A.} & P_1 = 760\text{ mm.} \\
V_2 = x & T_2 = 293°\text{A.} & P_2 = 750\text{ mm.}
\end{array}$$

$$\frac{2.8\text{ l.}}{x} = \frac{273°}{293°} \times \frac{750\text{ mm.}}{760\text{ mm.}}$$

$$x = 3.0\text{ l. } O_2 \text{ at } 20°\text{C. and } 750\text{ mm.}$$

EXERCISES

In solving these problems, use values for the atomic weights to the nearest whole number, but in the case of chlorine use 35.5.

1. How many grams of sodium chloride are formed when 10 g. of sodium hydroxide is neutralized with hydrochloric acid? *Ans.* 14.6 g.

2. What volume of hydrochloric acid (gas) is obtained under standard conditions from five moles of chlorine? *Ans.* 224 l.

3. A sodium chloride solution is subjected to electrolysis with the result that 20 g. of sodium hydroxide is formed. What volume of chlorine is formed at the same time under standard conditions?

4. The following reaction involves substances all of which are gases at 150°C. and 1 atm.:

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

Under these conditions, what volume of oxygen will react with 200 ml. of ethane, C_2H_6, and what volumes of carbon dioxide and of water vapor are formed?

5. What volume of hydrochloric acid at 91°C. and 380 mm. pressure can be obtained from 117 g. of sodium chloride?

6. What weight of water must be decomposed by electrolysis to obtain 10 l. of hydrogen at 20°C. and 770 mm.?

7. What weight of oxygen is required to burn one ton of coal completely, assuming the coal to be pure carbon? How many cubic feet of oxygen does this weight occupy under standard conditions? How many cubic feet of air will contain this volume of oxygen?

8. What volume of liquid water must be subjected to electrolysis to obtain 10 liters of oxygen under standard conditions?

9. A gram-atomic weight of a certain metal reacts with an acid and liberates 33.6 liters of hydrogen. What is the valence of the metal?

10. The dry powder for a lime-sulfur spray is made up by mixing three moles of sulfur with one mole of lime, CaO. How many kilograms of lime must be mixed with 3 kg. of sulfur to maintain these proportions?

CHAPTER TWENTY-THREE

THE HALOGENS

To John Dalton the atoms of the elements were hard, impenetrable spheres, each ultimately small and devoid of any structure. The properties of each element were unique and to be explained in terms of its peculiar atom. As the science of chemistry developed during the first half of the nineteenth century, elements of similar properties were discovered and grouped together. As early as 1816, Döbereiner pointed out that several groups of three similar elements exist and that the atomic weight of the middle element of each such triad is nearly the average of those of the other two.

Element	Atomic weights	Mean	Element	Atomic weights	Mean
Calcium	40.08		Chlorine	35.46	
Strontium	87.63	88.72	Bromine	79.92	81.19
Barium	137.36		Iodine	126.92	

As it turned out, other elements were discovered which obviously should be added to these groups, *e.g.*, radium to calcium, strontium, and barium, and fluorine to chlorine, bromine, and iodine. Therefore the triad lost significance. But the important relationship remained to indicate that atoms of these related elements are similar. This could be the case only if these atoms have similar structures. The concept of valence bonds created another need for a theory of atomic structure by which atom combination could be explained. Finally, the discovery of the periodic law by Newlands and Mendeléeff pointed out the interrelationship of the atoms of all the elements and was a clear indication of atomic structure. This important law will be the subject of the next chapter; but first we shall study a group of closely related elements in order to be better able to appreciate the significance of this law.

1. The halogens are the group of closely related nonmetals fluorine, chlorine, bromine, and iodine. The properties of chlorine have already been discussed. There is always the temptation to pass over lightly the striking similarity of the other three halogens to chlorine in order to avoid dreary repetition. But it should be kept in mind, when differences in properties are pointed out, that the similarities in behavior are far more impressive.

The halogens are the most active nonmetals. As free elements, they are composed of diatomic molecules. As the atomic and, therefore, the molecular weights of the free elements increase from fluorine to iodine, the van der Waals forces become stronger. Thus fluorine and chlorine are gases, bromine is a liquid, and iodine a solid under normal conditions. The vapor pressures of bromine and iodine are high, an indication that the forces of intermolecular attraction are relatively weak. The vapor pressure of iodine is so high at ordinary temperatures that it may be readily sublimed. Its melting point is 90.1°C.

As active nonmetals, the halogens react readily with metals to form salts. Each halogen atom gains an electron from a metal atom and becomes a halide ion with a change of −1. Strong Coulomb forces hold the metal and halide ions together in the crystal structures of the resulting salts. Since relatively large amounts of energy are liberated, the salts formed are very stable. The ease of reduction is greatest with fluorine, least with iodine.

On the other hand, the halogens do not react directly with oxygen. The oxides are prepared by indirect methods and, except in the case of iodine, are unstable and even dangerously explosive. In these and in their oxygen acids and oxygen salts, the valence number of the halogen atoms is positive. In such compounds, the halogen atoms are readily reduced and, therefore, the compounds are excellent oxidizing agents.

TABLE 18.—PROPERTIES OF THE HALOGENS

Halogen	Molecular formula	Atomic weight	State at S. T. P.	Critical temperature, °C.	Boiling point, °C.
Fluorine......	F_2	19.00	Pale yellow gas	.....	−187
Chlorine.....	Cl_2	35.457	Greenish-yellow vapor	144.0	−34.6
Bromine.....	Br_2	79.916	Red liquid	302	58.78
Iodine........	I_2	126.92	Gray solid	553	184.35

A fifth member of the halogen family probably exists in nature but has not as yet been definitely isolated. However, it has been prepared by transmutation of another element in the cyclotron (29-11).

As in the case of chlorine, the other halogens are poisonous. When inhaled in any but very low concentrations, they destroy the tissues of the nose, throat, and lungs. Liquid bromine produces painful, slow-healing burns when spilled on the skin. Even the relatively dilute tincture of iodine is destructive of healthy tissue, and its use as an antiseptic is decreasing. Powdered sulfanilamide derivatives are replacing it. All reactions involving the use of free halogens are best carried out under a hood.

2. Occurrence.—Negative ions of all the halogens occur in solution in sea water to the extent of 10,000, 67, 7, and 3 parts per million for the chloride, bromide, iodide, and fluoride ions, respectively. Although fluorine occurs to only a slight extent in the sea, largely because its compounds are so sparingly soluble, nevertheless it is the twentieth element in abundance. Among its most abundant compounds are fluorspar, CaF_2, used extensively as a flux by the steel industry, and cryolite, Na_3AlF_6, which when melted serves as the solvent in the electrolytic preparation of aluminum.

In addition to the occurrence of bromides in sea water, magnesium and sodium bromide are associated with sodium chloride in the salt deposits of Stassfurt in Germany and of Michigan, West Virginia, and Ohio in the United States.

Iodine is found as sodium iodate, $NaIO_3$, associated with sodium nitrate in the deposits of Chile saltpeter and as iodides in certain California brine wells. Its low concentration in sea water makes the accomplishment of its concentration by marine plants and animals all the more praiseworthy. It was once obtained from the ashes of seaweeds. The hormone thyroxin, a secretion of the thyroid gland, is an organic compound of iodine which plays a basic role in animal metabolism. Iodine deficiency in food is the common cause of goiter.

3. Oxidation-reduction Relationships.—Since an element in its compounds must have either a positive or a negative valence number, its liberation as a free element with a valence of 0 is accompanied by a valence change. Therefore, the preparation of any free element invariably involves an oxidation-reduction reaction. In such reactions, you will remember that the oxidation of one element causes the reduction of another. The substance that contains the element reduced in the reaction is called the *oxidizing agent* (17-2c); whereas the substance that contains the element oxidized is the *reducing agent.* The strength of an oxidizing agent depends upon the ease with which an element in it may be reduced. Similarly, the strength of a reducing agent is determined by the ease with which one of its constituent elements may be oxidized.

The halogens are active nonmetals. They react readily with hydrogen or with metals, and in so doing their valence numbers are reduced from 0 to -1. Hence in the free state they are oxidizing agents. Consider the following reactions:

$$\begin{aligned} H_2 + F_2 &\rightarrow 2HF + 76{,}000 \text{ cal.} \\ H_2 + Cl_2 &\rightarrow 2HCl + 44{,}000 \text{ cal.} \\ H_2 + Br_2 &\rightarrow 2HBr + 17{,}000 \text{ cal.} \\ H_2 + I_2 &\rightarrow 2HI - 13{,}000 \text{ cal.} \end{aligned}$$

The heat given out in each case is a measure of the ease with which the reduction of the halogen takes place. Hence fluorine is the most readily and iodine the least easily reduced. Free fluorine is the best oxidizing agent of all the halogens.

The preparation of a free halogen from its compound with hydrogen or with a metal involves oxidation from a valence of -1 to one of 0. Hence such reactions are the reverse of those considered in the last paragraph. The greater the ease with which the free halogen is reduced, the more difficult is its preparation by oxidization in the reverse process. The preparation of iodine from an iodide by oxidation is easy, but that of fluorine from a fluoride is so difficult that only after 75 years of persistent effort was fluorine prepared for the first time. Iodides are excellent reducing agents; fluorides are extremely poor ones.

To summarize the relative activity:

As an oxidizing agent: $F_2 > Cl_2 > Br_2 > I_2$
As a reducing agent: $HF < HCl < HBr < HI$

4. Preparation of the Halogens.—With the exception of sodium iodate, the halogens occur as halides in nature. Their preparation whether by commercial or by laboratory methods involves the oxidation of a halide by an oxidizing agent or by electrolysis.

We have already pointed out that free chlorine will displace bromine or iodine; *e.g.*,

$$Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$$

In this reaction chlorine is reduced

$$Cl^0 \rightarrow Cl^{-1}$$

and bromine, oxidized

$$Br^{-1} \rightarrow Br^0$$

This bears out what we have been considering since chlorine is more readily reduced but less readily oxidized than bromine. In general, it follows that fluorine displaces all the other halogens; chlorine displaces bromine and iodine; bromine displaces iodine only; and iodine lacks the ability to displace any other halogen.

The commercial preparation of bromine from sea water is based on this type of reaction. The development of the use of tetraethyl lead as an antiknock compound in gasoline (52-12) increased the annual consumption of bromine from 2 million pounds in 1921 to 9 million pounds in 1931. Ethylene treated with bromine is converted into ethylene dibromide from which in turn tetraethyl lead is prepared. Bromine had been prepared from natural brines, but this sharp increase in the demand led to the use of sea water as a virtually inexhaustible supply of bromide ion. Despite the fact that only 67 parts of bromide per million of water are found in the sea, a large plant located at the mouth of the Cape Fear River in North Carolina is extracting 15,000 lb. of bromine per day from the Atlantic Ocean. The bromide ion is converted into free bromine by bubbling chlorine gas into sea water:

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$$

or

$$Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$$

Then bromine is driven out of solution by a stream of air. The bromine vapor is absorbed by a spray of sodium carbonate (soda-ash) solution with which it reacts to form both sodium bromide and sodium bromate:

$$3Na_2CO_3 + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$$

At this point we seem to be back where we started in the deep blue sea. But the bromine is now much more concentrated. By treating the bromide-bromate solution with sulfuric acid, bromine is liberated:

$$5NaBr + NaBrO_3 + 3H_2SO_4 \rightarrow 3Na_2SO_4 + 3H_2O + 3Br_2$$

Balancing this equation by the valence changes involved is an interesting problem. Bromine in the bromate is reduced to free bromine:

$$Br^{+5} + 5e^- \rightarrow Br^0$$

whereas the bromine in the bromide is oxidized to free bromine:

$$Br^{-1} \rightarrow Br^0 + 1e^-$$

Thus five bromine atoms are oxidized for every one reduced. Sodium bromide is the reducing agent and sodium bromate, the oxidizing agent.

This one plant daily extracts bromine from 200,000,000 gal. of sea water with 90 per cent efficiency.

Iodine is produced commercially from oil-well brines in and near Long Beach, Calif., in which the concentration of iodides is 30 to 70 parts per million. This is high as compared with that of 7 parts per million in the sea and suggests an interesting possibility. At an earlier time, this section of the coast was under the Pacific Ocean. Here beds of giant kelp extracted iodine from the water. Subsequent decomposition produced petroleum and a salt brine rich in iodides.

After these brines have been clarified, the equivalent amount of silver nitrate is added to precipitate silver iodide:

$$AgNO_3 + NaI \rightarrow AgI\downarrow + NaNO_3$$

Fortunately the iodide of silver is less soluble than the chloride. This precipitate is allowed to settle, and the supernatant brine is run off. The iodide is treated with dilute hydrochloric acid and with iron scrap, whereupon the iron replaces the silver and a solution of ferrous iodide is obtained:

$$Fe + 2AgI \rightarrow FeI_2 + 2Ag$$

The silver, treated with nitric acid, is converted back into silver nitrate to be used again in the process. Chlorine or some other oxidizing agent is then used to liberate the iodine:

$$FeI_2 + Cl_2 \rightarrow FeCl_2 + I_2$$

By these means, enough iodine is obtained to break the Chilean monopoly. The production amounts to a little over 200 tons a year.

5. Preparation Using Oxidized Agents.—No element exists which is more readily reduced than fluorine. Hence none exists by whose reduction fluorine may be oxidized to the free state. It is, therefore, impossible to liberate fluorine from a fluoride by the use of an oxidizing agent. Manganese dioxide may be used to oxidize hydrobromic or hydriodic acids in the laboratory preparation of bromine or iodine:

$$MnO_2 + 4HBr \rightarrow MnBr_2 + Br_2 + 2H_2O$$
$$MnO_2 + 4HI \rightarrow MnI_2 + I_2 + 2H_2O$$

These are in every way similar to the laboratory preparation of chlorine. Indeed they proceed more readily since both hydrobromic and hydriodic acids are stronger reducing agents than hydrochloric.

The difference in the strength of these acids as reducing agents is well brought out by their behavior when treated with hot, concentrated sulfuric acid. The sulfur atom in the molecule of this acid has a valence of +6 which may be reduced to +4 if the acid is treated with a sufficiently strong reducing agent. Hydrochloric acid is not strong enough as a reducing agent to reduce sulfuric acid. However, both hydrobromic and hydriodic acids are:

$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$
$$2Br^{-1} \rightarrow Br_2 + 2e^-$$
$$S^{+6} + 2e^- \rightarrow S^{+4}$$

Sulfur dioxide is the only compound, in which sulfur has a valence number of +4, which is stable in acid solutions. When hydriodic acid is used, the reduction of the sulfur may be so great that it appears as hydrogen sulfide in the products:

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$$
$$8I^{-1} \rightarrow 4I_2 + 8e^-$$
$$S^{+6} + 8e^- \rightarrow S^{-2}$$

6. Preparation by Electrolysis.—As we might suspect, the preparation of fluorine proved to be the most difficult of all the halogens. We have seen that the electric current may be used to oxidize chlorine from the chloride ion to the free element at the anode by electrolysis. Fluorine was finally prepared by this method by Moissan in 1886. Two difficulties were encountered.

In the first place, melted fluorides are extremely poor conductors of electricity. Moissan solved this difficulty by dissolving potassium fluoride in dry, liquid hydrofluoric acid. The choice of a material for the electrolysis cell presented another problem. Because of its activity, fluorine reacts with all but the most inert metals. It also reacts with glass to form the gaseous compound silicon tetrafluoride, SiF_4. It would have been embarrassing to have the successful preparation heralded by the disintegration of the apparatus. Moissan used an alloy of the two inert metals platinum and iridium out of which to construct a U tube. Fluorine was evolved at a graphite anode:

$$2F^- \rightarrow F_2 + 2e^-$$

and hydrogen at the cathode:

$$2H^+ + 2e^- \rightarrow H_2$$

Since the fluorides of copper and of nickel are not attacked by either fluorine or hydrofluoric acid, the cell may be constructed of a less expensive alloy of these metals called Monel metal.

Bromine and iodine may also be prepared by electrolysis, but the method is of no importance.

7. Preparation of Iodine from Sodium Iodate.—Most of the world's supply of iodine is prepared by the reduction of sodium iodate, which makes up about 0.2 per cent of the Chile saltpeter, $NaNO_3$, beds. After separation from the sodium nitrate the iodate is treated with sodium bisulfite which acts as the reducing agent:

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

8. Reactions and Uses of the Halogens.—The reactions of the halogens are so similar to those of chlorine (17-4) that they need not be repeated here.

Bromine and iodine are used in the preparation of organic compounds. Bromides are used as sedatives in medicine, and silver bromide is used in photography (49-6). The familiar tincture of iodine is a solution of iodine in alcohol. Sodium iodide is added in small amounts to table salt to be used in regions where the iodine content of the drinking water is insufficient to meet the requirements of the thyroid gland.

HYDROFLUORIC, HYDROBROMIC, AND HYDRIODIC ACIDS

9. Preparation.—*Hydrofluoric acid* is prepared by treating calcium fluoride with concentrated sulfuric acid, a method analogous to the preparation of hydrochloric acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF\uparrow$$

This acid is a gas under normal conditions. Unlike the other binary acids of the halogens, its molecules are associated so that the formula $(HF)_n$ would be more accurate than the simple HF. However, the use of such a formula would needlessly complicate equations for reactions in which this acid plays a part.

Hydrobromic and *hydriodic acids* cannot be prepared by heating their salts with concentrated sulfuric acid. These are such strong reducing agents that sulfuric acid is reduced to sulfur dioxide, *e.g.*,

$$2NaBr + H_2SO_4 \rightarrow Na_2SO_4 + 2HBr$$
$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$

The phosphorus atoms in a phosphate are, however, much harder to reduce. Hence phosphoric acid heated with a bromide or an iodide can be used successfully in preparing these acids:

$$NaBr + H_3PO_4 \rightarrow NaH_2PO_4 + HBr\uparrow$$

Phosphorus and bromine or iodine combine directly to form the corresponding trihalide of phosphorus:

$$2P + 3Br_2 \rightarrow 2PBr_3$$

which reacts with water to form phosphorous acid and the desired binary acid:

$$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr$$

These acids may also be synthesized by passing bromine or iodine vapor mixed with hydrogen through a spiral coil of heated platinum wire:

$$H_2 + Br_2 \rightarrow 2HBr$$

10. Properties.—Each of the four binary acids is a gas which fumes in moist air and is very soluble in water. Each is extremely irritating to the mucous membranes of the nose and throat. As reagents, they are used in aqueous solution.

Each, with the exception of hydrofluoric, is a strong acid and *enters into all reactions typical of acids, e.g.*,

$$2HBr + Zn \rightarrow ZnBr_2 + H_2$$
$$2HBr + CaO \rightarrow CaBr_2 + H_2O$$
$$3HBr + Al(OH)_3 \rightarrow AlBr_3 + 3H_2O$$
$$2HBr + Na_2CO_3 \rightarrow 2NaBr + H_2O + CO_2$$

All the acids, except hydrofluoric, are *reducing agents* with hydriodic acid the most powerful reducing agent of the group:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$
$$MnO_2 + 4HBr \rightarrow MnBr_2 + Br_2 + 2H_2O$$
$$MnO_2 + 4HI \rightarrow MnI_2 + I_2 + 2H_2O$$
$$H_2SO_4 + HCl \rightarrow \text{no reaction}$$
$$H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2 + 2H_2O$$
$$H_2SO_4 + 8HI \rightarrow H_2S + 4I_2 + 4H_2O$$

but $$H_3PO_4 + HCl,\ HBr,\text{ or }HI \rightarrow \text{no reaction}$$

When silver nitrate is added to solutions of any chloride, bromide, or iodide, the *corresponding silver salt* precipitates:

$$AgNO_3 + HCl \rightarrow \underset{\text{white}}{AgCl\downarrow} + HNO_3$$
$$AgNO_3 + NaBr \rightarrow \underset{\text{cream}}{AgBr\downarrow} + HNO_3$$
$$AgNO_3 + KI \rightarrow \underset{\text{yellow}}{AgI\downarrow} + HNO_3$$

Of these, the iodide is the least soluble.

Hydrofluoric acid is unique in that it attacks silicon dioxide, or sand, and any silicate. The gas silicon tetrafluoride is formed:

$$SiO_2 + 4HF \rightarrow SiF_4\uparrow + 2H_2O$$

Glass is essentially a solution of sodium and calcium silicates. Hydrofluoric acid etches glass by the following reactions:

$$Na_2SiO_3 + 6HF \rightarrow 2NaF + SiF_4\uparrow + 3H_2O$$
$$CaSiO_3 + 6HF \rightarrow CaF_2 + SiF_4\uparrow + 3H_2O$$

A coating of paraffin is used to protect the glass; the design to be etched is cut through this film; and the liquid acid is poured over the film. The glass is thereby etched wherever it has been exposed.

11. Tests for the Halogens.—Chlorine may be recognized by its odor or by the fact that it liberates bromine from a bromide and iodine from an iodide:

$$Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$$
$$Cl_2 + 2NaI \rightarrow 2NaCl + I_2$$

These halogens are much more soluble in carbon tetrachloride than in water, and carbon tetrachloride is insoluble in water. If a solution containing free chlorine is shaken with a bromide or an iodide and a little carbon tetrachloride, the bromine or iodine liberated is concentrated in the carbon tetrachloride layer where it may be recognized by its color.

A very delicate test for free iodine is available. This halogen reacts with starch to form a deep blue color.

12. Oxygen Compounds of the Halogens.—We have mentioned that the halogens do not combine directly with oxygen. Oxides may be prepared indirectly but are relatively unimportant because of their instability. The following oxyacids and salts of chlorine are typical:

$HClO$, hypochlorous acid	$NaClO$, sodium hypochlorite
$HClO_2$, chlorous acid	$NaClO_2$, sodium chlorite
$HClO_3$, chloric acid	$NaClO_3$, sodium chlorate
$HClO_4$, perchloric acid	$NaClO_4$, sodium perchlorate

Hypochlorous acid may be prepared by the reaction of chlorine with water:

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

The reaction is incomplete since it is reversible. However, if chlorine is passed into a cold solution of sodium hydroxide, the reaction proceeds to completion with the formation of the corresponding salts:

$$Cl_2 + 2NaOH \rightarrow NaClO + NaCl + H_2O$$

If the solution is warm, the hypochlorite undergoes a simultaneous oxidation-reduction reaction:

$$\begin{aligned} 3NaClO &\rightarrow NaClO_3 + 2NaCl \\ 2Cl^{+1} + 4e^- &\rightarrow 2Cl^{-1} \\ Cl^{+1} &\rightarrow Cl^{+5} + 4e^- \end{aligned}$$

Chlorates are prepared commercially by the electrolysis of warm solutions of sodium or potassium chloride. They are powerful oxidizing agents. Mixtures of a chlorate and such reducing agents as phosphorus, sulfur, or carbon are dangerously explosive.

Perchlorates are slightly more stable than chlorates. They may be prepared by heating chlorates at a temperature just below that at which decomposition into chlorides and oxygen takes place:

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

Although in general safer to handle than chlorates, they have been known to explode violently when mixed with organic reducing agents.

EXERCISES

1. Explain in terms of the atomic structures of the halogens why the ease with which their atoms gain electrons decreases from fluorine to iodine.

2. Why does the state in which each halogen exists under normal conditions depend on its molecular weight?

3. Why does iodine sublime?

4. List the halide ions in the order of their ease of oxidation.

5. Why is chlorine an excellent oxidizing agent? Write five equations that illustrate this property.

6. Write equations for four reactions by which bromine may be prepared from sodium bromide.

7. Why cannot hydrobromic acid be prepared by the action of concentrated sulfuric acid on sodium bromide?

8. Write equations for two methods for preparing hydrobromic acid from bromine.

9. Write an equation for a reaction that illustrates the reducing action of hydriodic acid.

10. How does hydrofluoric acid etch glass?

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CHAPTER TWENTY-FOUR

THE PERIODIC TABLE

About the time of the Civil War, chemistry was emerging from a chaos of inadequate theory. In September of the year 1860, Stanislao Cannizzaro had explained clearly to a convention of chemists assembled at Karlsruhe the ideas of his teacher Avogadro on the relationship between atoms and molecules and had distributed to the delegates copies of his "Summary of a Course of Chemical Philosophy." After he had studied this pamphlet, the German chemist Lothar Meyer wrote, "The scales seemed to fall from my eyes. Doubts disappeared and a feeling of quiet certainty took their place." For the first time, chemists were able to determine atomic weights with certainty and to count the atoms in molecules of a compound. Correct formulas for these molecules could now be determined. From that time on, the science of chemistry grew as it never had grown before.

1. History of the Determination of Atomic Weights. — Dalton, you will remember, proposed his atomic theory early in the nineteenth century, and Avogadro's hypothesis followed shortly thereafter. The stage was set for the use of modern theory, but the great chemists of that day refused to play their parts. Berzelius would not accept Avogadro's hypothesis with its implication that atoms of the same kind are combined in the molecules of the common elementary gases. The science had to wait for a Cannizzaro and a more receptive generation of chemists.

Nevertheless, Berzelius was one of the first to try to determine atomic weights. Without the principle of Avogadro to guide him, he could do little but determine equivalent weights and trust to luck that these were true atomic weights. This we now know would be the case only if the element were univalent (21-10). As early as 1810, he published determinations of equivalent weights, and after a little over 10 years' work he had determinated these weights for no less than 50 elements by the preparation, purification, and analysis of no less than 2,000 of their compounds. When we stop to consider that analytical methods were then not only crude but more often nonexistent, we can realize in some measure the magnitude of his task. By making certain assumptions but by spurning the use of Avogadro's hypothesis, he converted his combining weights into atomic weights. A comparison of some of the atomic weights that he published in 1826 with those of the International Table of Atomic Weights of 1944 will reveal the surprising accuracy of his results:

TABLE 19

Element	Atomic weight	
	Berzelius, 1826	International Table, 1944
Chlorine	35.41	35.457
Lead	207.12	207.21
Nitrogen	14.05	14.008
Potassium	39.19	39.096
Silver	108.12	107.880
Sulfur	32.18	32.06

The pioneer work of Berzelius was carried on by Jean Servais Stas (1813–1891), a Belgian, and still later by Theodore William Richards (1868–1928) of Harvard. The latter determined the atomic weights of no less than 22 elements with unequaled precision. He was the first American to receive the Nobel Prize in chemistry (1914).

A table of atomic weights may be accepted gratefully with bows to the men whose patient, painstaking work made it possible and may then be used as the basis of all chemical calculations. The majority of chemists, who believed that they had no time to inquire into the hidden significance of such a table, made their bows and went to work. A few, however, paused to consider its possible implications.

2. The Discovery of the Periodic Law.—In 1866, John Newlands read a paper before the Chemical Society in which he reported a remarkable discovery. By arranging the then known elements in the order of their increasing atomic weights a regular, periodic recurrence of elements of similar properties was revealed. By following his example, this will become apparent. Omitting hydrogen, which should head the list because its atomic weight is the lowest but whose properties are unique, we proceed as shown in Table 20.

TABLE 20

Group	Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
I	Lithium	7	Sodium	23	Potassium	39
II	Beryllium	9	Magnesium	24	Calcium	40
III	Boron	11	Aluminum	27		
IV	Carbon	12	Silicon	28		
V	Nitrogen	14	Phosphorus	31		
VI	Oxygen	16	Sulfur	32		
VII	Fluorine	19	Chlorine	35		

The first seven elements are arranged in a vertical column, or period. The period starts with an active metal lithium and ends with the very active halogen fluorine. *The elements of the second column*, starting with sodium and ending with chlorine, *resemble the corresponding elements in the first column.* The first two elements in the third column fit nicely into their proper places. Beyond calcium, the relationships are more complicated and Newlands was not too successful in clarifying them. However, in the first part of his table, each element resembles the eighth element before it and the eighth element that follows. So close was the resemblance to the musical scale that it was referred to as the law of octaves. Unfortunately insofar as this simile was concerned, the subsequent discovery of the group of inert gases added an element to the end of each period. We find, then, a curious periodicity, or repetition, instead of a continuous progression of properties, which may be stated as the *periodic law:* the properties of the elements are a periodic function of their atomic weights.

One might well imagine the applause that greeted this revealing announcement by Newlands. As a matter of fact, far from applauding, the distinguished members of the society stooped to ridicule. A certain member, whose accomplishments have long since been forgotten, asked facetiously if Newlands had considered arranging the elements alphabetically. His paper was refused publication by the society, although his idea had been published earlier in the *Chemical News*. He retired from the thin ice of speculation to the comparative security of the sugar industry. In 1882, however, the Royal Society awarded him the Davy medal for his discovery of the periodicity of the elements.

3. Dimitri Ivanowitch Mendeléeff.—Although Newlands, perhaps largely because of his youth, failed to convince his colleagues, the Russian Mendeléeff did. A man of striking appearance whose face was endowed with magnificent hirsute appendages, his presentation of the periodicity of the elements was masterful and captured the imagination. In 1869, Mendeléeff published a preliminary paper on the classification of the elements arrived at in a way similar to that of Newlands of whose work he had no knowledge. This paper was followed by a second in 1871 in which the validity and value of his classification was so strongly pointed out that it received immediately, as it deserved, the serious attention of chemists all over the world. In this paper he made the daring prediction that in the course of time three elements would be discovered and proceeded to predict their atomic weights and properties. Before 25 years had elapsed, these elements were discovered, and their properties proved to be those which he had predicted. How closely Mendeléeff's predictions approximated those of one of the elements may be seen in Table 21.

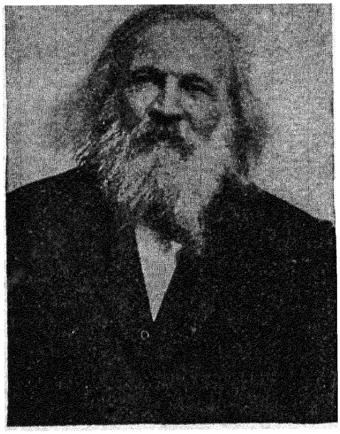

FIG. 75.—Dimitri Ivanowitch Mendeléeff. (*Courtesy of Journal of Chemical Education.*)

TABLE 21

Properties	Ekasilicon, predicted by Mendeléeff in 1879	Germanium, discovered by Winkler in 1887
Atomic weight	72	72.6
Density of the metal	5.5	5.47
Formula of oxide	EkO_2	GeO_2
Formula of chloride	$EkCl_4$	$GeCl_4$
Boiling point of chloride	Below 100°C.	86°C.

4. The Periodic Table.—Table 22 is a modern periodic table with all the now known elements arranged as in Mendeléeff's table. In this form, each group of elements of similar properties is in the same vertical column. To the eight groups of his table has been added Group 0 which contains the inert gases. With the exception of hydrogen, each of the first 20 elements up to and including calcium fit logically in their places. But scandium, the element that follows calcium, does not fall naturally under aluminum. Not until the thirty-first element gallium is reached does an element appear that resembles aluminum closely enough to be placed without reservations in the same group. Indeed none of the elements from scandium (21) to zinc (30) closely resemble elements of lower atomic weight in the table. Further, in the middle of this sequence are found three elements, iron (26), cobalt (27), and nickel (28), which resemble each other so closely that Mendeléeff placed them together in a new group VIII. From gallium (31) on, the elements again resemble those of lower atomic weights in the upper part of the table. Thus germanium resembles silicon; arsenic, phosphorus; selenium, sulfur; and bromine, chlorine.

To overcome these perplexing difficulties, Mendeléeff divided each of his original groups into two subgroups beyond calcium in the table. Members of one subgroup appear at the left and of the other at the right of their boxes. Thus in Group I the alkali metals lithium, sodium, potassium, rubidium, and cesium form one subgroup and copper, silver, and gold, the other. One has to remember only that the alkali metals are the most active of all the metals whereas copper, silver, and gold are at the bottom of the electromotive series to realize that these two subgroups of Group I are strange companions.

5. The Extended Table.—Within recent years the extended periodic table (Table 23) has been regarded with increasing favor. This is the form in which we shall use the periodic table. Each series of elements, *i.e.*, each horizontal row, starts with an alkali metal and ends with an inert gas. Subgroups are avoided by starting new groups, numbered with Arabic numerals, with the element scandium. Roman numerals are retained for the elements which resemble those near the top of the table.

The first period is made up of two elements hydrogen and helium. Hydrogen's unique properties, which will be explained

TABLE 22.—THE PERIODIC TABLE
(Based on the classification of Mendeléeff)

	Group									
	0	I	II	III	IV	V	VI	VII	VIII		
1		1 H 1.0080									
2	2 He 4.003	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.0000	9 F 19.00			
3	10 Ne 20.183	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457			
4	18 A 39.944	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69
5		29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916			
6	36 Kr 83.7	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43 Ma ?	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
7		47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92			
8	54 Xe 131.3	55 Cs 132.91	56 Ba 137.36	57–71 Rare Earths	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23
9		79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po 210?	85			
10	86 Rn 222	87	88 Ra 226.05	89 Ac 230?	90 Th 232.12	91 Pa 231	92 U 238.07				

The Rare Earths

57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il ?	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 164.94
				68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99			

TABLE 23.—THE PERIODIC TABLE OF THE ELEMENTS

Atomic numbers in italic

Atomic weights in roman

	Groups																	
	I	II	3	4	5	6	7	8			1	2	III	IV	V	VI	VII	0
	Valences																	
	+1	+2	+3	Variable									+3	−4 +4	−3 +5	−2 +6	−1 +7	0
Periods 1	*1* H 1.0080																	*2* He 4.003
2	*3* Li 6.940	*4* Be 9.02											*5* B 10.82	*6* C 12.010	*7* N 14.008	*8* O 16.0000	*9* F 19.00	*10* Ne 20.183
3	*11* Na 22.997	*12* Mg 24.32											*13* Al 26.97	*14* Si 28.06	*15* P 30.98	*16* S 32.06	*17* Cl 35.457	*18* A 39.944
4	*19* K 39.096	*20* Ca 40.08	*21* Sc 45.10	*22* Ti 47.90	*23* V 50.95	*24* Cr 52.01	*25* Mn 54.93	*26* Fe 55.85	*27* Co 58.94	*28* Ni 58.69	*29* Cu 63.57	*30* Zn 65.38	*31* Ga 69.72	*32* Ge 72.60	*33* As 74.91	*34* Se 78.96	*35* Br 79.916	*36* Kr 83.7
5	*37* Rb 85.48	*38* Sr 87.63	*39* Y 88.92	*40* Zr 91.22	*41* Cb 92.91	*42* Mo 95.95	*43* Ma	*44* Ru 101.7	*45* Rh 102.91	*46* Pd 106.7	*47* Ag 107.880	*48* Cd 112.41	*49* In 114.76	*50* Sn 118.70	*51* Sb 121.76	*52* Te 127.61	*53* I 126.92	*54* Xe 131.3
6	*55* Cs 132.91	*56* Ba 137.36	*57* La 138.92 *58 to 71* rare earths	*72* Hf 178.6	*73* Ta 180.88	*74* W 183.92	*75* Re 186.31	*76* Os 190.2	*77* Ir 193.1	*78* Pt 195.23	*79* Au 197.2	*80* Hg 200.61	*81* Tl 204.39	*82* Pb 207.21	*83* Bi 209.00	*84* Po	*85*	*86* Rn 222
7	*87*	*88* Ra 226.05	*89* Ac	*90* Th 232.12	*91* Pa 231	*92* U 238.07												

Rare earths

58 Ce 140.13	*59* Pr 140.92	*60* Nd 144.27	*61* Il	*62* Sm 150.43	*63* Eu 152.0	*64* Gd 156.9	*65* Tb 159.2	*66* Dy 162.46	*67* Ho 164.94	*68* Er 167.2	*69* Tm 169.4	*70* Yb 173.04	*71* Lu 174.99

later in terms of the structure of its atom, are somewhat like those of the alkali metals and to a lesser extent like those of the halogens. Its valence number of +1 in its compounds with nonmetals is common to all the alkali metals; but in metallic hydrides, *e.g.*, CaH_2, it resembles the halogens in that its valence number is −1. It is placed in Group I with the alkali metals with strong reservations. Helium, on the other hand, clearly belongs in Group 0 as a typical inert gas.

The second and third periods each contain 8 elements which are placed in the Roman-numeral groups. The fourth and fifth periods are composed of 18 elements. These include sequences of elements, from scandium to zinc in the fourth and from yttrium to cadmium in the fifth, which resemble none of the elements in the Roman-numeral groups closely. In the extended table, these elements are placed in the Arabic-numeral groups. The sixth period contains 32 elements. In the box of this period and of Group 3 there appears a group of 15 elements whose atomic weights follow in sequence and whose properties are so similar that their separation from one another is extremely difficult. These are the rare-earth metals. To save space they appear under the table. The seventh period is incomplete and ends with the ninety-second element, of greatest atomic weight, uranium.

6. Usefulness of the Periodic Table.—From the foregoing description of the complexities of the table, one might at first sight assume that it could not be very useful. Such, however, is decidely not the case. In the first place, the Roman-numeral groups include most of the common elements, and fortunately the properties of these elements are relatively simple. Let us consider the information contained in the table about the elements in these groups and omit consideration for the time being of the elements in the Arabic-numbered groups.

Each period starts with an alkali metal the valence of which is +1. These metals are very active chemically. The next element in Group II is a slightly less active alkaline-earth metal with a valence of +2. The third element is a still less active trivalent metal. In Group, IV nonmetallic properties appear; the maximum positive valence number is 4; and the valence number of −4, the first negative valence, appears. In Group V, the nonmetallic properties are more pronounced and the valence numbers are +5 and −3. In Group VI, we find yet more active nonmetals with valence numbers of +6 or −2. Group VII belongs to the halogens which we know are the most active nonmetals. Their maximum valence number is +7 and their minimum, −1.

To summarize, as one goes *from left to right across a period the metallic character decreases and the nonmetallic properties increase.* We find the metals in the lower numbered groups and the nonmetals in those of higher number. The value for the positive valence number is the same as the group number. The negative valence number, which nonmetals alone possess, is equal numerically to the difference between 8 and the group number.

We have learned in the case of the halogens that the most active member of this group is fluorine, the element of lowest atomic weight. In general, *as the atomic weight increases in a group of nonmetals, the activity decreases. The reverse is true of the metals.* Cesium is the most active alkali metal and is at the bottom of the group. In Group IV in the middle of the Roman-numeral groups, the nonmetals carbon and silicon are found at the top and the metals tin and lead, at the bottom. As a matter of fact, the transition from a typical metal to a typical nonmetal is not abrupt. The elements near the middle of the table have both metallic and nonmetallic properties. We have been purposely rather vague as to what constitutes a metal or a nonmetal. Nor do we propose to go into detail here. Later, after we have studied the theory of ionization, the difference will be discussed (41-11).

The elements in the Arabic-numbered groups are, in general, metals. Most of these form several series of compounds corresponding to a number of different valences. In their lower valences they act as metals, but as the valence increases they become predominently nonmetallic. Consequently, their chemical properties are more complex than those of the Roman-numeral groups.

7. Undiscovered Elements.—We have as yet left unexplained the method by which Mendeléeff was able to predict the properties of elements yet to be discovered. We hope his method has been surmised by the reader. In 1871, the elements scandium, gallium, and germanium had not been discovered. Hence in constructing the table Mendeléeff found that titanium followed calcium. This would place titanium in Group III, whereas its properties indicate clearly that it belongs in Group IV. This would leave a space in Group III which indicated to Mendeléeff the existence of an unknown element. Similarly, spaces appeared in his original table which gallium and germanium now occupy.

The properties of an element can be predicted with some degree of accuracy from its position in the table. Hence Mendeléeff was able to foretell the properties of these unknown elements. He called the element, which was to occupy the position in Group III, series 4 of his table, ekaboron. Its atomic weight must lie between those of calcium (40.07) and titanium (47.90). By taking their average, or ½ (40 + 48), he was able to predict an atomic weight of 44. After scandium had been discovered, a determination of its atomic weight gave the value 45.10, so that his prediction was a fair approximation. Knowing the characteristic valence of Group III to be 3, Mendeléeff had no trouble in deriving the formulas of the compounds that this element would form with other elements. The formulas for its chloride and oxide would be $EkCl_3$ and Ek_2O_3, respectively.

In 1938, four spaces remained empty in the periodic table. If we number the elements consecutively from hydrogen as number 1 to uranium, number 92, these spaces correspond to elements 43, 61, 85, and 87. The discovery of elements 43, masurium, and 61, illinium, had been reported, but sufficiently convincing confirmation of their discovery was lacking. The last of the alkali metals of Group I, element number 87, was detected by Mlle. Peréy and its discovery reported in 1939. Element 85, a halogen, was prepared by a transmutation (29-11) of bismuth and its properties determined. It has not as yet been discovered in nature. Element 43 in Group 7 was made artificially by the transmutation of molybdenum. Finally element 61, a rare earth, was formed by the transmutation of neodymium.

8. The Inconsistencies of the Periodic Table.—One might suppose from the preceding that the periodic table presents all the facts of chemistry in a convenient, concentrated form. Unfortunately such is not the case.

An inconsistency appears in the table where the order of the atomic weights does not place elements in their proper places. Thus iodine has a lower atomic weight than tellurium, and yet iodine belongs in Group VII with the other halogens and tellurium in Group VI. Similarly, argon and potassium, and cobalt and nickel are reversed. At the time the table was first proposed, the atomic weights of indium, uranium, cerium, yttrium, and others did not place them properly. Mendeléeff suggested that their atomic weights had been determined incorrectly, and so later and more accurate determinations proved. Yet there remain the three pairs, argon and potassium, iodine and tellurium, and nickel and cobalt, whose atomic weights have been determined with the greatest accuracy, curiously reversed. Thus in these cases the fundamental principle by which the elements were arranged in the table had to be sacrificed to avoid obvious misplacements. This suggests that there may be some property of the atoms more fundamental then their weight. We shall see later what this property is.

9. The Interrelatedness of the Atoms.—One cannot study the periodic table of the elements without becoming impressed by a sense of the interrelatedness of the atoms. The fact that the elements within a group resemble one another is a clear indication that their atoms have similar structures. Otherwise the periodicity of the elements must be considered as pure chance. When one calculates the probability of such a coincidence, it is found to be so inconceivably small as to be practically impossible. For atoms to have similar structures implies the existence of structure units. Inescapably the conclusion must be drawn that the atoms are not the ultimate particles of matter; that there exist subatomic particles of which the various atoms are built. As we proceed more deeply into the structure of matter, a majestic simplification results. There are one-half million different molecules made up of the atoms of the 92 elements, and each of these in turn is made up of one or, at the most, a few fundamental particles.

EXERCISES

1. What is the basis of the arrangement of the elements in the periodic table?

2. How do the properties of the elements in a period vary as the atomic weight increases? In a group?

3. An element of atomic weight 224 is discovered. Describe its properties.

4. Explain the need for new groups beginning with the element scandium.

5. What inconsistencies are present in the arrangement of the elements in the table?

6. How did the discovery of the periodic law lead to the discovery of elements?

7. What valences are characteristic of each group in the table?

8. Write the formulas for the following compounds: indium chloride, cesium nitrate, an oxide of tellurium, radium phosphate, antimonic acid.

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CHAPTER TWENTY-FIVE

SUBATOMIC PARTICLES

Our knowledge of the molecular structure of the states of matter we owe mainly to the physicist, whereas the chemist has revealed the atomic nature of molecular structure. Undoubtedly the work of Mendeléeff, a chemist, pointed the way to the structure of the atom. When the particles that make up this structure were discovered, it was only natural for chemists to consider them as their own. But, fortunately for the chemist, these particles were discovered by physicists, with the result that both sciences have gained by joining forces in the study of the structure of atoms.

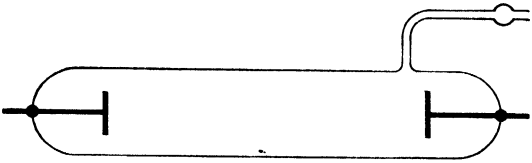

FIG. 76.—Cathode-ray tube.

1. Cathode Rays.—Electrons were the first of the subatomic particles to be discovered. They are to be found in every atom, but atoms had been studied by chemists for nearly a century without suspecting their existence. Only when they are momentarily freed from the atoms of matter can they be studied and their properties ascertained. In every electrical discharge, from the tiny spark that jumps across the terminals of a spark plug in an engine to the flash of lightning, free electrons are present. However, in the tiny spark on the one hand and in the majestic lightning, on the other they are difficult to study.

At atmospheric pressure, air and gases in general are poor conductors; at high voltages their conductivity is increased as the pressure is lowered until it reaches a maximum, at lower pressures than which the conductivity again decreases. The apparatus for carrying out investigations of the conductivity of gases at low pressures is very simple. It (Fig. 76) consists of a tube into which two metallic electrodes are sealed and which is provided with a side arm to be connected to a vacuum pump. If the electrodes are connected to the secondary of a suitable induction coil, discharge will take place almost as soon as the pump is started. At first, it consists of a crackling discharge along narrow, flickering lines between points on both electrodes; but, as the exhaustion proceeds, the discharge broadens until it fills the entire tube. A luminous glow covers the surface of the cathode, or negative electrode, about which is the so-called Crookes dark space. A luminous cylinder, called the positive column (Fig. 77), extends from the positive electrode, or anode, as far as the edge of the Faraday dark space. The positive column is usually broken up into alternate lighter and darker layers across the path of the discharge, which broaden as the degree of exhaustion increases.

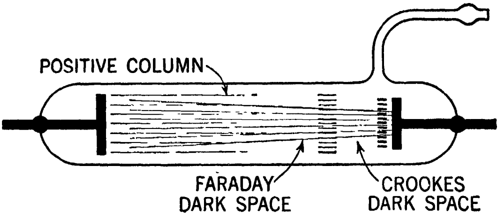

Fig. 77.—The discharge in a cathode-ray tube.

If the pressure is made still lower, of the order of 0.001 mm., the positive column becomes faint and inconspicuous but the Crookes dark space increases in volume until it occupies most of the space within the tube. The glass wall of the tube opposite the cathode glows with a greenish fluorescence. Certain minerals, placed within the Crookes dark space, fluoresce with a color characteristic of the minerals. The dark space is traversed by a discharge known as the cathode rays which stream out at right angles to the surface of the cathode regardless of the position of the anode. These rays can be faintly discerned as streaks of bluish light as they cross the Crookes dark space. Whenever they impinge upon the glass, the greenish fluorescence, noted above, is produced. These rays were first discovered by Plücker in 1859 and their properties described some years later by Hittorf. The discovery of the nature of these cathode rays gave to science its first insight into the nature of the structure of the atom.

2. The Nature of Cathode Rays.—The explanation of the nature of these rays was not immediately obvious. At first sight they seemed to be light. But snap judgments are never safe in science. The light of the rays might be a secondary effect caused by some more fundamental phenomenon. In 1869, Hittorf placed obstacles between the cathode, the source of the rays, and the glass and observed a sharp shadow of the obstacles on the glass. Six years later Goldstein confirmed these results and concluded that these rays were light. However, in 1879 Sir William Crookes passed cathode rays between the poles of an electromagnet and observed that their former straight-line path was bent into an arc. To a physicist this was astounding and could mean but one thing. These rays are material and are electrically charged. Light never behaves this way. Crookes was badly puzzled. He thought he had found a fourth state of matter and suggested that cathode rays were radiant matter.

3. The Work of Sir J. J. Thomson.—The stage was set for the epoch-making research of Sir J. J. Thomson, director of the Cavendish Laboratory of Experimental Physics at Cambridge. At the age of twenty-eight, successor to Clerk Maxwell and Rayleigh, he was to gather together a group of brilliant young physicists who were to reveal the secrets of the atom under his direction. He discovered that cathode rays can be deflected in an electrical as well as a magnetic field and that the rays are bent toward the positively charged plate. Hence they must be negatively charged. Then in April, 1897, he announced to the Royal Society the results of 20 years of work. He postulated that cathode rays are composed of particles of negative electricity much lighter than the hydrogen atom. He had discovered the existence of a particle of matter lighter than the lightest of Dalton's atoms.

By measuring the deviations produced by magnetic and electrical fields of known strength, it was possible for him to calculate not only the velocity at which these particles were moving, but also the ratio, e/m of their charge e to their mass m. The ratio found was 1.768×10^7 electromagnetic units per gram.

The value for e/m obtained was independent of the metal of which the cathode was made and of the nature of the residuum of gas left within the tube. This indicated that the nature of the corpuscles from various metallic electrodes was the same. It was also discovered by Rutherford, a student of Thomson, that the *e/m* for the beta particles, emitted by radioactive elements, was identical with that of the corpuscles of the cathode rays. Corpuscles of the same kind were found to be emitted from heated metallic filaments and metallic oxides and when metals were illuminated with *x*-rays. In every case, the measured *e/m* was the same within the limits of experimental error as is shown in Table 24. Strong evidence had begun to accumulate, therefore, that these corpuscles are to be found in all matter and that, whatever their source, they are identical. Dr. G. Johnstone Stoney, as early as 1891, suggested the name "electron" for the "natural unit of electricity." This was, of course, before the discovery of the corpuscles in cathode rays. This term was adopted as a logical one for these corpuscles.

TABLE 24.—THE RATIO *e/m* DETERMINED BY VARIOUS METHODS

Observer	Source of corpuscles	*e/m*, e.m.u./g.
Classen	Cathode rays	1.774×10^7
Classen	Hot calcium oxide	1.776×10^7
Woltz	β-Rays from radium	1.767×10^7

The ratio of the charge to the mass *e/m* of the electron, although it does not tell us the exact value for either the charge or the mass, is nevertheless significant. The same ratio had been determined for various other charged particles. The smallest of these is the hydrogen ion, a positively charged hydrogen atom that is found in water solutions of all acids. Its *e/m* was found to be 9,649.4 electromagnetic units per gram which is some 1,830 times smaller than 1.77×10^7, the ratio *e/m* of the electron. Two inferences may be made from this comparison: either the charge on an electron is some 1,830 times greater than that of the hydrogen ion, both having the same weight, or both carry the same charge but the electron is some 1,830 times lighter than the hydrogen ion. If the latter alternative were true, then a particle of matter lighter than the lightest atom had been discovered. The only way to find out which of the two was correct was to determine the mass of the electron directly or to determine its charge and by substituting the latter for *e* in the ratio *e/m* calculate the mass.

4. The Determination of the Charge of the Electron.—The charge of an electron was first determined by Townsend in 1897 and independently by C. T. R. Wilson, both of the Cavendish Laboratory at Cambridge, of which Thomson was the director. The most accurate determinations of the electron's charge have been carried out by Robert Andrews Millikan. For this work, which was started at the University of Chicago in 1909, he received the Nobel Prize in physics. Millikan calculated the amount of charge on electrically charged oil droplets from data obtained by measuring their rate of fall due to gravity and their rate of rise between electrically charged brass plates. The charge on each droplet must be equal either to that of an electron or to some integer multiple of it. If, for example, the charge on the droplet is made up of nine electrons, it must obviously be nine times greater than the charge on a single electron. By taking the greatest common factor of the charges on many oil droplets, a value for the charge on a single electron can be obtained. This might, of course, be the charge on two or even three electrons, provided no droplets with charges of less than two or three electrons were studied, but the approximate value for e, obtained by other methods, agrees with Millikan's value. His most accurate value for the charge of an electron is equal to 4.774×10^{-10} electrostatic unit.

An extremely significant feature of these experiments was that although the charge on a droplet might be either positive or negative yet, regardless of its sign, it was in magnitude an integer multiple of the charge of an electron. There exist, therefore, in all probability positive as well as negative subatomic particles. Of these positive particles, or protons as they are sometimes called, more will be said later.

5. The Calculation of the Mass of the Electron.—We have learned that e/m, the ratio of the charge to the mass of the electron, is equal to 1.768×10^7 electromagnetic units per gram. Since e has now been determined, the mass of the electron m can be calculated:

$$\frac{e}{m} = 1.768 \times 10^7 \text{ e.m.u./g.} = 5.304 \times 10^{17} \text{ e.s.u./g.}$$

$$e = 4.774 \times 10^{-10} \text{ e.s.u.}$$

Hence

$$\frac{4.774 \times 10^{-10} \text{ e.s.u.}}{m} = 5.403 \times 10^{17} \text{ e.s.u./g.}$$

$$m = \frac{4.774 \times 10^{-10}}{5.304 \times 10^{17}} = 0.9001 \times 10^{-27}\text{ g.}$$
$$m = 9.001 \times 10^{-28}\text{ g.}$$

The mass of the hydrogen atom, 1.650×10^{-24} g., was the smallest mass known prior to the discovery of the electron. The electron is 1,833 times lighter. A thousand million million million million electrons weigh a little more than a gram.

Making certain assumptions, it has been possible to estimate the radius of an electron as 2×10^{-13} cm. This is about 50,000 times smaller than the radius of an atom. This figure is based on the assumption that an electron is spherical in shape. Of the existence of electrons in all matter, there can be no longer any doubt. The electrical conductivity of gases, solutions, and metals, the generation of *x*-rays, various optical phenomena, and many other physical and chemical phenomena point to their existence.

6. Protons.—The discovery of electrons in the cathode-ray tube naturally suggested a search for rays emanating from the anode which might be composed of positively charged corpuscles. At moderately low pressures (of the order of 0.1 mm.) in the Crookes tube a luminous sheath, violet in color, surrounds the cathode but does not touch it. As the pressure is reduced, its inner surface moves away from the cathode, until at fairly low pressures a distance of some 2 cm. intervenes between the cathode and the inner surface of the sheath of violet light. At the same time, orange-colored rays emanate from the inner surface of the sheath toward the cathode, and as they approach the latter, their luminosity becomes more intense. The fact that these rays originate in the sheath and move toward the cathode can be proved by interposing some object between the inner surface of the sheath and the cathode. A sharply defined shadow of the object will be thrown on the surface of the cathode. The fact that these rays moved toward the cathode suggested at once that they might consist of positively charged corpuscles similar in nature to the electrons but of opposite charge.

In 1886, Goldstein, a German physicist, using a cathode pierced by a cylindrical hole, or canal, succeeded in obtaining a pencil of these positive rays behind the cathode (Fig. 78). The rays, passing through the canal, can travel through several centimeters into the space behind the cathode. Because of this method of isolation, the rays became known as canal rays. They were investigated in the same way as were the cathode rays, *i.e.*, by the method of deflection by means of magnetic and electrical fields. The velocity of the particles, of which canal rays are composed, is much less than that of the electrons of the cathode rays. The ratio of their charge to their mass e/m is much smaller and varies with the nature of the residual gas left in the tube. When the tube contains hydrogen, the particles bear positive charges, each of which is equal but of opposite sign to that of an electron. The mass of each, however, is that of the hydrogen atom. In the cases of other gases, the particles, of which the canal rays are composed, are the respective atoms of these gases bearing one or more unit positive charges. In no case has it been possible to isolate a unit-positive charge on any particle of lesser mass than that of the hydrogen atom in such tubes. This is strong evidence that the unit-positive charge, the proton, unlike the electron, is always bound up on the atoms of the elements and can never appear alone. There is strong evidence that the neutral hydrogen atom is composed of one proton and one electron only. Hence the proton may be considered as a hydrogen atom that has been deprived of its electron.

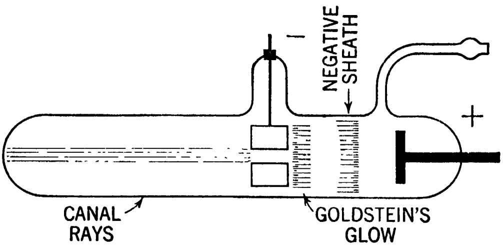

FIG. 78. --Canal rays.

7. The Electron and Proton Compared.—Let us now summarize what has been learned of the electron and the proton. The electron is a unit charge of negative electricity (4.774×10^{-10} e.s.u.), having a mass (9.001×10^{-28} g.) which is some 1,800 times lighter than that of the hydrogen atom. Its radius is of the order of 2×10^{-13} cm., or about 50,000 times shorter than that of the smallest (hydrogen) atom. The proton consists of a unit charge of positive electricity equal in amount to the charge on an electron but of opposite sign. Since the hydrogen atom consists of one electron and of one proton only, it is apparent that the mass of the proton is practically equal to that of the hydrogen atom and, therefore, about 1,800 times the mass of the electron. It is probable that the radius of the proton is not greater than 10^{-16} cm., which is about 1,800 times shorter than that of the electron. The proton is, therefore, 1,800 times heavier but 1,800 smaller than the electron.

8. The Neutron and the Positron.—Prior to 1932, physicists and chemists were agreed that the ultimate particles, of which the atoms of the elements are composed, were two in number—the electron and the proton. Then the discovery of the neutron was announced by Chadwick of the Cavendish Laboratory of Cambridge. It was found among other products when certain atoms of low atomic weight are bombarded by alpha particles (29-7). The neutron, as its name implies, is electrically neutral, which accounts for the delay in its discovery since it is unaffected by electrical and magnetic fields. Hence the determination of its mass has proved difficult. It now appears to have a mass approximately equal to that of the proton.

The positron was discovered by C. D. Anderson of the California Institute of Technology. The discovery was made quite by accident during the progress of a research on cosmic rays. A positron wrote the history of its movements in a magnetic field including its passage through a sheet of lead 6 mm. thick. A photograph of the path that it followed was made by an ingenious method previously developed by C. T. R. Wilson. A subatomic particle moving at high speed through a gas, actually passes through those atoms of the gas which are in its path. In so doing, it frequently jars an electron loose from a neutral atom thus leaving charged particles, or ions, in its wake. If the gas is supersaturated with water vapor, these ions act as centers upon which water molecules condense as fine droplets. The path of the subatomic particle is thus defined by the line of fog droplets that it leaves behind.

In the Wilson cloud chamber, the fog track of the first positron known to man was photographed. The curvature of its path in the magnetic field and the spacing of the fog droplets indicated that it was a positively charged particle of the same mass and amount of charge as that of the negative electron. Since this historic photograph (Fig. 79), many positrons have been detected among the products of transmutation (29-9).

The positron leads a transitory existence. Created from the energy of cosmic rays or from the protons within atoms under powerful bombardment, it is soon captured by a neutron with the formation of a proton, or it may join an electron in mutual suicide with the formation of energy from their mass. Because its independent existence is so short, it is of little importance in the study of atomic structure.

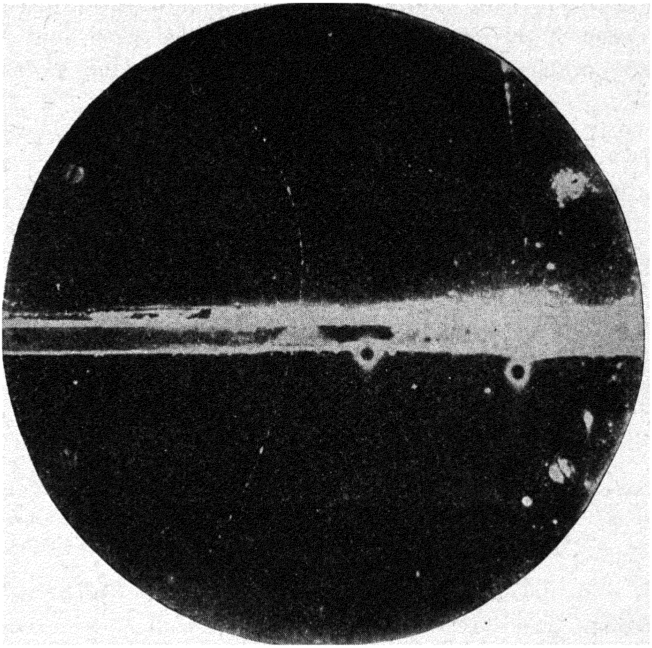

FIG. 79.—Track of a positron passing through a lead barrier and moving in a magnetic field. (*Courtesy of Dr. Carl D. Anderson.*)

9. The Work of Moseley.—In the trenches of Gallipoli in the summer of 1915, Moseley, one of the most brilliant of the younger British physicists, was shot and instantly killed. At the age of twenty-seven he had completed one of the most significant pieces of research of the last half century.

When a stream of cathode rays is allowed to fall upon some obstacle, which stops the electrons of the rays, there are generated x-rays of frequencies characteristic of the element of which the obstacle is composed. Moseley used obstacles, or anticathodes, of most of the known elements and measured the frequencies (26-1) of the x-rays emitted in each case. If the elements are arranged in the order of increasing frequency of the characteristic x-rays, which they emit, they form a series in which the order of the elements is the same as that of their increasing atomic weights. Moseley assigned an *atomic number* to each of the known elements which indicates the place of the element in this series. These atomic numbers are given in the table on the inside of the rear cover of this text together with the corresponding atomic weights. The order of the atomic weights is identical with that of the atomic numbers except in three cases: argon and potassium, cobalt and nickel, and tellurium and iodine in which cases the order is reversed. It will be remembered that these exceptions gave trouble in connection with the problem of finding proper places for the elements involved in the periodic table (24-8). The order of their atomic weights had to be reversed to fit them into the proper groups of the table. The atomic number order, however, fits each element into its proper place. Figure 80 is derived from a series of photographs of corresponding lines in the spectra of a series of elements from atomic numbers 33 to 38. The spectrum of krypton, a gas of atomic number 36, is not included, for obviously no anticathode could be made of it. The position of the line along the horizontal axis of the photograph corresponds to its frequency. Moseley found that the square root of the frequency of a characteristic line in the spectra of such a series of elements varies directly as the atomic numbers of the

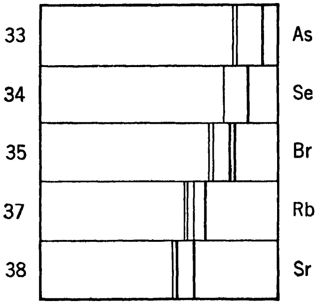

Fig. 80.—X-ray spectra.

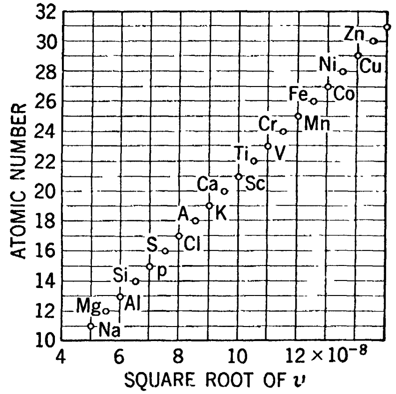

Fig. 81.—The atomic numbers as a function of the x-ray frequency.

corresponding elements. Thus by plotting the square root of these frequencies against the atomic numbers of the corresponding elements, a nearly straight line is obtained indicating a direct proportionality (Fig. 81).

The significance of Moseley's atomic numbers lies in the fact that the frequency of light emitted by the atoms of a given element is determined by the structure of these atoms, *i.e.*, by the arrangement and number of the electrons and protons of which each atom is composed. Hence the atomic number of an element must be connected in some way with the structure of its atoms. Even before Moseley's work a Dutch physicist, van den Broek, suggested that the number of electrons in the atom of an element was equal to its order number in the list of elements arranged according to atomic weight, the latter, of course, being equal to its atomic number. Later, owing to the work of Rutherford on the scattering of α-particles from radioactive elements and the development of the Bohr theory of atomic structure, it became apparent that *the atomic number of an element is equal to the number of positive charges on the nucleus of its atom and also to the number of electrons, which revolve about this nucleus* much as planets do about the sun.

10. Rutherford's Nuclear Atom.—In 1911, Rutherford demonstrated that *the positive electricity of an atom is concentrated in an exceedingly small nucleus at its center about which the electrons revolve.* His method of investigation involved the use of α-particles from a radioactive element. These particles are positively charged with an amount of electricity equal to the charge of two protons. Their mass is some four times that of a proton and hence about 7,300 times the mass of an electron. Such particles are emitted at tremendous velocities by the atoms of certain radioactive elements. A stream of these particles was passed through a small opening across a highly evacuated chamber and allowed to fall on a zinc sulfide screen. As this substance fluoresces under a bombardment of α-particles, a bright spot whose edges were sharply defined appeared on the screen. Then a thin metallic plate of known thickness was placed over the opening in such a way that the stream of α-particles had to pass through the plate in order to reach the screen. Owing to their high velocity and to the spaces between and within the atoms of the metal of which the plate was composed, the α-particles easily passed through. The spot of light on the zinc sulfide screen, however, was no longer sharply defined but had broadened out to fill a greater area on the screen. In some instances, momentary flashes of light could be detected at some distance from the main spot of light. This fact indicated that in passing through the metallic plate the α-particles had suffered numerous deflections from their original straight-line path. In fact, in some cases it was found that the deflection was so great than an occasional particle would emerge from the plate on the same side from which it had entered. By applying the theory of probability to analyze these deflections, it became apparent that the minor deflections were due to electrons in the atoms of the metal, but that the major deflections, which were in some instances so great as to reverse the direction of the particle, were due to the repellent effect of charges of positive electricity concentrated in tremendously small volumes. The latter were the nuclei of the metallic atoms.

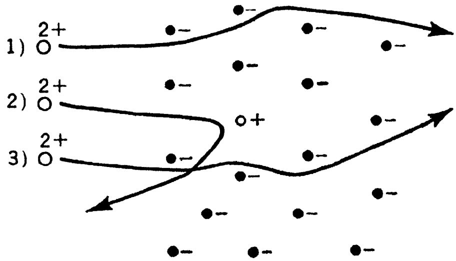

FIG. 82.—Paths of α-particles through an atom.

Figure 82 will help you to visualize the mechanism of these deflections. The first and third α-particles approach close enough to electrons to be attracted by them and hence suffer a change in path. The second α-particle is violently repelled when it approaches an atomic nucleus in its path and emerges on the same side of the metal plate. By continuing further experiments along these lines, Rutherford was able to show that the diameters of the atomic nuclei were of the order of 10^{-12} to 10^{-13} cm. He was also able to calculate the amount of positive charge on the nuclei of the metallic atoms by applying the theory of probability to the observed scattering of α-particles. In the case of every metal out of which the various plates that he used were composed, *the positive charge on the nucleus of its atom was found to be equal to its atomic number.*

11. The Number of Planetary Electrons.—Thus far we have learned that the number of unit-positive charges' on the nucleus of an atom is equal to its atomic number; that the nucleus is of exceedingly small volume; and that it acts as a kind of sun about which the planetary electrons revolve. Since the atoms of a chemically uncombined element are electrically neutral, *the number of these planetary electrons must be equal to the positive charge on the nucleus and hence also to the atomic number.*

12. The Helium Atom.—Helium is the second lightest atom and has, therefore, an atomic number of 2. This indicates that there are two planetary electrons in each of its atoms and that the charge on the nucleus is +2 or, in other words, a charge equal to that of two protons. If these were the only particles in the helium atom, it should be twice as heavy as the hydrogen atom. Actually, it is four times as heavy since its atomic weight is 4. This apparent paradox is resolved by the theory for which there is abundant evidence that the helium nucleus contains two neutrons in addition to the two protons. Since the mass of a neutron is very nearly the same as that of a proton, its atomic weight of 4 and its nuclear charge of +2 are explained.

13. The Composition of Atoms.—The atomic number of an element is symbolized by Z and its mass number, or its atomic weight to the nearest whole number, by M. In general *Z is equal to the number of planetary electrons in the neutral atom and to the number of protons in its nucleus. The number of neutrons in the nucleus is equal to the difference between the mass number and the atomic number* ($M - Z$). Thus the aluminum atom ($M = 27$, $Z = 13$) is composed of a nucleus of 13 protons and 14 neutrons and 13 planetary electrons.

14. The Arrangement of the Planetary Electrons.—Of the fact that the planetary electrons are arranged in some orderly fashion in the atom, there can be no doubt. But as to the nature of this arrangement there is little definite evidence, and what evidence there is may be interpreted in several different ways. Two methods of attacking this problem have been used. A method based on chemical evidence, developed mainly by G. N. Lewis and Irving Langmuir, has given a very plausible explanation of such phenomena as the periodicity of the elements and valence. The physicist, on the other hand, developed a theory of the arrangement of the planetary electrons based on such evidence as that of the nature of the light emitted by luminous atoms.

EXERCISES

1. Compare the properties of an electron with those of a proton.
2. What evidence leads to the assumption that the nucleus of the helium atom contains two neutrons?
3. What is the atomic number of an element?
4. What is the mass number?
5. If the atomic and mass numbers of an atom are known, how is it possible to determine of what subatomic particles it is composed?
6. What is the composition of an atom whose atomic and mass numbers are 9 and 19, respectively?
7. What is a positron, and why is it relatively unimportant in the study of atomic structure?

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CHAPTER TWENTY-SIX

ATOMIC STRUCTURE

In the last chapter we have learned that the atoms of the elements are composed of three subatomic particles: electrons, protons, and neutrons. The next step toward developing a satisfactory theory of the nature of the atoms is to endow them with a *structure* that will explain their properties. The chemist is interested primarily in why atoms combine, in the nature of valence, and in the forces that bind the atoms in their compounds. These forces determine in large measure the stability and the reactivity of compounds. When gases are heated sufficiently or are subjected to a discharge of electricity, they become luminous (25-1). The light they emit is a composite of colors, characteristic of the atoms of the elements in the gas. Indeed so characteristic are these colors that they may be used to identify the elements present. Now the study of light and of radiation, in general, falls within the province of physics. Further, when light is emitted by an atom, the process must in some way be connected with its structure. Hence it was only natural that physicists should have developed theories of atomic structure to explain how atoms emit radiation.

1. The Nature of Radiation.—Since many of you may not have studied physics, it will not be amiss to consider briefly the theories of the nature of radiation. The impressive factual evidence that light as it travels through space is a wave phenomenon need not be considered here. The wave motion, associated with the transmission of light, cannot be due to matter in motion since light travels easily through empty space. About 1865, James Clerk Maxwell predicted that light waves are electromagnetic in character, *i.e.*, they are associated with energy and not with matter. This prediction was demonstrated experimentally by the great German physicist Heinrich Hertz by measuring the speed at which electromagnetic impulses, generated by a discharge of electricity, are propagated through space. This proved to be identical with the velocity of light.

Let us learn how the properties of light may be interpreted in terms of a wave theory. Every wave is characterized by its length (Fig. 83), its amplitude, and the velocity with which it is propagated. The *wave-length* of a beam of visible light determines its *color*. In general, the wave-length is symbolized by the Greek letter lambda, λ. The *amplitude* determines its *intensity*, *i.e.*, its brightness. All forms of radiation travel through space at a velocity of 186,000 miles, or 2.9986×10^{10} cm./sec. This constant velocity is symbolized by the letter *c*. The *frequency* nu (ν) of a train of waves is defined as the number of waves that pass a given point in a second. It is a function of the wave-length and of the velocity of light. Since the velocity is the distance traveled in 1 sec. when it is divided by the wave-length, the number of waves per second is obtained.

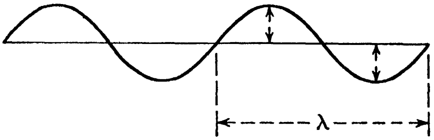


FIG. 83.—Wave-length and amplitude.

$$\nu = \frac{c}{\lambda}$$

The frequency is, therefore, inversely proportional to the wave-length.

2. Spectrum of Visible Light.—The wave-length of light of a certain color may be measured in several different ways, which need not be discussed here. It may then be expressed in any convenient length, such as centimeters or millimeters. One of the units commonly used is the angstrom unit, equal to 10^{-8} cm. The human eye is sensitive to light of a very narrow range of wave-lengths only, *viz.*, between 4,000 Å. (4×10^{-5} cm.) for the shortest wave of violet light to 8,000 Å. for the longest red light.

TABLE 25.—WAVE-LENGTHS OF THE COLORS OF THE VISIBLE SPECTRUM

Color	Wave-length, Å.	Color	Wave-length, Å.
Red	7,500–6,500	Green	5,750–4,900
Orange	6,500–5,900	Blue	4,900–4,550
Yellow	5,900–5,750	Violet	4,500–3,950

3. The Spectroscope.—When white light, a mixture of all colors, is passed through a prism, the various colors are spread out into a spectrum (Fig. 84). This is due to *refraction*, a change in the direction of the path of a beam of light when it leaves one medium and enters another. The angle through which the light is bent is greater, the shorter its wave-length. Thus red light is bent less than violet. A dispersion of the colors of white light by a prism results in a rainbowlike effect called a spectrum.

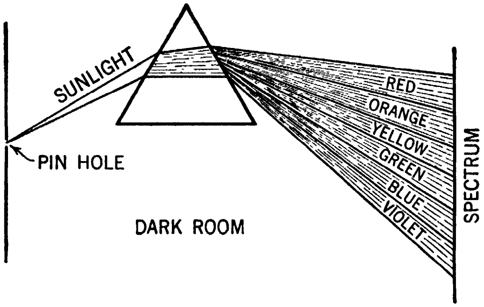


FIG. 84.—Dispersion of white light by a prism.

Bunsen and Kirchhoff in 1854 invented an instrument called the spectroscope which makes use of a prism to analyze the light given off by luminous gases. A diagram of this instrument is shown in Fig. 85. The collimator *C* consists of a slit at one end and a lens, for producing a parallel beam, at the other. After leaving the collimator, the light is analyzed into its colors by the prism *P*, and each color is then focused by means of a lens in the telescope *T*. Each color appears as an image of the slit against a dark background at the eyepiece. A scale, placed in the eyepiece above the bright colored lines, permits the observer to determine their wave-lengths. Since the atoms of a given element emit light of characteristic wave-lengths, its bright-line spectrum as seen in the spectroscope serves as a means for its identification.

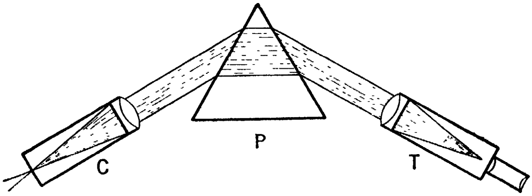


FIG. 85.—A spectroscope.

The spectrum of a gaseous element can be obtained most readily by passing a current of electricity at high voltage through a glass tube that contains the gas at low pressure. Such tubes have found extensive commercial application as letters in advertising signs. Tubes filled with neon glow with a brilliant red light.

4. The Complete Electromagnetic Spectrum.—To the great pioneers of the study of optics, Newton and Huygens, radiation consisted of the relatively insignificant band of wave-lengths that constitute visible light. Soon after the invention of photography, it was discovered that the photographic plate is affected by radiation of shorter wave-lengths than visible light. This radiation is called ultraviolet light. In 1895, Roentgen discovered that radiation of yet shorter wave-lengths is produced when high-speed electrons are suddenly stopped. These were later called *x*-rays. The gamma-rays, which are associated with radioactive disintegration (28-6), are of the shortest wave-lengths known (Fig. 86).

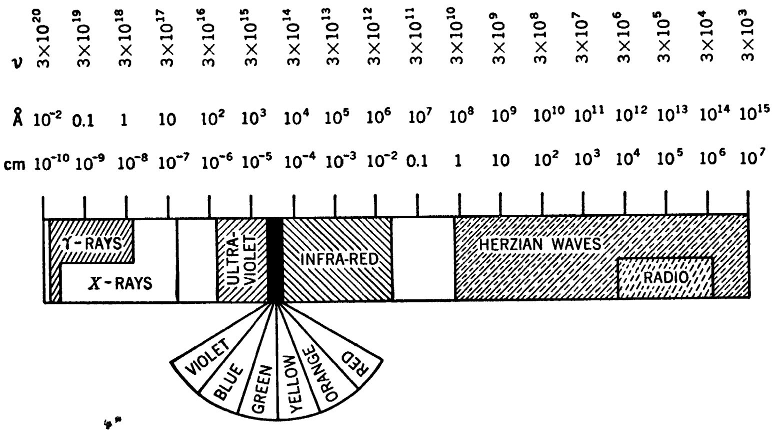


Fig. 86.—The electromagnetic spectrum.

Early in the study of optics, the infrared region of radiant heat waves was discovered. These are readily absorbed by matter and converted into molecular heat motion. They do not affect the ordinary photographic plate as might be expected, since the red rays of the visible spectrum can be used as a "safe" light when films are being developed. However, the emulsion of the photographic plate can be made sensitive to light in the red and infrared regions by means of certain dyes. These color sensitizers are of great help in airplane photography because the predominating colors of the ground are reds and browns. Beyond the infrared region and of yet greater wave-lengths are the Hertzian waves used in radio. These are the gigantic ocean rollers of the electromagnetic waves, some of which are hundreds of meters in length.

5. The Hydrogen Spectrum.—The bright-line spectrum of the element hydrogen is, as one might expect, the simplest of all the elements. It can easily be studied by observing in a spectroscope the light emitted by the luminous gas. It consists of three lines: red, light blue, and violet. When the spectrum of hydrogen is photographed with plates that have been made sensitive to infrared light, many other bright lines in the infrared and ultraviolet are discovered. The complete hydrogen spectrum is shown in Fig. 87. The lines appear to be arranged in three separate groups, or series, in each of which the lines come closer together as each series approaches a limiting wave-length, shown in each case by a dotted line in the figure.

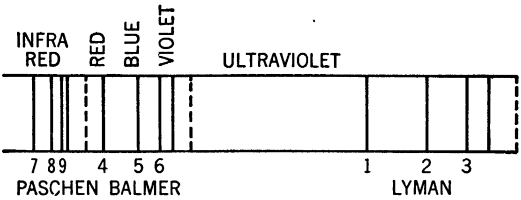


Fig. 87.—The hydrogen spectrum.

The various wave-lengths of light corresponding to the bright lines of the hydrogen spectrum are produced by some mechanism associated with the structure of the hydrogen atom. These lines may be compared with a chord of music sounded by some hidden musical instrument. Could a physicist hope to describe the structure of such an instrument by analyzing the frequencies of the sound waves that it sends forth? Has it been possible for physicists to construct a thought model of the hydrogen atom by analyzing the frequencies of light that it emits? One of the major triumphs of modern physics has made possible an affirmative answer to this question.

The single electron in the hydrogen atom cannot occupy a fixed position. Remember the nucleus—in this case a single proton—is positively charged. The Coulomb force of attraction between the electron and the proton would compel the electron and the proton to come together and be annihilated in a burst of energy. An electron, which rotates about the nucleus as the earth rotates about the sun, is a much more plausible system, for the centrifugal force of its orbital motion would balance the force of attraction of the nucleus. However, according to the classical theory of electrodynamics, a body charged with electricity, like an electron, and moving in a circular or elliptical orbit, must be constantly radiating energy into space. Since this energy must come from its energy of motion, the electron should be slowing up, moving in orbits of smaller radius, in short, spiraling into the nucleus. Again this model predicts the demise of the hydrogen atom.

6. The Quantum Theory of Radiation.—The clue to the solution of this puzzling problem was given in the statement of the quantum theory of radiation by Max Planck in 1900. He assumed that an electron in an atom does not give out radiation continuously; but that when radiation is emitted, it is given off in definite amounts, or *quanta*. He further postulated that the energy in such a quantum of radiation, E, is directly proportional to its frequency:

$$E \propto \nu$$
$$E = h\nu$$

In this equation the constant h is known as Planck's constant. According to this theory, light is composed of discrete packets of energy the magnitude of which determines the frequency of the accompanying electromagnetic wave. In support of this theory, there has accumulated an impressive amount of experimental evidence.

7. The Bohr Theory of the Hydrogen Atom.—In 1913, Niels Bohr, a Danish physicist, proposed a theory of the mechanism of light emission and absorption by the hydrogen atom. He assumed that the amount of energy $h\nu$ possessed by a quantum of light of the frequency ν, corresponding to a line in the hydrogen spectrum, is equal to the difference between two amounts of energy E' and E as shown in the following equation:

$$h\nu = E' - E$$

From this equation, Bohr next proceeded to picture the behavior of the electron in the hydrogen atom in absorbing or emitting a quantum of energy. He postulated that the electron can revolve about the nucleus in certain orbits only. No other orbits are possible. These permissible orbits are shown in Fig. 88. The electron in any one orbit possesses an amount of energy which is characteristic of that orbit. These orbital energies have been labeled E_0, E_1, E_2, E_3, E_4, E_5 . . . E_∞ in the figure.

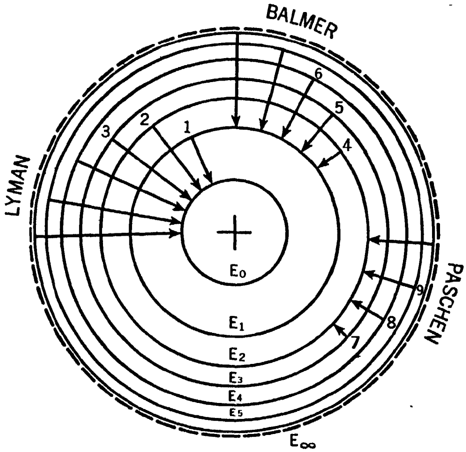


Fig. 88.—Energy levels in the hydrogen atom.

The amount of energy possessed by the electron becomes greater as the electron moves from an inner to an outer orbit owing to the fact that energy is absorbed when oppositely charged particles are moved farther apart. The electron, when in the innermost orbit, is unable to emit any radiant energy. This is the normal, or ground, state of the atom. Whenever the atom is excited by exposure to some external source of energy, such as an electrical discharge or an exposure to light of the proper frequency, the electron can absorb a quantum of energy by jumping to one of the outer orbits. This process of absorption can be stated mathematically as follows:

$$
\begin{aligned}
E_0 + h\nu &= E_1 \text{ (from orbit 0 to orbit 1)} \\
E_0 + h\nu' &= E_2 \text{ (from 0 to 2)} \\
E_1 + h\nu'' &= E_2 \text{ (from 1 to 2), etc.}
\end{aligned}
$$

The electron in any but the innermost orbit is in an excited state and is capable of emitting a quantum of radiant energy by reversing the process and jumping back to an inner orbit:

$$E_2 = E_1 + h\nu'' \text{ (from 2 to 1)}$$
$$E_2 = E_0 + h\nu' \text{ (from 2 to 0)}$$
$$E_1 = E_0 + h\nu \text{ (from 1 to 0), etc.}$$

The light emitted when the electron jumps from one orbit to an inner one is of a definite frequency and corresponds to a line in the hydrogen spectrum. For example, a jump from orbit 1 to orbit 0 results in the emission of ultraviolet light of the frequency corresponding to the line numbered 1 in Fig. 87 of the hydrogen spectrum. A jump from 2 to 1 gives rise to the red line, number 4 of Fig. 87, etc. The outermost orbit, in which the electron has an energy of E_∞, represents the maximum energy content that it can have and yet remain in the atom. If it absorbs a greater amount of energy than this, it will fly away from the influence of the positive nucleus out of the hydrogen atom.

The Bohr theory has been somewhat modified, but its essential features have remained unchanged. It has been enlarged by Bohr himself to include the helium atom and by others to include the atomic structures of the other elements. We are by no means certain that any one of these is correct, since the proof of their structure cannot be obtained by a mathematical analysis of their spectral lines. However, there is good evidence that usually only the electrons in the outer orbits of an atom, the so-called valence electrons, take part in the emission or absorption of radiant energy.

Although the Bohr theory has been extensively modified, the essential idea of electrons arranged about the nucleus in quantum levels has been retained. Heisenberg pointed out that it is impossible to predict with certainty both where an electron is and how it is moving. Schrödinger showed how the probable future movements of an electron could be predicted by means of a differential equation which describes a wave motion. As a result the modern, so-called wave-mechanical, treatment of atomic structure came into being. Unfortunately this treatment presents no clear-cut picture of atomic structure and demands a knowledge of mathematics far beyond that of a college freshman before it can be understood and applied. However, it is the most satisfactory means of predicting the behavior of atoms and subatomic particles available at the present time. Fortunately it is possible to present a relatively simple picture of atomic structure which will prove of practical value not only to a student of elementary chemistry but also to the professional chemist in the solution of many of the problems with which chemistry deals.

8. The Lewis-Languir Theory.—This simple theory of the arrangement of the planetary electrons was developed originally and independently by Kossel and by G. N. Lewis in 1916. Three years later, it was considerably enlarged and modified by Irving Langmuir. *The clue to the number of electrons in a given quantum level is given by the structures of the chemically inert gases of Group* 0 *of the periodic table and by the valences of the elements in general.*

The single electron of the hydrogen atom is in the n = 1 quantum level. As we proceed from one element to the next in the periodic table, the nuclear charge increases by one unit and an electron is added. The two electrons of the helium ($Z = 2$) atom are in the first quantum level also. Now helium is one of the elements of Group 0 all of which are chemically inert, *i.e.*, they show no tendency to form compounds with other elements. This is an indication of an atomic structure of extraordinary stability. Hence *two electrons completes the quota of the first quantum level.* The lithium atom ($Z = 3$) has 2 electrons in the first and one in the second level. The atoms of the remaining elements in the second period, beryllium ($Z = 4$), boron (5), carbon (6), nitrogen (7), oxygen (8), fluorine (9), and neon (10), each have 2 electrons in the first level and 2 (Be), 3 (B), 4 (C), 5 (N), 6 (O), 7 (F), and 8 (Ne) electrons, respectively, in the second level. Neon, the last of this period, is another inert element of Group 0. Therefore, *eight electrons is the quota of the second quantum level.* In the third period which includes the elements from sodium ($Z = 11$) through argon (18), the atoms of each element are made up of 2 electrons in the first and 8 in the second levels with 1 electron in the case of sodium to 8 in the case of argon in the third level. Again *eight electrons is the quota for the third level,* when this is the outer level of an atom, since argon is an inert gas. The information contained in this paragraph is summarized in Fig. 89.

9. The Long Periods.—A complete tabulation of the arrangement of the planetary electrons in the atoms of the elements has been made in Table 26. You will remember that in the first period of 18 elements, period 4, members of the Arabic-numeral

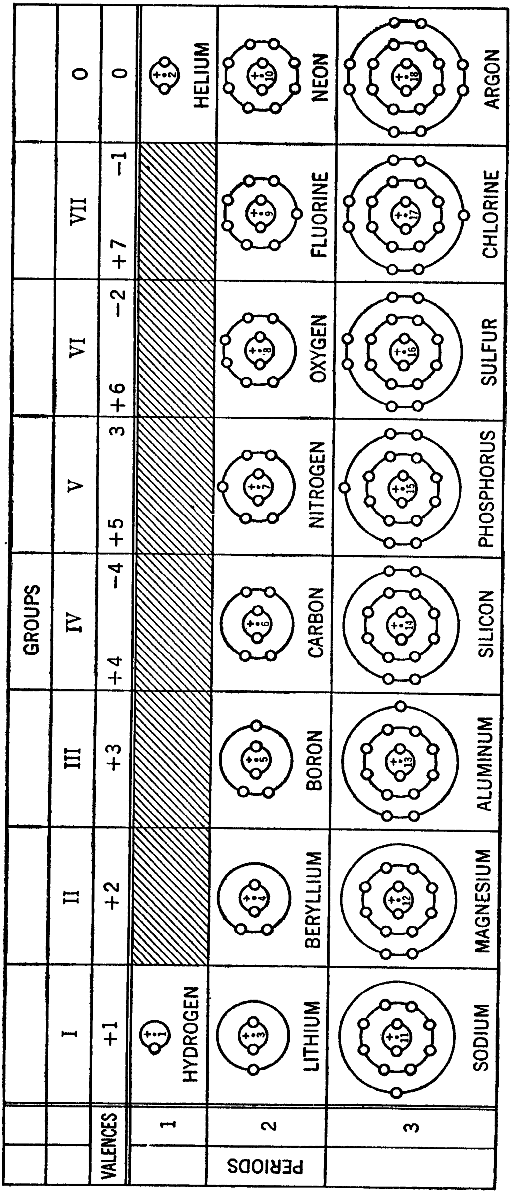


FIG. 89.—Atomic structures of the elements of the first, second, and third periods.

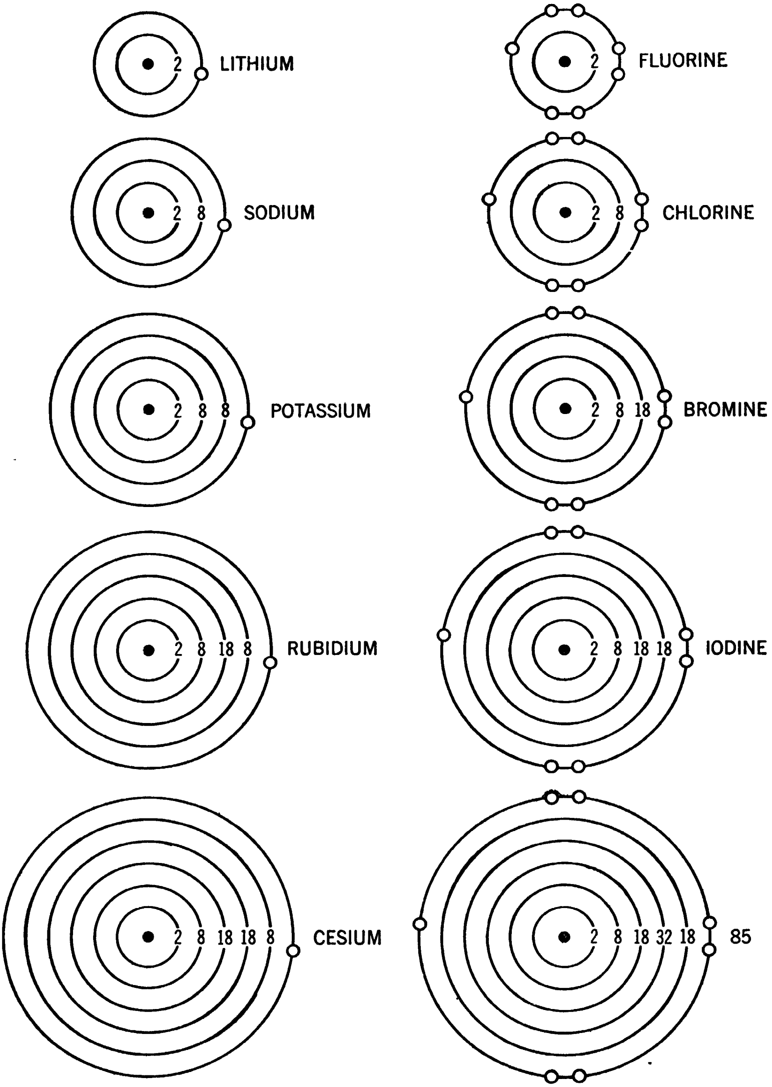
Table 26.—Electron Arrangement in Atoms

Groups

Periods	Levels	I	II	3	4	5	6	7	8			1	2	III	IV	V	VI	VII	0
1		H																	He
	1	1																	2
2		Li	Be											B	C	N	O	F	Ne
	1	2	2											2	2	2	2	2	2
	2	1	2											3	4	5	6	7	8
3		Na	Mg											Al	Si	P	S	Cl	A
	1	2	2											2	2	2	2	2	2
	2	8	8											8	8	8	8	8	8
	3	1	2											3	4	5	6	7	8
4		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	2	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
	3	8	8	9	10	11	13	13	14	15	16	18	18	18	18	18	18	18	18
	4	1	2	2	2	2	1	2	2	2	2	1	2	3	4	5	6	7	8
5		Rb	Sr	Y	Zr	Nb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	2	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
	3	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
	4	8	8	9	10	12	13	14	15	16	18	18	18	18	18	18	18	18	18
	5	1	2	2	2	1	1	1	1	1		1	2	3	4	5	6	7	8
6		Cs	Ba	Rare earths	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
	1	2	2		2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	2	8	8		8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
	3	18	18		18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
	4	18	18		32	32	32	32	32	32	32	32	32	32	32	32	32	32	32
	5	8	8		10	11	12	13	14	15	16	18	18	18	18	18	18	18	18
	6	1	2		2	2	2	2	2	2	2	1	2	3	4	5	6	7	8
7		—	Ra	Ac	Th	Pa	U												
	1	2	2	2	2	2	2												
	2	8	8	8	8	8	8												
	3	18	18	18	18	18	18												
	4	32	32	32	32	32	32												
	5	18	18	18	18	18	18												
	6	8	8	9	10	11	12												
	7	1	2	2	2	2	2												

Rare Earths

		La	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	2	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
	3	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
	4	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
	5	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
	6	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2



ALKALI METALS
GROUP I

HALOGENS
GROUP VII

Fig. 90.

groups appear for the first time (24-4). The first two elements of this period potassium and calcium start off normally each with two, eight, and eight electrons, respectively, in the first, second, and third levels. Potassium has one electron and calcium two electrons in the fourth level. The next element scandium in Group 3 has only two electrons in the fourth quantum level of its atom. The additional electron has been added to the third and not to the fourth level. So through the elements of the Arabic-numeral groups of the fourth period, the third quantum level is built up until it contains 18 electrons in the copper atom. Then only are electrons added to the outermost level, the fourth, until it reaches a total of eight in the atom of the inert gas krypton. The fifth period closely resembles the fourth. In the sixth period, the group of rare earths appears. As the atomic numbers increase in this group of elements, electrons are added to the third from the outer level, *i.e.*, the fourth level. The number of its electrons is increased from 18 to 32.

10. Group Properties and Electron Arrangement.—The elements of a given group in the periodic table resemble one another closely. The explanation of such resemblance must be found in similar atomic structures. For the elements in the Roman-numeral groups, *the number of electrons in the outermost level is the same for the atoms of each element in a given group and is equal to the group number.* Thus the atoms of the halogens in Group VII have seven electrons in the outermost quantum levels (Fig. 90). The alkali-metal atoms of Group I have one electron (Fig. 90). As we shall see more clearly in the next chapter, one of the most important factors in determining the chemical properties of an element is the number of electrons in the outermost quantum level of its atom. In the case of no atom does the number of electrons in the outer level exceed eight.

11. The Electrons in Space.—There is strong evidence for the theory that the eight electrons in the outer level of a typical inert-gas atom are arranged *in pairs* at the corners of an imaginary tetrahedron. Thus the electrons of the argon atom might be imagined as illustrated in Fig. 91*a*. This tendency of planetary electrons to pair off seems odd at first since their like charges of electricity produce a force of repulsion that should tend to drive them apart. Some other force of attraction must be present to balance the force of repulsion. This force is called an *exchange* *force* and is due to the fact that each electron is spinning about an axis. A pair of electrons, spinning in opposite directions, attract each other. We shall soon see that electron-pair formation plays an important role in holding atoms together in molecules.

The picture of the tetrahedral structure of the argon atom in Fig. 91*a* may be further simplified with a great saving in artistic effort, as shown in Fig. 91*b*. A further simplification may be accomplished by the device shown in Fig. 91*c*. Here the symbol A stands for *the kernel* of the argon atom, *i.e.*, *its nucleus and the planetary electrons of all but the outermost level.* In a similar manner the potassium, iodine, and aluminum atoms may be written:

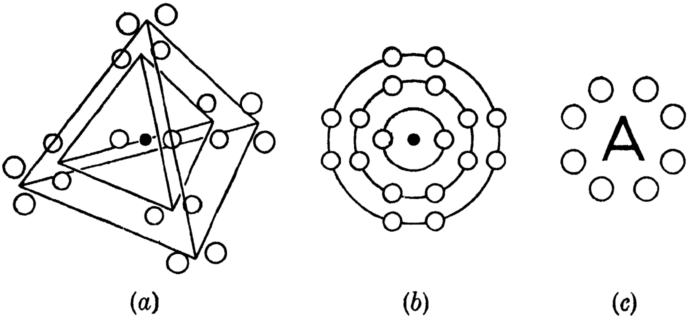
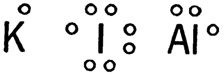


FIG. 91.—Three methods of indicating the arrangement of planetary electrons in the argon atom.



$$\overset{\circ}{\mathrm{K}} \qquad {}^{\circ}\overset{\circ\,\circ}{\underset{\circ\,\circ}{\mathrm{I}}}\,{}^{\circ}_{\circ} \qquad \overset{\circ\,\circ}{\mathrm{Al}}{}^{\circ}$$

Since the electrons of this outer level are usually the only ones involved in chemical changes, the simplified device usually suffices.

It is well to remember that in any drawing of the structure of an atom the distances between electrons and between the electrons and the nucleus are not drawn to scale. With the electrons the size illustrated, the distances between would be of the order of a few hundred feet and we should have to hunt for the nucleus with a microscope. An atom is mainly empty, which is small comfort when the atoms in our head make contact with the atoms of a door in the dark. If the subatomic particles were not charged, atoms could pass freely through one another. Charged with negative electricity, the electrons in one atom strongly repel those of another and thus prevent interpenetration.

EXERCISES

1. Upon what facts is the theory of the arrangement of the planetary electrons in the atoms based?

2. In what way do the atomic structure of the elements in a given group in the periodic table resemble one another?

3. How are the eight electrons in the valency quantum level of an inert-gas atom arranged in space?

4. What is the kernel of an atom?

5. The atomic and mass numbers of a certain atom are 11 and 23, respectively. Draw a diagram of its atomic structure. In what group is it in the periodic table? Is it a metal or a nonmetal?

6. How many electrons are there in the valency quantum level of the iodine atom?

7. Does a quantum of ultraviolet radiation contain more or less energy than a quantum of yellow light?

8. How did Bohr explain the mechanism by which the hydrogen atom emits light?

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CHAPTER TWENTY-SEVEN

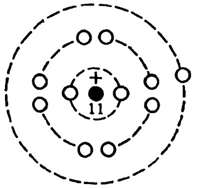
THE NATURE OF VALENCE

When atoms combine, the compounds formed have widely different properties. Why, when sodium and chlorine combine, is the resulting compound a solid of high melting point but of no odor? Why is this compound readily soluble in water? Why does this compound when melted or dissolved in water conduct electricity? Why do common salt and salts in general have these properties? On the other hand, why is carbon dioxide a gas under normal conditions? Why does not liquid carbon dioxide conduct electricity? Why does Dry-ice, the solid form of carbon dioxide, sublime? Why are the compounds of carbon so numerous and, again, why are these organic compounds so different from the vast majority of inorganic compounds? We have discussed the answers to some of these questions briefly. We are now in a position to consider them more fully in the light of our more complete knowledge of atomic structure.

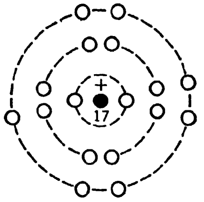
1. The Mechanism of Chemical Combination.—The atoms of the inert gases of Group 0 are the only ones that will not combine with other atoms. Their planetary electrons are arranged in so stable a fashion that nothing could be gained in stability by the loss of electrons from or the addition of electrons to these atoms. Each quantum level, which contains any electrons at all, has its full quota. On the other hand, the outer quantum levels of the atoms of all other elements are incomplete, and this accounts for their chemical reactivity. In combining with other atoms, the atoms of an element *strive to attain the stable arrangement of electrons that characterizes the inert atoms of the elements of Group* 0. This is done by the process of gaining, losing, or sharing electrons.

2. The Combination of Sodium and Chlorine.—The alkali metals of Group I combine readily with the halogens of Group VII to form binary salts. As in the case of all salts, these are solids of relatively high melting point and show no measurable tendency to sublime. They are readily soluble in water, and the resulting solutions conduct electricity. The manner in which these atoms combine must be able to explain these properties.

Every alkali-metal atom when uncombined has one electron in the outer level. The sodium atom is typical:



In the outer level of every halogen atom, when uncombined, there are seven electrons. We may use chlorine as a typical example:



By losing one electron, the sodium atom would attain the planetary electron structure of the inert gas, neon, nearest to it in the periodic table. Having lost this electron, the sodium atom would not have become a neon atom, since its nucleus still bears a positive charge of 11 units and hence belongs to the element of atomic number 11, *i.e.*, sodium. The 10 remaining electrons, however, cannot neutralize the charge of +11 on the nucleus, and the atom as a whole has a net positive charge of one unit. Since a charged atom or group of atoms is called an ion, the sodium atom upon losing an electron becomes a sodium ion.

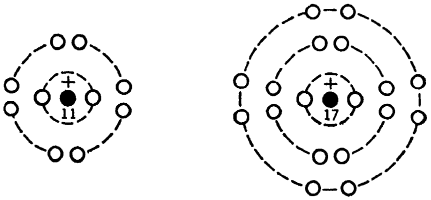


FIG. 92.—A positively charged sodium ion and a negatively charged chloride ion as found in the salt, sodium chloride.

The chlorine atom, on the other hand, by gaining one electron would complete its outer level with a total of eight electrons. Thus it would attain the electron structure of argon. The electron, gained by the hitherto neutral atom, would confer a charge of −1 on the atom as a whole, changing the neutral chlorine atom into the negatively charged chloride ion.

When the metal sodium combines with the nonmetal chlorine, large numbers of neutral sodium atoms each lose an electron to each of an equally large number of chlorine atoms. The ions formed have different properties than those of the corresponding neutral atoms. The sodium ions bear electrical charges opposite in sign to those of the chloride ions. Hence relatively strong Coulomb forces pull the oppositely charged ions together. The result is a crystalline compound in which sodium and chloride ions are packed closely in a regular pattern, or crystal lattice, the form of which is determined by the relative diameters of the two kinds of ions. In the case of sodium chloride, the crystals formed are cubes with the arrangement of ions shown in Fig. 93. Here each sodium ion is in contact with six equidistant chloride ions, and vice versa. It is obvious that the ions are not paired and that no molecules of sodium chloride exist in such crystals.

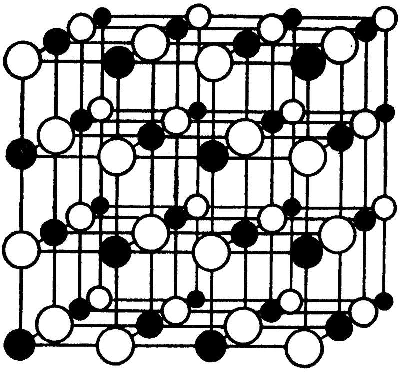


FIG. 93.—Ions are the structure units in the crystals of a salt like sodium chloride.

The relatively high melting point of salt (804°C.) is to be attributed to the strength of the Coulomb forces that bind the crystal together. So also is the lack of any measurable sublimation at ordinary temperatures. However, common salt and salts in general are for the most part readily soluble in water. This solvent has the almost unique property of drastically reducing the Coulomb forces between charged particles. Hence it dissolves salts as separate ions from their crystals. This phenomenon will be discussed in greater detail later. When a salt crystal melts or is dissolved in water, we have good reason to believe that the ions lead a separate existence. Hence melted or dissolved salts conduct electricity.

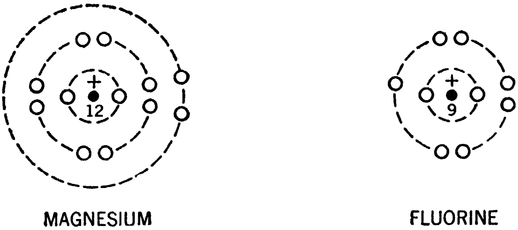


Fig. 94.—Neutral magnesium and fluorine atoms.

3. Other Examples.—Let us consider a few more examples of this type. Magnesium atoms are divalent, and fluorine atoms univalent. The atomic structures of the neutral atoms of these elements, before combination has taken place, are shown in Fig. 94. Each magnesium atom has two electrons in its outer shell to lose, and each fluorine atom has only one empty place to be filled by an electron in its outer shell. Therefore one magnesium atom will lose an electron to each of two fluorine atoms (Fig. 95).

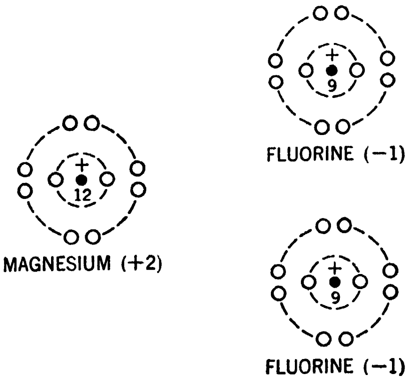


Fig. 95.—One magnesium and two fluoride ions as found in magnesium fluoride.

One more example, in the formation of sodium sulfide, two atoms of univalent sodium combine with one divalent atom of sulfur. The union of these atoms is pictured in Fig. 96.

4. Electrovalence, or Ionic Valence.—In general, when atoms of metals combine with atoms of nonmetals, a transfer of electrons from the metal atoms to those of the nonmetal takes place. The metal atoms are, therefore, left positively charged, and the nonmetal atoms acquire a negative charge. The valence "bond" in such cases is one of electrostatic attraction between oppositely charged ions. Valence bonds of this type are called *electrovalent.*

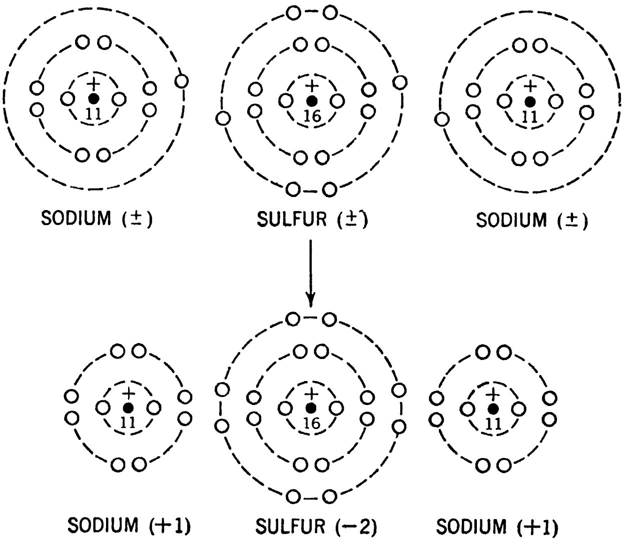


FIG. 96.

In each of the three examples that we have been considering, a metal combines with a nonmetal, the atoms of the metal losing the electrons that the nonmetallic atoms gain. It will be remembered that the metals are in the low-numbered groups of the periodic table; therefore, the number of electrons in the outer levels of their atoms is in general less than half the quota for the shell (Fig. 89). It is logical to expect that metallic atoms tend to deplete their outer levels by giving up electrons to the atoms with which they combine rather than to complete levels by gaining additional electrons. In losing electrons, the metallic atoms will become positively charged or, in other words, will exhibit a *positive valence.* The amount of this positive charge, or valence, *will be equal to the number of electrons that are lost from the outer level.* Thus the atoms of the uncombined elements in Group I of the periodic table have one electron in their outer levels; and when this is lost in combining with other atoms, these atoms acquire a unit-positive charge or, in other words, a positive valence of 1. Similarly, the metals of Group II show valences of +2, since their atoms lose the two electrons of their outer levels when combining with the atoms of other elements, and so on for the other metallic groups.

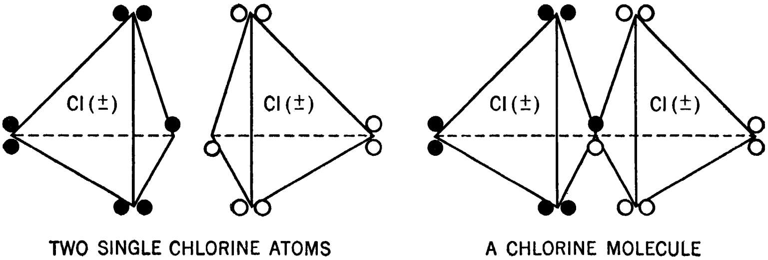


Fig. 97.

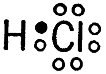
The nonmetals, on the other hand, are in the higher numbered groups. Hence the outer levels of their atoms contain nearly their quota of electrons. There is, therefore, a greater tendency to gain rather than to lose electrons when these atoms combine with the atoms of metals. Under these circumstances, the nonmetallic atoms become negatively charged and exhibit, therefore, a negative valence. *The negative valence of a nonmetal is equal to the number of electrons that its atom must gain to complete the quota of the outer level of its atom.* Hence the characteristic valence of the nonmetals of Group V is −3; of Group VI, −2; and of Group VII, −1.

5. Covalence.—In many cases, atoms combine with no actual transfer of electrons but attain the stable structure of the inert gas atoms *by sharing pairs of electrons.* This type of combination is easier to picture than to describe. As an example, let us consider the structure of the molecule of free chlorine which contains two chlorine atoms. These are joined by a pair of electrons shared by the two atoms as illustrated in Fig. 97. The electrons of one of the atoms are filled in, not because they differ in any way from those of the other atom, but in order that the electrons belonging to each atom may be the more readily visualized. Atoms linked in this way remain electrically neutral since neither has lost any of its electrons. Such a linkage is called a *covalent linkage.* Here we meet another example of electron-pair formation in which the two electrons have opposite spins.

The tendency of atoms to combine through the formation of covalent linkages is shown to the greatest degree by the atoms of the elements in the middle groups of the periodic table and by hydrogen atoms. The hydrogen atom needs only one electron pair to complete the first level. Hence hydrogen forms diatomic molecules in the free state:

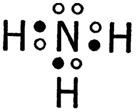
$$\mathrm{H{:}H}$$

The hydrogen and chlorine atoms in the molecules of hydrochloric acid are linked by a covalent bond:



$$\mathrm{H}\begin{smallmatrix}\bullet\\\circ\end{smallmatrix}\overset{\circ\circ}{\underset{\circ\circ}{\mathrm{Cl}}}\begin{smallmatrix}\circ\\\circ\end{smallmatrix}$$

The molecules of ammonia, NH_3, contain three covalent bonds:

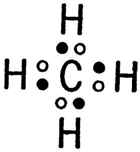


$$\begin{array}{c}\mathrm{H}\begin{smallmatrix}\bullet\\\circ\end{smallmatrix}\overset{\circ\circ}{\mathrm{N}}\begin{smallmatrix}\circ\\\bullet\end{smallmatrix}\mathrm{H}\\ \bullet\circ\\ \mathrm{H}\end{array}$$

AMMONIA

Here the nitrogen atom shares three of its five electrons (Group V) with three hydrogen atoms. The two remaining electrons form a *lone pair.*

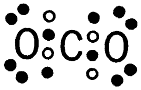
Carbon in the fourth group with, therefore, four electrons in the outer shells of its atoms invariably forms covalent bonds with other atoms. The simplest hydrocarbon, methane, CH_4, has a molecular structure in which four electron pairs join the central carbon to four hydrogen atoms:



$$\begin{array}{c}\mathrm{H}\\ \bullet\circ\\ \mathrm{H}\begin{smallmatrix}\circ\\\bullet\end{smallmatrix}\mathrm{C}\begin{smallmatrix}\bullet\\\circ\end{smallmatrix}\mathrm{H}\\ \circ\bullet\\ \mathrm{H}\end{array}$$

METHANE

When oxygen combines with elements of Group III or higher numbered groups, the atoms are held by covalent bonds, *e.g.*, carbon dioxide:



CARBON DIOXIDE

In molecules in which dissimilar atoms are joined by covalent linkages, it is highly probable that the shared pairs of electrons are nearer one kind of atom than the other because of the magnitudes of the positive charges on the different nuclei. When either metals or nonmetals combine with oxygen, it is probable that the shared pairs of electrons are nearer to the oxygen nuclei than to those of the other atoms. Hence the oxygen atoms in such compounds are more negative than are the metallic or the nonmetallic atoms with which they are combined, and vice versa, the other atoms are more positive than the oxygen atoms.

The valence number of an element in molecules in which the atoms are held together by covalent linkages is equal to the number of pairs of electrons that it shares with other atoms.

Compounds, which are composed of molecules in which all the atoms are linked by covalent bonds, are usually gases or liquids, and only if of high molecular weight are they solids. All the examples of covalence discussed thus far are gases under ordinary conditions. Free bromine, whose molecules are diatomic and similar to those of chlorine, is a liquid because of its greater molecular weight—160 as compared with chlorine, 71. Iodine with a molecular weight of 254 is a solid. Sugar, $C_{12}H_{22}O_{11}$, in whose molecules the atoms are bound by covalent linkages, has a molecular weight of 342 and is a solid. Such facts are not difficult to explain. When atoms share electrons, neither becomes electrically charged. The resulting molecules are also neutral. Hence the intermolecular, or van der Waals, forces between such molecules are much weaker than the Coulomb forces between charged ions. Even those molecular compounds which are solids have relatively low melting points and usually sublime readily. Iodine is a case in point. Both the low melting point and the ease of sublimation are definite evidence of weak forces holding molecular crystals together. Solids like naphthalene (mothballs), camphor, menthol, and iodine may be easily detected by their odor, which indicates that their molecules have found their ways into our noses via sublimation.

The crystal structures of iodine and solid carbon dioxide (Dry-ice) are shown in Figs. 98 and 99. In both, the molecules are the crystal-structure units and are held together by relatively weak van der Waals forces. Within each molecule, the atoms share pairs of electrons; hence they are held together by exchange forces.

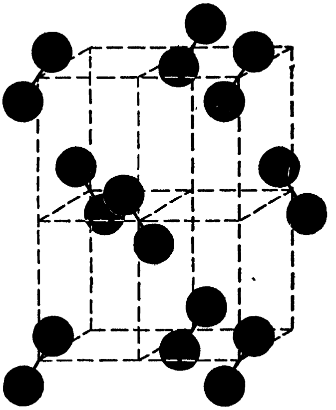


Fig. 98.—Iodine, a molecular crystal.

6. Giant molecules in which large numbers of atoms are linked together have been discussed previously. Here the type of linkage is covalent throughout the entire molecule. If the macromolecule is built up in three dimensions, the entire crystal is a single molecule. Such crystals, of which the diamond is an example, are very hard and melt at extremely high temperatures.

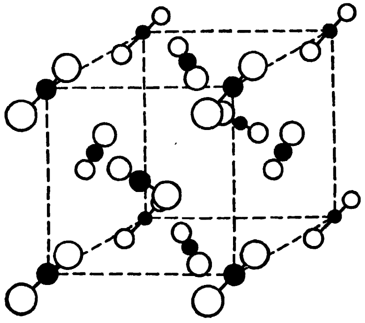


Fig. 99.—Carbon dioxide crystal structure.

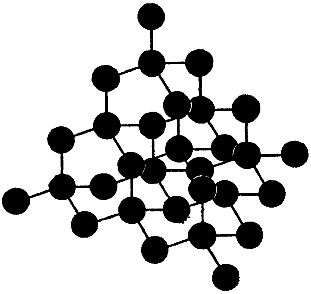
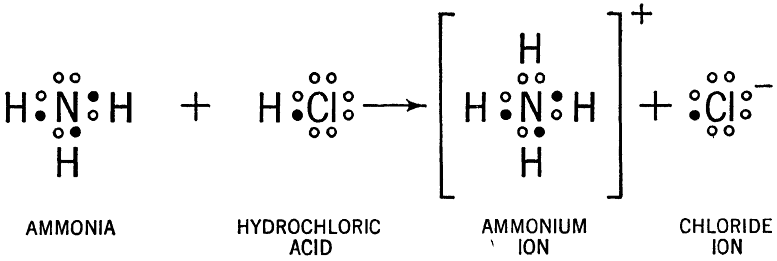


Fig. 100.—The diamond, a macromolecular crystal.

7. Coordinate Covalent, or Dative, Bonds.—There is a special type of covalence in which both the electrons of the shared pair came originally from one of the two atoms linked by the covalent bond. This type is called dative, or coordinate, covalence. We have mentioned that the nitrogen atom in the ammonia molecule has a lone pair of electrons that does not serve as a valence bond (27-5). Ammonia reacts with acids to form the corresponding ammonium salts, *e.g.*,

$$NH_3 + HCl \rightarrow NH_4Cl$$

In this case, the ammonium chloride formed is a salt whose crystals are composed of ammonium and chloride ions in equal numbers. When we examine this reaction in terms of the planetary electrons involved, the formation of a dative bond becomes clear:



The hydrogen atom in the hydrochloric acid molecule is sharing its electron (black) and one of the chlorine atom in a normal covalent bond. The symbol H stands for the kernel of the hydrogen atom which is a single proton. (Why?) The reaction involves the transfer of this positively charged proton to the ammonia molecule. Here it shares the pair of electrons that constituted the lone pair of the nitrogen atom. The positive charge of this added proton converts the neutral ammonia molecule into an ammonium ion. The electron of the transferred proton remains with the chlorine atom; hence the latter becomes a chloride ion.

8. Formulas of Salts.—We have learned that salts are composed of ions and not of molecules. The formula of a salt indicates the relative numbers of ions of each kind in its crystals and in its solutions. Thus $BaCl_2$ indicates that in the crystals of barium chloride there are half as many barium ions as chloride ions. In many salts, groups of atoms act as single ions. A case in point is the ammonium ion, which we have just considered. Here and in similar cases, the atoms grouped together in a single ion are joined by covalent bonds. But the group as a whole has either lost or gained electrons, and hence is no longer neutral but an ion. In the formation of ammonium chloride, the hydrogen atom of the hydrochloric acid leaves its electron behind when it joins the ammonia molecule. Hence the ammonium ion bears a unit positive charge.

The formula Na_2SO_4 indicates that crystals of the salt sodium sulfate contain twice as many sodium as sulfate ions. Since the uncombined sodium atom has one electron in its outer, or valency, level, each of two sodium atoms has contributed an electron to the sulfate group and the latter has become an ion bearing two unit negative charges. In Fig. 101, the electrons from the sodium atoms are represented by ●, from the oxygen atoms by ⊗, and from the sulfur atom by ○. See if you can find two examples of each type of linkage in this compound.

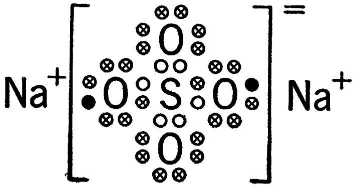


FIG. 101.

Since molecules of salts do not exist under ordinary conditions, it is improper to refer to the molecular weight or to a mole of a salt, although this is common practice. The terms formula weight and gram-formula weight are better.

EXERCISES

1. An element of atomic number 9 combines with one of atomic number 19. In terms of their atomic structures, explain what happens when these elements combine. What type of valence does their union illustrate?

2. Will the resulting compound be solid, liquid, or gaseous under normal conditions? Explain your answer.

3. Hydrogen combines with an element of atomic number 7. Show the manner in which these elements combine. Describe the properties of the resulting compound.

4. To what are the positive valence of a metal and the negative valence of a nonmetal equal?

5. What type of force binds elements together which share a pair of electrons?

6. What is a dative bond?

7. Explain the properties of common salt, iodine, and a diamond in terms of their structures.

8. Mercuric chloride may be readily purified by sublimation. What type of valence holds its atoms together?

9. Why is sulfur dioxide with a molecular weight of 64 a gas whereas lithium fluoride, LiF, whose formula weight is 26, melts at 870°C.?

10. What is meant by polar covalence?

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CHAPTER TWENTY-EIGHT

RADIOACTIVITY

Radioactivity and transmutation are processes associated with the nuclei of atoms. Perhaps such topics had best be discussed in physics courses. However, most of the spectacular results in these fields have been due to collaboration of physicists and chemists. It may be that your instructor may not assign this chapter and the next for study in which case read them over anyhow.

1. The Discovery of Radioactivity.—In 1895, Roentgen discovered x-rays while investigating the nature of the fluorescence of the glass walls of Crookes tubes (25-1). These rays, he found, possessed the ability to penetrate matter opaque to visible light. This ability may be easily demonstrated by wrapping an unexposed photographic plate in lightproof, black paper and placing it near the fluorescing wall of a Crookes tube. The x-rays penetrate the paper and expose the plate.

It was then well known that a number of naturally occurring substances were fluorescent, *i.e.*, they had the ability to absorb light and to reemit it, changed to a color characteristic of the fluorescent substance but not of the light by which the fluorescence was produced. The possibility that the emission of x-rays was characteristic of all fluorescence suggested itself to Henri Becquerel, a French physicist, and he began a series of simple experiments similar to those which had enabled Roentgen to discover x-rays. Fluorescent substances were placed upon the opaque wrapping of unexposed photographic plates to test whether x-rays were emitted by them. The results were negative, *i.e.*, the photographic plates remained unexposed, except in one instance. Fortunately he had included certain compounds of the element uranium which fluoresce with a beautiful greenish-yellow light. These compounds of uranium, unlike the others tested, exposed the photographic plate. This immediately suggested to Becquerel that the element uranium emits rays, which are either x-rays or very similar to them.

2. Pierre and Marie Curie.—In 1897, Marie Sklodowska Curie, working at the Sorbonne in Paris, undertook the investigation of the newly discovered phenomenon of radioactivity which was destined to make her famous. By using an electrometer she was able to devise a very reliable method of measuring the intensity of the rays emitted by radioactive substances. She found that the radioactivity of uranium compounds remained constant over long periods of time, that it was exhibited by all uranium compounds, and that in the case of pure uranium compounds the activity was proportional to the amount of uranium in the compound. From these results, she formed the conclusion that the radioactivity was a property of uranium atoms and not of the other atoms in the molecules of uranium compounds.

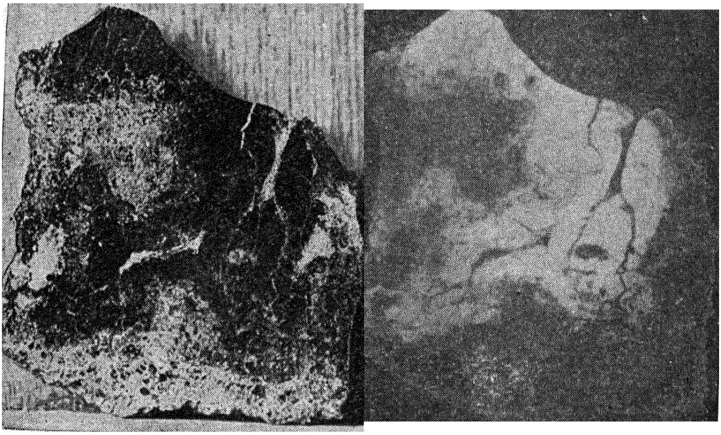


FIG. 102.—A radioactive ore takes its own picture.

FIG. 103.—Marie Sklodowska Curie.

Madame Curie next carried out a systematic investigation of the other elements to determine whether any of them were radioactive. This search led to the discovery that of the then known elements only thorium, other than uranium, possessed this remarkable property. A comparison of the properties of these two elements revealed that they resemble each other only in their radioactivity and in the fact that they are the elements of the two greatest atomic weights. The latter fact proved to be very significant as we shall see later.

3. The Discovery of Polonium and Radium.—A most surprising fact was revealed by her next discovery. She measured the radioactivity of natural minerals containing uranium and thorium, expecting to find an activity proportional to the amounts of these elements in the minerals. What was her surprise when she found an activity greater than could have been predicted. In one sample of the uranium ore pitchblende the activity was found to be four times as great as that predicted from its uranium content. This result suggested the presence of yet unknown elements in the ores whose radioactivity must be far greater than that of thorium and uranium.

Madame Curie was then joined by her husband Pierre in the search for these traces of powerfully radioactive elements. The result was the discovery of polonium and radium. The very high grade of pitchblende ore from which the Curies isolated these elements contained about 60 per cent uranium. The ratio of radium to uranium in such ores is 3.4 parts of radium to every 10,000,000 parts of uranium. One ton of the ore would contain about 0.2 g. of radium. This gives an idea of the task undertaken by the Curies. The Austrian government generously presented them with a ton of pitchblende ore residues from which the uranium had been extracted and with the financial assistance given them by several scientific societies and friends interested in their work the Curies were able to separate 0.1 g. of very pure radium chloride from these residues as the result of an exceedingly tedious separation. With this sample the atomic weight of radium was determined and its spectrum photographed.

In 1903, Mme. Curie received the degree of *Docteur des sciences physique* for her thesis on the discovery of radium and within a few months thereafter shared with her husband and Becquerel the Nobel Prize. In 1906, her husband was killed by a heavy wagon drawn by two horses as he was crossing the *Rue Dauphine* in Paris. This blow nearly cost Mme. Curie her life. However, she slowly recovered and consecrated her life anew to her two children and her work. In 1910, she succeeded in preparing radium as a free element and in the following year was again awarded the Nobel Prize, the first to receive this distinction for the second time.

4. The Properties of Radium.—The discovery of radium revealed a group of phenomena that were unique in the history of science. Its tremendous radioactivity, some 3,000,000 times the activity of uranium, at once captivated the public interest. Here was an element capable of giving out energy in the form of light and heat at a rate that remained constant regardless of external conditions. At high temperatures and at the temperature of liquid hydrogen, its activity remained the same. Here too was an element emitting rays that could penetrate lightproof paper and take photographs of the internal structure of opaque objects and could render air a conductor of electricity. Small wonder that the discovery of radium caught and held the public interest as had no other scientific discovery.

5. The Discovery of Other Radioactive Elements.—The discovery of other radioactive elements was the direct result of the research that was stimulated by the discoveries of Becquerel and the Curies. In 1899, Debierne, working in Mme. Curie's laboratory, discovered actinium. In 1901, Hofmann and Strauss discovered a form of lead which was radioactive. In 1900, Rutherford discovered a radioactive gas associated with thorium compounds; in the same year Dorn showed that a similar gas could be obtained from radium. In 1907, Boltwood discovered ionium in uranium minerals. Soon many others were added to the list.

6. The Nature of Radioactivity.—During this period of discovery, the rays emitted by radioactive elements were being investigated. The greater part of this research was carried out by Sir Ernest Rutherford of the University of Manchester. There were found three types of radiation: α- and β-particles and γ-rays, the properties of which may be summarized as follows:

α-Particles are the nuclei of helium atoms and, therefore, consist of two protons and two neutrons. For this reason they bear a net positive charge of two units. Because of this charge, their mass and the amount of charge could be determined by methods analogous to those used by Thomson and others for determining the mass and the charge of the electron. A stream of α-particles will be bent out of its straight-line path toward the negatively

charged plate of a condenser. The two protons and two neutrons these particles contain make it four times as heavy as the hydrogen atom. α-Particles are emitted from the atoms of certain radioactive elements at tremendous velocities, sometimes equal to one-fifteenth of the velocity of light. Because of this velocity, α-particles will plough through 2.6 to 8.6 cm. of air at ordinary pressure, knocking off electrons from many of the 200,000 atoms of nitrogen and oxygen through which each on the average passes before its energy is spent. Rutherford was able to prove that, after an α-particle had picked up two stray electrons, it became a typical neutral helium atom, the two electrons becoming the planetary electrons of its atomic structure.

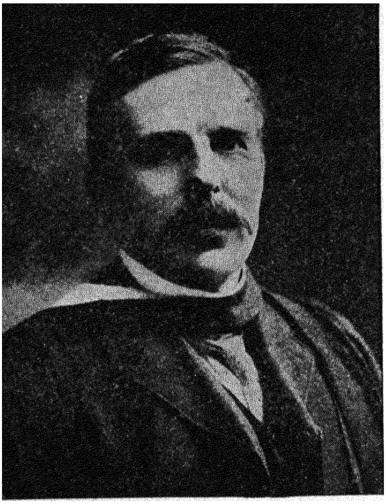


FIG. 104.—Ernest Rutherford. (*Courtesy of Journal of Chemical Education.*)

β-Particles are electrons, emitted by the atoms of certain radioactive elements with extraordinary velocities, which in some instances have been known to exceed nine-tenths of the velocity of light. They also knock off electrons from the atoms of gases through which they pass, thus rendering them conductors of electricity. Since they are negatively charged, a stream of β-particles will be deflected by an electrical field toward the positive plate of a condenser. By studying this deflection quantitatively, their identity with the electrons was established.

Associated with the emission of β-particles are the *γ-rays*. These are very similar to the *x*-rays and consist of light of exceedingly short wave-length because of which they possess the power of penetrating matter to an extraordinary degree. These are chiefly responsible for the exposure of photographic plates wrapped in lightproof paper. Only one-half the intensity of a stream of γ-rays is absorbed by a half-inch of lead. They differ from visible light in wave-length only, their waves being less than one-thousandth of the shortest visible light wave. They travel with the velocity of light and are not deflected by magnetic or electrical fields.

7. The Rutherford-Soddy Disintegration Theory.—To explain the source of these radiations, Rutherford and Soddy in 1902 proposed their disintegration theory of radioactivity, which was nothing short of revolutionary in the light of the accepted scientific concepts of that time. They stated their theory as follows:

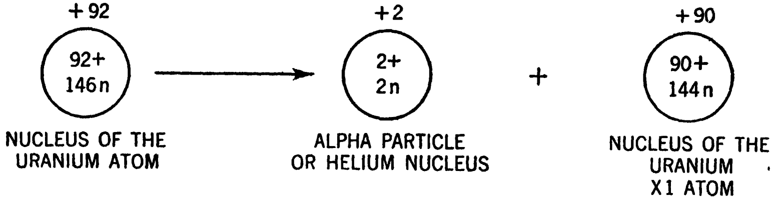
> The atoms of radioactive elements disintegrate giving rise to a new element, which may or may not disintegrate as did its parent. The atom resulting from the disintegration of the parent has different chemical properties from the parent. This disintegration is accompanied by corpuscular emissions and radiations, which afford a comparative measure of the rate at which disintegration takes place.

With one stroke, the theory of the changeless character of the elements was overthrown. This view had been strikingly stated by James Clerk Maxwell before the British Association in 1873:

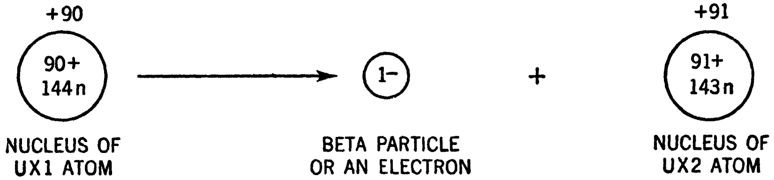
> Natural causes, as we know, are at work which tend to modify, if they do not at length destroy, all the arrangements and dimensions of the earth and the whole solar system. But though, in the course of ages, catastrophes have occurred and may yet occur in the heavens, though ancient systems may be dissolved and new systems evolved out of their ruins, the molecules (atoms) out of which these systems are built—the foundation atoms of the universe—remain unbroken and unworn.

Yet the disintegration theory, which proposed that the atoms of the radioactive elements are continually changing into other atoms, has been proved beyond a shadow of doubt.

8. Radioactive Transformations.—The disintegration theory pictures a whole family of elements starting with the head of a family line, followed by its offspring and its offspring's offspring, and so on down through the family tree. Such a family of radioactive elements is headed by the element uranium. The atom of this element characteristically emits an α-particle and, in so doing, becomes a new element uranium X1, which in its turn emits a β-particle and becomes uranium X2, and so on down the line. These particles are emitted from the nucleus of the atom and result in a change in the charge and sometimes in the mass of the nucleus as will become apparent when we stop to analyze the change. Uranium has an atomic weight of 238 and an atomic number of 92. Hence its nucleus will be made up of 92 protons and 146 neutrons with a nuclear charge of +92. About this nucleus in the neutral uranium atom are revolving 92 planetary electrons, which take no part in the radioactive changes under consideration. The concentration of so many protons and neutrons within the nucleus results in an instability, which seeks to adjust itself to a more stable condition by the emission of an α-particle. We may picture the emission of this particle from the nucleus of the uranium atom as follows:



What is left of the uranium nucleus, after the emission of an α-particle, is the nucleus of another element with an atomic weight of 234 and an atomic number of 90 (nuclear charge). Since the nuclear charge determines the element to which an atom belongs, the change in this charge from +92 to +90 signifies a transmutation of one element into another. This new element in its turn is radioactive and characteristically emits a β-particle:



The emission of an electron from a nucleus which at first sight seems to contain none is explained when we recall that a neutron may be regarded as an electron-proton pair. The loss of a β-particle, therefore, changes a neutron into a proton.

The new element, produced in this way, will have the same atomic weight as UX1, since the weight of the β-particle (electron) lost is negligible, but an atomic number of 91. It must be always kept in mind that it is the charge on the nucleus, or the atomic number, which determines the number and arrangement of the planetary electrons and, therefore, the chemical properties of the corresponding element. Atoms with different nuclear charges are atoms of different elements. The complete genealogy of the uranium family will be found summarized in Table 27. In every case, the emission of an α-particle results in the formation of a new element, four units less in atomic weight and two units less in atomic number. On the other hand, the emission of a β-particle is accompanied by no change in atomic weight and an increase of one unit of atomic number. It will be noted that radium itself is one of the progeny of uranium and

TABLE 27.—THE URANIUM SERIES OF RADIOACTIVE ELEMENTS

Element	Atomic weight	Neutrons	Atomic number, protons	Particle emitted	Half life
Uranium 1	238	146	92	α	5 × 10^9 yr.
↓					
Uranium X1	234	144	90	β	24.6 days
↓					
Uranium X2	234	143	91	β	69 sec.
↓					
Uranium 2	234	142	92	α	2 × 10^6 yr.
↓					
Ionium	230	140	90	α	69,000 yr.
↓					
Radium	226	138	88	α	1,690 yr.
↓					
Radon	222	136	86	α	3.85 days
↓					
Radium A	218	134	84	α	3.0 min.
↓					
Radium B	214	132	82	β	27 min.
↓					
Radium C	214	131	83	β	20 min.
↓					
Radium C′	214	130	84	α	
↓					
Radium D	210	128	82	β	16.5 yr.
↓					
Radium E	210	127	83	β	5 days
↓					
Polonium	210	126	84	α	136 days
↓					
Lead	206	124	82	Not radioactive	

that lead, an element that is not radioactive, is the last member of the family.

The radioactive elements are those of the highest atomic weights and atomic numbers and, therefore, those whose atoms are the most complex. The packing together of such a large number of neutrons and protons into a single nucleus results in an instability of structure in which electrical stresses exist. These stresses are relieved by the emission of electrons or helium nuclei until an atom with a stable nucleus results. This is the nucleus of the lead atom in the series under consideration. In the two other series of radioactive elements, the thorium and the actinium series, lead is also the end of the series.

9. The Rate of Radioactive Decay.—The emissions that accompany the disintegration of a radioactive element provide a measure of the rate at which the disintegration proceeds. A quantitative study of the rate of radioactive disintegration showed that the number of atoms disintegrating in a unit time is in all cases proportional to the total number of atoms of the radioactive element present. This rate is also proportional to the characteristic tendency of the atoms of the radioactive element under consideration to disintegrate. We have seen, for example, that radium atoms show some 3,000,000 times the activity of uranium atoms. This factor will have a different value for each radioactive element and will be large for those elements whose atoms show a great tendency to disintegrate and small for those elements whose radioactivity is slight.

Since the rate of decay varies in this way, it follows that in a definite interval of time a definite fraction of the total number of atoms of a given radioactive element will disintegrate. For example, let us suppose that in the case of a hypothetical radioactive element one-fourth of the total number of its atoms present dissociate every day. At the end of the first day, one-fourth of the number of atoms, present at the start, will have disintegrated and three-fourths will remain. At the end of the second day, one-fourth of the remaining three-fourths will have disintegrated, leaving three-fourths of three-fourths, or nine-sixteenths, of the original number of atoms undissociated. Obviously it will take an infinite time for all the original atoms to dissociate under these circumstances. The full life of every radioactive element, therefore, is the same—infinity—and for this reason it is not significant. The time that it takes half of a certain number of atoms of a given element to disintegrate, however, can be readily calculated and is characteristic of each radioactive element. This *half-life period*, as it is called, will be a measure of the activity of the element, since the shorter this period is, the greater will be the fraction of the total number of atoms changing in a given interval of time.[1] Thus radium with a half life of 1,690 years is some 3,000,000 times as active as uranium whose half life is 5×10^9 years. Radon, the radioactive gas into which radium atoms disintegrate, is half disintegrated after 3.85 days. It would take only a very small number of radon atoms to show the same α-ray activity as that of a relatively much greater number of radium atoms.

10. Radioactive Equilibrium.—A given amount of radium will disintegrate into radon at a rate that will remain practically constant over a period of several months owing to the comparatively long life of radium. The radon atoms when formed will start to disintegrate into radium A at a rate that is proportional to the number of radon atoms present and to their tendency to disintegrate. At first, this rate is slow since as yet only a few radon atoms have been formed; but, as more and more are formed from radium, the number disintegrating in a unit time becomes greater and greater. Eventually, the rate at which radon atoms are disintegrating will become equal to the rate at which they are being formed from radium. Then the amount of radon will remain constant; for the rates at which it is being formed and at which it is disintegrating are the same. If we start with the long-lived patriarch of the series, uranium itself, in time all its disintegration products will come into a similar equilibrium in which each member of the series is disintegrating as rapidly as it is being formed. When such an equilibrium has been established, the amount of each element present will be inversely proportional to its characteristic tendency to disintegrate, because the less the tendency of a certain element to disintegrate, the greater the number of its atoms necessary to produce the same rate of disintegration, and vice versa.

The following analogy has been often used to help explain the nature of a radioactive equilibrium. Figure 105 shows a series

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[1] The "half-life" periods of the elements of the uranium series will be found in the last column of Table 27.

of receptacles placed at different levels with holes of different sizes in their bottoms. A stream of water enters the uppermost vessel at a constant rate through a small hole in the bottom of a large reservoir. In time, water will accumulate in each of the receptacles and will come to a constant level in each. Under these conditions, the rate at which water enters a given receptacle will be equal to that at which it leaves. The smaller the hole at the bottom, the greater will be the depth of water in a given container. If we liken the series of containers to a series of radioactive elements, letting the depth of water in each correspond to the amount of each element at equilibrium and letting the size of the holes correspond to the respective tendencies of the various elements to disintegrate, the analogy becomes clear.

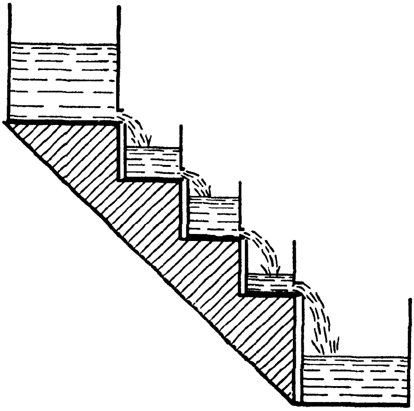

Fig. 105.—Analogy to a radioactive equilibrium.

11. The Age of the Earth.—In such a series of radioactive elements in equilibrium, the amounts of each element will remain constant, for each is being formed at the same rate at which it is disintegrating. The last element in the series, however, does not disintegrate; hence it increases in amount at a perfectly constant rate. Such an element corresponds to a receptacle with no hole out of which water can escape. In 1905, Boltwood pointed out the fact that lead was always found in uranium-containing minerals and concluded that this element was the end product of the uranium series. Since the lead in these minerals had been accumulating at a constant rate through the ages, he was able to calculate how long it would take the amount of uranium found in the mineral, to produce the amount of lead present in the same mineral and so to determine the age of the mineral. In this way he found that certain minerals were as old as 1,640,000,000 years. Geologists had always demanded millions of years for the age of the earth, but previous to Boltwood's method, no absolute proof had been advanced that the earth was so old.

12. The Energy of Radioactive Processes.—The energy associated with α- and β-particles and with γ-rays is tremendous, considering the exceedingly small quantities of the radioactive elements which produce it in disintegrating. When these emanations strike the atoms of matter, their energy is transformed into heat. The heat, generated every hour in this way by 1 g. of radium, is sufficient to raise the temperature of 1 g. of water from its freezing to its boiling point. This energy is emitted at practically a constant rate over a long period of years. At the end of 1,690 years, only half the energy, which will eventually be released by a given sample of radium, will have been liberated.

The source of this energy was a puzzling question for a long time after its discovery. It seemed to disprove the law of conservation of energy; for here was a liberation of energy from no known source. It is now known that radioactive changes involve the conversion of almost infinitesimal amounts of matter into energy. The weight of the products is actually less than that of the reactants. We shall see in the next chapter that relatively enormous amounts of energy are formed from the destruction of small quantities of matter.

13. The Commercial Production of Radium.—Radium will always remain a rare and costly element. Uranium itself is far from abundant in nature, although it is widely distributed through the earth's crust. Since radium is one of the disintegration products of uranium, these two elements occur together in minerals. Radium is also widely distributed but in exceedingly small amounts. The ratio of radium to uranium in an old uranium mineral can never exceed 1 to 3,000,000, since this represents the proportions of these two elements which are in radioactive equilibrium. The element uranium does not occur chemically uncombined in nature but occurs in its purest form as an oxide, U_3O_8 (pitchblende), which contains about 85 per cent of uranium. Every 3.9 short tons of such a high-grade ore contain only 1 g. of radium.

Previous to 1913, the principal sources of radium were pitchblende, an impure uranium oxide from St. Joachimsthal, Czechoslovakia, and autunite, a calcium uranium phosphate from Portugal. From 1913 until about 1925, the deposits of carnotite, a potassium uranyl vanadate, from Colorado and Utah were worked for their radium content. From these American deposits, over 160 g. of radium have been extracted. In 1922, the production of radium began from the rich radium-bearing ores located in Belgian Congo. This soon stopped production in America. However, in 1931, deposits of pitchblende were discovered on the rim of the Arctic Circle on Great Bear Lake some 2,000 miles north of Edmonton, Canada. From this remote region, the ore is transported by air, rail, and water to Port Hope for refining.

It is beyond the scope of this book to give a detailed description of the methods used to extract radium from its ores, but the following data will give an idea why the process is so expensive. The carnotite ore, from which radium was extracted in America, averaged a little less than 2 per cent uranium oxide. Some 2,500 tons of this mineral and the rock with which it was mixed were the source from which only 1 g. of pure radium bromide could be produced. By hand-sorting this immense amount of material, about 500 tons of milling ore were obtained which contained about 0.003 g. of radium per ton. The chemicals required in the extraction of 1 g. of radium amounted to between 450 and 500 tons together with approximately 10,000 tons of distilled water and 1,000 tons of coal. A plant employing 300 men could produce 1 g. of radium per month. Small wonder that radium cost $60,000 a gram. It can be extracted from the richer Canadian ores and sold at a profit for less than half these figures.

14. The Uses of Radium.—The greatest amount of radium is used in the treatment of disease—particularly in the treatment of cancer. Applications of radium bromide or of radon, the radioactive gas into which radium disintegrates, send out emanations that check the growth of cancerous cells and are said to stimulate the growth of healthy tissue. Radium is not a cure for cancer, nor has it replaced surgery in the treatment of the disease. Mixed with a special form of phosphorescent zinc sulfide, it is made up into luminous paint for painting the numerals on watches and other instruments. As little as 10 to 25 parts per million of radium will produce a glow that can be seen in a dark room.

EXERCISES

1. Summarize the properties of α- and β-particles and γ-rays.

2. Why is radioactivity assumed to be a property of the nucleus of an atom?

3. Why does a radioactive disintegration result in the formation of atoms of a different element?

4. An element of atomic number 88 and mass number 226 is in Group II of the periodic table. This element emits an α-particle. What are the atomic and mass numbers of the disintegration product, and in what group is it?

5. How does the emission of a β-particle change the atomic and mass numbers of an atom?

6. To what is the rate of radioactive decay proportional?

7. Why is it not a function of the temperature?

8. What is the nature of a radioactive equilibrium?

9. How may the age of a uranium-containing mineral be estimated?

10. Why is radon radioactive but chemically inert?

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CHAPTER TWENTY-NINE

THE NUCLEUS

The number of electrons in the outer shell of an atom determines in large measure its chemical properties. Yet this number in turn depends upon the more fundamental charge on the nucleus. This charge determines the element to which the atom belongs. The nucleus at the center of the atom, protected by a sheath of planetary electrons, remains unchanged by conditions of temperature and pressure which exert such a profound effect on the velocity of chemical reactions. The atom remains one of a given element through all the countless physical and chemical changes through which it may have passed. To convert it into an atom of another element must involve a method of changing its nuclear charge. We have learned that such changes take place spontaneously when radioactive atoms disintegrate. The means by which atoms may be transmuted into others at will have been discovered only recently. Alchemy remained an unsuccessful art during the centuries of its existence. The science of nuclear physics and chemistry is but an infant; but young though it may be, its achievements have been spectacular. "Atom smashing" has reached the headlines.

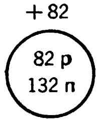
1. **Isotopes.**—Shortly after he had discovered the radioactive element ionium, Boltwood had occasion to separate a mixture of this element with the element thorium. He was completely unsuccessful, although he tried in many ways. He concluded that, although these elements had different atomic weights, they were identical in every other respect. Once these elements were mixed, their separation was impossible because of the identity of their chemical properties. Soon it was found that the lead formed in radioactive minerals, although like common lead in all other respects, possessed a lower atomic weight.

In 1886, Sir William Crookes made an amazing statement in his address to the Chemical Society of the British Association at Birmingham. He suggested that the atoms of a given element might not all be of the same weight, although their properties in all other respects were identical. He said in part:

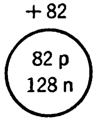
> I conceive, therefore, that when we say that the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number 38 or 42, and so on. . . . This may seem an audacious speculation, but I do not think it beyond the power of chemistry to test its feasibility.

This idea was contrary to the universally accepted atomic theory of Dalton, but as we have seen, the study of radioactivity gave the first indication of the correctness of his prophecy. Soddy suggested the name *isotopes* for the atomic species of the same element which differ in atomic weight but are identical in chemical properties.

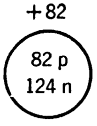
If we refer to Table 27 (page 291), we find that radium B, radium D, and lead have the same atomic numbers. Therefore, they are atoms of the same element. Their atomic weights differ, however, and hence they are isotopic. Since they have the same atomic numbers, the net charges on their nuclei and the number of their planetary electrons must be the same. Hence, in chemical properties, they must be identical. However, the number of neutrons in each kind of atom must be different since the atomic weights are not the same. The nuclei of these three isotopes are composed as follows:



RADIUM B



RADIUM D



LEAD

Since the structure of the nucleus determines the radioactivity, these atoms will show different tendencies to disintegrate or, as in the case of lead, will not disintegrate at all.

In 1912, Sir J. J. Thomson discovered that neon, an inert gas of Group 0, is composed of at least two isotopes of atomic weights 20 and 22. During the years that followed, over 400 isotopes of the chemical elements have been discovered. Very few of the elements are composed of only one kind of atom.

2. The Mass Spectrograph.—The method most commonly employed for the separation of isotopes is based on the original one of Thomson. It has been developed to its present state of perfection by the outstanding work of F. W. Aston, also of the Cavendish Laboratory, and, more recently, by Dempster, Costa, and Bainbridge. Let us consider the modified method of Bainbridge.

The free element in the gaseous state or one of its gaseous compounds is ionized by means of an electrical discharge. The positive ions are then accelerated by an electrical field and passed through a velocity filter (Fig. 106). This is an ingenious device that lets through only those ions which are moving with a certain velocity. The ions emerging from the filter enter the field of a powerful magnet which bends their hitherto straight-line paths into arcs of circles. The ions of different mass corresponding to the various isotopes of the element follow arcs of different circles. The heavier an ion, the more difficult it is for the magnet to deflect it from its original path. Hence the heavier ions follow arcs of greater radii. The ions of the same mass, *i.e.*, of the same isotope, arrive at the same point on a photographic plate. Hence the number of exposed lines on the plate indicates the number of isotopes; and the positions of the lines permit the calculation of the atomic weight of each isotope. An instrument such as we have been describing is called a mass spectrograph. The precision now attained by its use is as high as 1 part in 100,000.

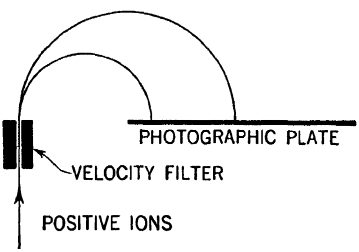


FIG. 106.—Mass spectrograph.

3. The Mass Defect.—The well-known unit of atomic weight "one-sixteenth of the weight of the oxygen atom" is now quite misleading, for there are three isotopic oxygen atoms known of masses 16, 17, and 18. The chemist's unit is really one-sixteenth of the weighted average weights of the three oxygen atoms in the proportions in which they are found mixed in nature. The physicist's unit, to which the masses of all isotopes are referred, is one-sixteenth of the mass of the oxygen-16 isotope. It is called the standard mass unit and is symbolized by M_s.

When we consider that all atoms are composed, in the last analysis, of equal numbers of electrons and protons and that the hydrogen atom is made up of one proton and one electron, it becomes apparent that the atomic masses of all isotopes should be integer multiples of the atomic mass of the hydrogen atom. That this is *not the case* is evident by an inspection of accurately determined atomic masses of isotopes such as are tabulated in Table 28. These are in every case slightly but significantly less than a whole-number multiple of the weight of the hydrogen atom. The weight of the helium atom, for example, is $4.00389M_s$. Now the helium atom consists of two planetary electrons and a nucleus of two protons and two neutrons. If we regard a neutron as an electron-proton pair, then the helium atom is made up of four electrons and four protons or, in other words, four hydrogen atoms. But four hydrogen atoms weigh

$$4 \times 1.00813M_s = 4.03252M_s$$

The whole helium atom weighs less than the sum of its parts by $0.02863M_s$.

TABLE 28.—ISOTOPES OF THE ELEMENTS OF LOW ATOMIC WEIGHT

Isotope	Mass, M_s	Isotope	Mass, M_s
${}_1H^1$	1.00813	${}_7N^{14}$	14.00750
${}_1H^2$	2.01473	${}_7N^{15}$	15.00489
${}_2He^4$	4.00389	${}_8O^{16}$	16.00000
${}_3Li^6$	6.01686	${}_8O^{17}$	17.00450
${}_3Li^7$	7.01818	${}_8O^{18}$	18.00369
${}_4Be^9$	9.01504	${}_9F^{19}$	19.00452
${}_5B^{10}$	10.01631	${}_{10}Ne^{20}$	19.99881
${}_5B^{11}$	11.01292	${}_{10}Ne^{22}$	21.99864
${}_6C^{12}$	12.00398	${}_{11}Na^{23}$	22.9961
${}_6C^{13}$	13.00761		

If we may imagine the formation of the helium atom from its constituent particles, we are considering a process that involves the destruction of 0.02863 standard mass units of matter. The old law of conservation of matter has broken down. Matter has not been destroyed exactly, but it has been converted into energy. To calculate the amount of energy created by the destruction of a certain amount of matter is not difficult. We are indebted to Einstein for the equation that makes such calculations possible:

$$E = mc^2$$

where c is the velocity of light. The destruction of one standard mass unit ($M_s = 1.55 \times 10^{-24}$ g.) gives rise to 935,000,000 electron-volts[1] of energy. Hence if we imagine the four electrons and the four protons of four hydrogen atoms merging to form a single helium atom, 27,000,000 electron-volts

$$(0.02863M_s \times 935{,}000{,}000 \text{ electron-volts}/M_s)$$

of energy would be liberated. Conversely, 27,000,000 electron-volts of energy would be required to smash a helium atom into its component particles.

The loss in mass seems to be due entirely to the formation of the nucleus. The packing together of subatomic particles in the small confines of a nucleus results in their weighing less than when they are farther apart. Since the energy produced when a nucleus is formed must be supplied to reverse the process, it follows that this may be considered as the binding energy holding the constituent particles of a nucleus together. The greater this binding energy, the more stable is the nucleus.

4. Fractional Atomic Weights.—Between the years 1815 and 1816, a London physician, Dr. William Prout, announced a hypothesis that was destined to make of him one of the major prophets of chemistry. In looking over the atomic weights of the elements that had been determined in his day, he was impressed by the fact that the majority of these were integer multiples of the atomic weight of hydrogen, the lightest element, within the limits of accuracy with which atomic weights could be calculated at that time. He, therefore, concluded that this could be no coincidence but that the atoms of all elements were merely aggregates of primordial hydrogen atoms. The oxygen atom, for example, he considered to be composed of 16 hydrogen atoms because of its atomic weight of 16. On the basis of this hypothesis, however, it was difficult to explain such an anomalous atomic weight as that of chlorine, 35.5, which could scarcely be farther away from a whole number. Either the values for the atomic weight of chlorine and of other elements with fractional atomic weights were in error, or Prout's hypothesis was wrong. Paradoxical though it may seem, both were right. Fifty years later, Stas of Ghent, who has been mentioned before in connection with

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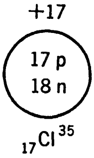
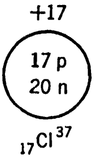
[1] An electron-volt is the quantity of energy that an electron will acquire by moving through a potential difference of one volt.

accurate atomic-weight determinations, found so many fractional atomic weights that he concluded, "I have arrived at the absolute conviction, the complete certainty, that the law of Prout is nothing but an illusion." Now a knowledge of atomic structure and of isotopes clearly indicates that Prout's guess was correct.

The element chlorine, for example, as it is found in nature consists of a mixture of two isotopes of atomic weights, 35 and 37, or, more accurately, 34.9796 and 36.9777. Every sample of chlorine found in nature contains 76 per cent of the 35 isotope and 24 per cent of chlorine-37. The atomic weight of this element determined by the method outlined in Chap. 21 is 35.457. This represents the weighted average atomic weights of the two isotopes.

These two isotopes of chlorine have the same net nuclear charge of +17 corresponding to chlorine's atomic number of 17 and, of course, the same planetary electron structure. Their nuclei, however, are different.





5. Deuterium and Heavy Water.—In 1931, Urey and Murphy of Columbia University and Brickwedde of the National Bureau of Standards reported the discovery of a heavy isotope of hydrogen of atomic mass 2. They succeeded in concentrating this isotope, which makes up only 0.02 per cent of hydrogen gas, by allowing large quantities of liquid hydrogen to evaporate, with the result that the molecules containing the lighter isotope evaporated at a faster rate. The heavy isotope was thus concentrated in the residue. Shortly thereafter, G. N. Lewis discovered the more efficient method of separation by the electrolysis of large amounts of water. Molecules containing the lighter hydrogen isotope are more readily liberated at the negative pole than are those of heavy hydrogen. The latter are thus gradually concentrated in the water that remains.

We have emphasized the fact that the properties of the isotopes of a given element are practically identical since each kind of atom has the same net nuclear charge and the same planetary electron system. However, in the case of the hydrogen isotopes, this resemblance is not so striking. An atom of heavy hydrogen has twice the mass of the ordinary hydrogen atom. Hence the ratio of the weights of the hydrogen isotopes is much greater than that of the isotopes of any other element. The difference in properties, though small, is sufficiently significant to warrant the use of a separate name for heavy hydrogen—*deuterium.* The nucleus of the deuterium atom consists of a proton and a neutron and is called a *deuteron.* The deuterium atom is given the symbol D or the equivalent H^2.

Water composed of deuterium atoms and oxygen atoms (D_2O) is called heavy water or deuterium oxide. Its density is 10 per cent higher than that of ordinary water. It freezes at 3.8°C. and boils at 101.6°C. Since water plays such an important role in chemical and biological phenomena, extensive research is being carried on to determine the effect of the substitution of heavy water for the more common form. Since organic compounds almost invariably contain hydrogen in addition to carbon, the substitution of deuterium atoms for hydrogen atoms in their molecules offers interesting possibilities. Furthermore the deuteron, the nucleus of the deuterium atom, has proved extraordinarily valuable as a subatomic projectile in transmutation experiments.

6. Transmutation, or the process of changing one element into another, was little more than an alchemist's dream 25 years ago. It was known to occur spontaneously in the disintegration of naturally radioactive elements, but this process is beyond the control of man. A radioactive element disintegrates at a constant rate which is determined by the nature of the nuclei of its atoms. These nuclei, protected from the shocks of collisions with other atoms by their planetary-electron sheaths, remain unaffected by high temperatures. To effect transmutation of a stable nucleus, some means had to be discovered by which the planetary-electron sheath could be penetrated and a blow struck with sufficient energy. For this purpose, none but subatomic particles were small enough and none save the α-particles, emitted at high velocities from naturally radioactive nuclei, had sufficient kinetic energy.

In 1919, Lord Rutherford announced the first successful transmutations. By bombarding the atoms of some of the elements of low atomic weight with α-particles, he succeeded in knocking protons from their nuclei. Since the number of protons in the nucleus of an atom determines the element to which the atom belongs, the loss of a proton indicates that a transmutation has been effected. α-Particles, you will remember, are nuclei of helium atoms and are composed of two protons and two neutrons. These are ejected from the nuclei of certain naturally radioactive atoms with velocities of the order of one-fifteenth of the velocity of light, fast enough to cover the distance of the earth's circumference thirty times in a minute. To give these doubly charged particles such a velocity would require a difference in potential of some 2,500,000 volts, far beyond attainment at the time Rutherford announced his first successful transmutations.

The use of α-particles from radioactive nuclei to accomplish transmutation was subject to severe limitations. These particles are ejected in all directions from a radioactive source. The radioactive atom cannot be persuaded to take careful aim at some target atom before letting the α-particle fly. Hence the efficiency of the process is extremely low, since atomic nuclei are very small, compared with the space between the planetary electrons and the space between atoms. Less than one in every 50,000 atoms found their mark in Rutherford's experiments. Further, since both the α-particles and the nuclei of the target atoms are positively charged, the forces of repulsion must be conquered before transmutation may take place. Since protons and deuterons, nuclei of ordinary and heavy hydrogen atoms, respectively, bear single positive charges, their use as agents of transmutation is more efficient. Unfortunately, these nuclei are not among the products of radioactive disintegration. Hence, they must be given sufficient kinetic energy by acceleration through a sufficiently large difference in potential.

7. "Atom-smashing" Machines.—The production of differences in potential as large as several million volts with which to accelerate subatomic particles presented interesting problems to experimental physicists. Several successful machines are in operation which produce such voltages directly. Of this type, the electrostatic generators, designed by Van der Graaff of the Massachusetts Institute of Technology, produce potential differences of 3 to 5 million volts.

One of the most ingenious, efficient, and successful machines is the cyclotron of E. O. Lawrence of the University of California at Berkeley. Instead of producing high voltages directly, protons, deuterons, or helium nuclei are accelerated a hundred or more successive times each through a difference in potential of the order of 100,000 volts. A stream of hydrogen gas is ionized into protons (or deuterons) and electrons through contact with an electrically heated filament. This occurs at the center of an evacuated chamber, cylindrical in shape and between the poles of a powerful electromagnet. Here they move in circular paths in the magnetic field and in the space within two hollow D-shaped electrodes. These look as if they had been formed from a gigantic, old-fashioned pillbox cut in half vertically. The electrodes are connected to a source of current which alternates their polarity at intervals equal to the time required by a proton to describe a half circle within a Dee.

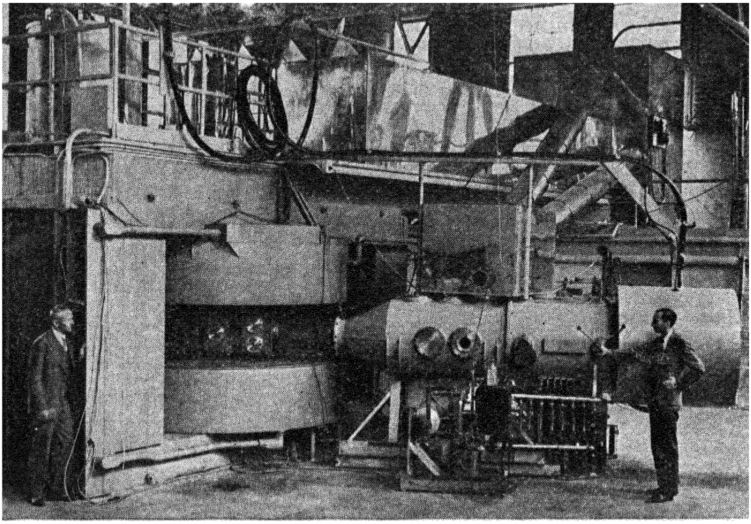


Fig. 107.—The "60-inch" cyclotron in the Radiation Laboratory at the University of California in Berkeley. (*Courtesy of Dr. Donald Cooksey.*)

As each proton enters the gap between the Dee's, it is attracted to the electrode of opposite polarity. Within this electrode and in the field of the magnet it describes a circular path. When it reaches the gap, the polarity of the Dee's changes and the proton gains in kinetic energy as it travels across the potential difference of the gap toward the other electrode which now is negatively charged. Since its velocity is greater when it enters this electrode, it moves in a circular path of greater radius. However, the time it takes to complete this greater distance is the same because of its increased velocity. Hence, it arrives at the gap at the instant the polarity again changes. After a hundred or more accelerations across the gap, its velocity is so great that its path follows the circumference of the Dee's. At this point, a negatively charged plate deflects the proton stream through a thin foil window into the target of the element in which transmutation is to be induced.

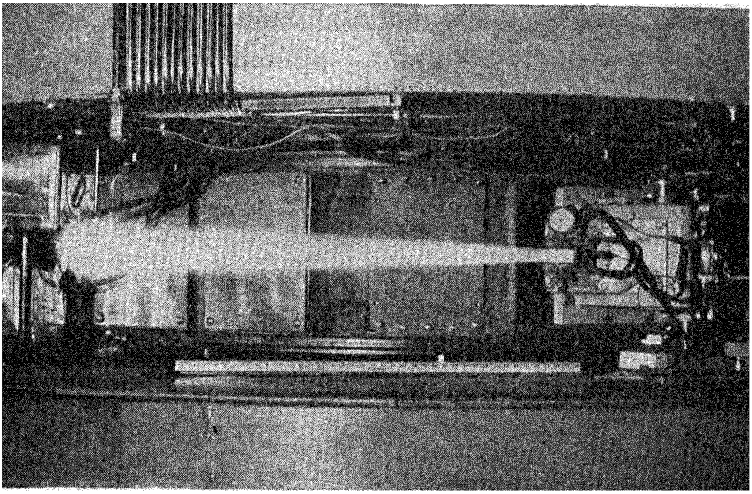


FIG. 108.—A beam of purple light marks the path of a stream of deuterons emerging from the cyclotron. (*Courtesy of Dr. Donald Cooksey and the Radiation Laboratory at the University of California.*)

There are now nearly 20 cyclotrons in operation in this country. By far the largest will be the one under construction at Berkeley, Calif. This instrument will use a chamber 20 ft. in diameter with 1,000,000 volts potential difference across the Dee's. It will accelerate protons to a kinetic energy of 100,000,000 electron-volts.

Neutrons have proved to be very effective agents of transmutation. Since they are without charge, they cannot be accelerated in a cyclotron. However, neutrons are easily generated by bombarding beryllium powder with α-particles from radon. Their effectiveness in transmutation is due to the lack of any force of repulsion between them and the target nuclei. Oddly enough, neutrons moving at low velocities are, in general, more effective than faster ones.

8. Transmutation Equations.—Transmutation reactions may be summarized by equations. The nuclei involved are designated by the symbols of the corresponding elements. The atomic number, or the charge on the particle, is placed below and to the left of each symbol; and its mass number, or isotopic mass to the nearest whole number, appears above and to the right. Thus, when Rutherford bombarded nitrogen with α-particles, or helium nuclei, the isotope of oxygen of mass number 17 and protons were formed:

$$_7N^{14} + {}_2He^4 \rightarrow {}_8O^{17} + {}_1H^1$$

In such equations the atomic numbers and the mass numbers balance.

9. Artificial Radioactivity.—In 1934, the Curie-Joliots discovered that the products of certain transmutation reactions are radioactive. When aluminum is bombarded with α-particles, neutrons are emitted and a radioactive isotope of phosphorus is formed:

$$_{13}Al^{27} + {}_2He^4 \rightarrow {}_{15}P^{30} + {}_0n^1$$

These phosphorus atoms enter into a radioactive disintegration by emitting positrons, or positive electrons:

$$_{15}P^{30} \rightarrow {}_{14}Si^{30} + {}_1e^0$$

Thus, for the first time radioactive isotopes of the elements of low atomic numbers were produced. As in the cases of naturally radioactive elements, the rate at which artificially radioactive atoms disintegrate is proportional to their number and to their inherent tendency to disintegrate. Each type of radioactive atom is characterized by a half-life period, the time taken for half the atoms, present at a given time, to disintegrate. Thus the half-life period of radiophosphorus, $_{15}P^{30}$, is 2.5 min. At the end of 5 min., one-fourth of the original number will remain; after 7.5 min., one-eighth; after 10 min., one-sixteenth; etc. The full life of any radioactive element is always infinite and, therefore, has no significance. The shorter its half-life period, however, the greater its radioactivity.

The discovery by the Curie-Joliots of artificial radioactivity was followed by the identification of many radioactive isotopes;

today, at least one such is known for each of the elements in the periodic table. A given kind of radioactive atom may be prepared by several different transmutation reactions. Thus, radiophosphorus may be prepared as follows:

$$
\begin{gathered}
{}_{13}\mathrm{Al}^{27} + {}_{2}\mathrm{He}^{4} \rightarrow {}_{15}\mathrm{P}^{30} + {}_{0}\mathrm{n}^{1} \\
{}_{16}\mathrm{S}^{32} + {}_{1}\mathrm{H}^{2} \rightarrow {}_{15}\mathrm{P}^{30} + {}_{2}\mathrm{He}^{4}
\end{gathered}
$$

Radioactive sodium results from several transmutations:

$$
\begin{gathered}
{}_{13}\mathrm{Al}^{27} + {}_{0}\mathrm{n}^{1} \rightarrow {}_{11}\mathrm{Na}^{24} + {}_{2}\mathrm{He}^{4} \\
{}_{12}\mathrm{Mg}^{24} + {}_{0}\mathrm{n}^{1} \rightarrow {}_{11}\mathrm{Na}^{24} + {}_{1}\mathrm{H}^{1} \\
{}_{11}\mathrm{Na}^{23} + {}_{1}\mathrm{H}^{2} \rightarrow {}_{11}\mathrm{Na}^{24} + {}_{1}\mathrm{H}^{1}
\end{gathered}
$$

However prepared, radiosodium disintegrates as follows:

$$
{}_{11}\mathrm{Na}^{24} \rightarrow {}_{12}\mathrm{Mg}^{24} + {}_{-1}\mathrm{e}^{0}
$$

The usefulness of a given radioactive isotope is in large measure determined by its half-life period. If this is too short, the isotope is too unstable to be useful. In Table 29, the properties of radioactive isotopes of the more common elements are listed. Under Source in this table are listed the symbols of the target elements followed by the bombarding particles in parentheses.

TABLE 29.—THE PROPERTIES OF RADIOACTIVE ISOTOPES OF COMMON ELEMENTS

Symbol	Particle emitted	Half-life period	Source
${}_{1}\mathrm{H}^{3}$	${}_{-1}\mathrm{e}^{0}$	31 yr.	H^{2}(d)
${}_{6}\mathrm{C}^{11}$	${}_{+1}\mathrm{e}^{0}$	20.5 min.	B(d), B(p), C(n)
${}_{6}\mathrm{C}^{14}$	${}_{-1}\mathrm{e}^{0}$	1,000 yr.	C^{13}(d), N(n)
${}_{7}\mathrm{N}^{13}$	${}_{+1}\mathrm{e}^{0}$	11 min.	B(α), N(n), C(d), C(p)
${}_{8}\mathrm{O}^{15}$	${}_{+1}\mathrm{e}^{0}$	126 sec.	N(d), O(n)
${}_{9}\mathrm{F}^{18}$	${}_{+1}\mathrm{e}^{0}$	112 min.	Ne(d)
${}_{11}\mathrm{Na}^{24}$	${}_{-1}\mathrm{e}^{0}$	14 hr.	Na(d), Na(n), Al(n), Mg(n), Mg(d)
${}_{12}\mathrm{Mg}^{27}$	${}_{-1}\mathrm{e}^{0}$	10.2 min.	Mg(d), Al(n), Mg(n)
${}_{14}\mathrm{Si}^{31}$	${}_{-1}\mathrm{e}^{0}$	170 min.	Si(d), P(n), Si(n)
${}_{15}\mathrm{P}^{32}$	${}_{-1}\mathrm{e}^{0}$	14.5 days	P(d), S(d), P(n), S(n), Cl(n)
${}_{16}\mathrm{S}^{35}$	${}_{-1}\mathrm{e}^{0}$	80 days	Cl(n)
${}_{17}\mathrm{Cl}^{34}$	${}_{+1}\mathrm{e}^{0}$	33 min.	P(α), S(d), Cl(n)
${}_{19}\mathrm{K}^{42}$	${}_{-1}\mathrm{e}^{0}$	12.2 hr.	K(n), Ca(n), K(d), Sc(n)
${}_{20}\mathrm{Ca}^{45}$	${}_{-1}\mathrm{e}^{0}$	180 days	Ca(n), Ca(d), Sc(n)
${}_{26}\mathrm{Fe}^{59}$	${}_{-1}\mathrm{e}^{0}$	40 days	Co(n), Fe(d)
${}_{53}\mathrm{I}^{128}$	${}_{-1}\mathrm{e}^{0}$	25 min.	I(n)

10. Detection of the Products.—Since the products of a transmutation, including those of radioactive disintegration, are moving in general with high velocities, they are able to strip electrons from the atoms of any gas in their paths. Charged gas ions are produced by these encounters, and the gas becomes a conductor of electricity. If such ionization occurs in a dust-free atmosphere supersaturated with water vapor, liquid water droplets condense on each gas ion. The track of the product of disintegration becomes visible and can be photographed. This, in brief, is the principle of the Wilson cloud chamber.

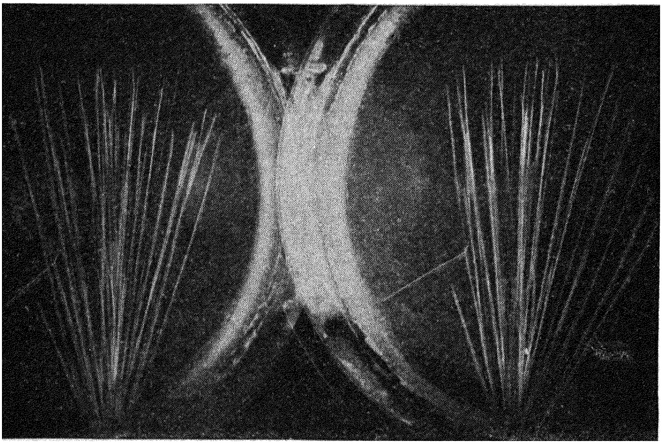


FIG. 109.—Two simultaneous pictures taken at different angles of cloud-chamber show tracks of α-particles one of which has collided with a sulfur atom nucleus. (*Courtesy of Dr. A. F. Kovarik and Dr. R. L. Anthony.*)

More frequently used, however, is the Geiger-Müller counter. This instrument consists of a cylindrical cathode and a wire anode placed at the axis of the cylinder. Both electrodes are sealed in a glass tube filled with a dry gas at a pressure of about 0.1 atm. The product of transmutation enters the counter through a thin window and creates ions by stripping electrons from the gas atoms in the tube. These ions are accelerated sufficiently toward the electrode of opposite charge to ionize additional gas atoms. The increased conductivity of the gas, owing to this ion formation, causes a momentary discharge in the tube which can be magnified in the external circuit by vacuum-tube amplification. The amplified current is sufficient to produce a "click" in a loudspeaker, a "count" in a counting device, or to move a stylus on a recording drum. Electrons, both negative and positive, emitted by the nuclei of radioactive atoms, can be readily detected by this device.

11. Synthesis of Atoms of Unknown Elements.—In 1934, four elements of atomic numbers 43, 61, 85, and 87 were known. The last of the alkali metals, 87, was detected by Mlle. Perey as a member of the actinium series of radioactive elements. Element 43 in Group 7 with manganese was prepared as a product of the transmutation of molybdenum under neutron or deuteron bombardment. The halogen of atomic number 85 was prepared by bombarding bismuth with α-particles. Finally element 61, a rare earth, was formed by the transmutation of neodymium by deuterons; but because of the similarity in the chemical reactions of the rare earths, its properties could not be determined. The properties of elements 43 and 85 have been determined, although only about 10^{-12} g. have been produced. Since these isotopes are radioactive, the part that they play in various chemical reactions can be followed. With this knowledge, it is possible to predict in what types of mineral they may be found and the steps to be taken in their extraction.

12. Properties of Tracer Isotopes.—It must be kept in mind that isotopes are atoms of the same element which differ only in the number of neutrons in their nuclei. The charge of the nucleus of each isotopic atom is the same, and so also is the number of planetary electrons. Hence, in their chemical properties, isotopes are identical. Most of the elements are mixtures of isotopes. However, the relative amounts of each isotope are the same in all samples of the element. The fact that these proportions have remained constant and that no concentration of one isotope at the expense of the others has occurred is excellent evidence that the isotopes of an element have the same chemical properties.

If radioactive atoms are mixed with nonradioactive atoms of the same element, they will thereafter be inseparable, regardless of the number of chemical changes through which the element passes. But throughout the course of these changes, the activities of the radioactive isotope, and therefore of the nonradioactive atoms of the element, may be followed by Geiger-Müller counters or other suitable means. Hence the name "tracer atoms" has been given to radioactive atoms used in this way to trace the course of an element through changes in all ordinary chemical, physical, and physiological systems.

If a process is known by which the stable isotopes of an element may be separated, it is possible to enrich a sample of an element with one of its isotopes. Thereafter, the presence of this enriched sample may be detected by means of a mass spectrometer. This is a more laborious process than the detection of radioactivity. Yet it must be resorted to when radioactive isotopes of long enough half-life periods are lacking.

13. Applications of the Products of Transmutation.— Tracer isotopes have found many and varied applications. In the field of animal nutrition, their use has given definite answers to many problems as to the fate of foods in our bodies. By feeding animals with synthetic fats and amino acids (55-10) in whose molecules tracer atoms are present, it has been possible to trace their subsequent histories. Using radioactive iron, the fate of this element in normal and anemic animals has been studied. Radioactive iodine is being used to study the functioning of the healthy and diseased thyroid gland, which plays such an important role in the regulation of growth and body heat. The mechanism of the all-important reactions of photosynthesis (55-1), by which plants store the energy of the sun's rays in sugar and starch, is being investigated using carbon dioxide in which are radioactive carbon atoms.

One cannot help being impressed by the rapidity with which discoveries in the field of nuclear physics have been put to practical use. Ten years ago, a cyclotron was a luxury that few universities could afford. Its products are formed in such meager amounts that they cannot be weighed. Ten years ago such research was pure science indeed. Today the products of transmutations are used in the steel mill and in the hospital. Physicists, chemists, and physiologists have pooled their knowledge and resources, and with such collaboration who can predict what will develop in the future?

EXERCISES

1. What are isotopes?

2. Explain how the masses of the isotopes of an element may be determined.

3. Why is not the mass of a given isotope a whole-number multiple of the mass of the hydrogen atom?

4. Why is the chemists' atomic weight of chlorine 35.457?
5. What is heavy hydrogen?
6. What is a deuteron?
7. How many different molecules of H_2O are possible? See Table 28.
8. What subatomic particles have been used successfully as agents of transmutation?
9. What does the following equation mean? ${}_3Li^6 + {}_1H^2 \rightarrow 2\,{}_2He^4$.
10. What is artificial radioactivity?

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CHAPTER THIRTY

IONIZATION OF SALTS

The theories of atomic structure that we have been studying offer a plausible explanation of the existence of ions. However, as early as 1887, before the existence of charged subatomic particles was known, Svante Arrhenius first clearly stated a theory of ionization based on experimental facts discovered by Faraday, van't Hoff, and others. The essential postulates of his theory have stood the test of time. However, modifications have been made from time to time as new experimental evidence was discovered. The original Arrhenius theory assumed that both acids and salts behaved similarly when dissolved in water. This is no longer considered sound theory. For this reason, we shall consider the theory of ionization as applied to salts, first, modifying the original Arrhenius theory to conform with the now known facts.

Hitherto, whenever we have had occasion to present a theory, we have tried to show how each of its postulates was derived from and explains the facts. As the theory background—we might call it the philosophy—of a science develops and becomes more elaborate, new postulates may be derived from more fundamental theory rather than directly from experimental facts. So in developing the postulates of the theory of ionization, some may be derived directly from facts but others from more fundamental theory.

1. Aqueous Salt Solutions and the Solution Laws.—When nonelectrolytes, like sugar and glycerin, are dissolved in water, the vapor pressure and the freezing point of the water are lowered and its boiling point is raised. Further, if such solutions are dilute, the lowering of the vapor pressure and of the freezing point and the rise in boiling point are proportional to the molecular concentration of the dissolved nonelectrolyte. Thus we have learned (20-3) that the freezing point of a solution, which contains one mole of any nonelectrolyte dissolved in 1,000 g. of water, is $-1.86°C$. This is decidedly not the case when solutions of the same molality of salts are considered.

Let us prepare 0.01m solutions in water of two nonelectrolytes, sugar and glycerin, and of two electrolytes, potassium chloride and potassium sulfate. These solutions will be sufficiently dilute so that the solution laws should hold. If the salts exist in solution as single molecules, each solution will be of the same molecular concentration. Table 30 summarizes the preparation of each solution and the results of the determination of the freezing-point lowering, ΔT_f, in each case.

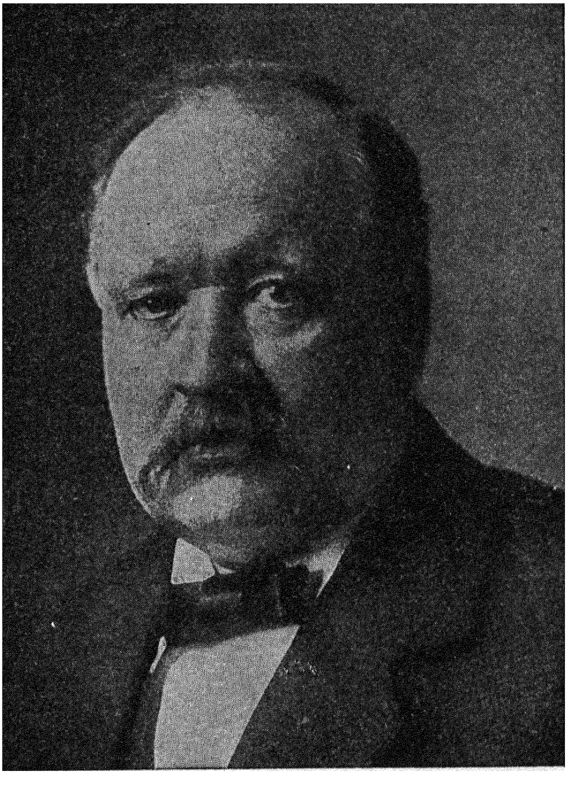

FIG. 110.—Svante Arrhenius. (*Courtesy of Journal of Chemical Education.*)

Thus the actual lowering of the freezing point in the case of the potassium chloride solution is actually nearly twice that of a solution of the same molality of a typical nonelectrolyte. In the case of potassium sulfate, the lowering is nearly three times as great. Had we measured the lowering of the vapor pressure or the rise in boiling point, the same effects would have been discovered.

TABLE 30.—FREEZING-POINT LOWERING IN AQUEOUS SOLUTIONS OF THE SAME MOLALITY

	Nonelectrolytes		Electrolytes	
	Sugar	Glycerine	Potassium chloride	Potassium sulfate
Formula	$C_{12}H_{22}O_{11}$	$C_3H_8O_3$	KCl	K_2SO_4
One mole	342 g.	92 g.	74.6 g.	174 g.
Number of molecules per mole	6.02×10^{23} in each case if the formulas represent single molecules			
0.01 molal solution (g./1,000 g. H_2O)	3.42	0.92	0.746	1.74
Molecular concentration	Same in each case if formulas represent single molecules in solution			
Theoretical ΔT_f	−0.0186° in each case if solute particles are single molecules corresponding to formulas			
Observed ΔT_f	−0.0186°	−0.0186°	0.0361°	0.0521°

In general, then, *salts in aqueous solution lower the vapor pressure and the freezing point and raise the boiling point nearly a small whole number times as much as do nonelectrolytes in aqueous solutions* **of the same molality.** The phrase "of the same molality" has been printed in boldfaced type to emphasize the fact that the effects are strictly comparable only when the solutions are of the same concentration. A lump of sugar in a cup of water will cause a far greater lowering of the freezing point than a pinch of salt in a swimming pool.

In discussing the reason why the vapor pressure of a liquid is lowered by the addition of a solute, it was pointed out that each particle of the solute takes the place of a solvent molecule (20-1). The solvent molecules are less concentrated in a solution than they are in the pure solvent. Hence the rate of evaporation of solvent from a solution is less, and so the vapor pressure is lower. When the solute particles are single molecules as in the case of nonelectrolytes like sugar and glycerine, each solute molecule, regardless of kind, takes the place of a water molecule. When equal numbers of solute molecules are dissolved in the same weight of water, the effect on the vapor pressure is the same. Since the freezing-point lowering and the boiling-point rise are determined by the vapor-pressure lowering, all three effects are determined by the number of solute particles in a given weight of water.

As shown in Table 30, the freezing-point lowering is the same for 0.01*m* solutions of sugar and glycerin. In these solutions, therefore, we assume that the number of solute particles per unit weight of water is the same. Since the same number of molecules (0.01 mole) of each was dissolved in 1,000 g. of water, we may further assume that each solute particle is a single molecule. If potassium chloride and potassium sulfate exist as molecules, corresponding to the formulas KCl and K_2SO_4, then the 0.01*m* solutions of these salts should freeze at the same temperature as those of the two nonelectrolytes. Actually, the lowering is nearly twice as great in the case of potassium chloride. This lowering indicates the presence of twice as many particles as would have been present if single KCl molecules were present. The evidence points definitely to the existence of potassium and chlorine atoms as the solute particles. In the case of potassium sulfate, the lowering, three times as great, indicates three times as many particles of solute as would have been the case if each particle were a K_2SO_4 molecule. Hence we suspect the existence in solution of two potassium atoms and one sulfate group instead of single K_2SO_4 molecules.

We must assume that *salts exist in aqueous solution as particles (ions) that are smaller than molecules.*

2. Electrical Conductivity of Salt Solutions.—*All aqueous salt solutions are conductors of electricity.* This fact leads to the assumption that electrically charged particles must exist in such solutions which can carry the current through the solution. Since only those solutions conduct electricity which have abnormally low freezing points, we must assume that *the particles, "smaller than molecules," in aqueous salt solutions are electrically charged.* These particles we shall call ions. *An ion is an electrically charged atom or group of atoms.*

3. Ionic Migration.—When salt solutions are subjected to electrolysis (17-2), metals or hydrogen are liberated at the negative electrode (cathode) and nonmetals are liberated at the positive electrode (anode). This seems to indicate that metal ions are attracted by and migrate to the cathode. Conversely, nonmetal ions must move to the anode. Since oppositely charged objects attract each other, we assume that *metal ions are positively and nonmetal ions negatively charged.* Positively charged ions are called *cations* since they migrate to the cathode, and nonmetal ions are called *anions* since they migrate to the anode.

4. Faraday's Law and the Charge on an Ion.—Michael Faraday was the first to discover the fundamental relationship between the quantity of electricity that may be passed through a solution and the amount of chemical action that it produces. *The same quantity of electricity liberates weights of different elements at the electrodes which are proportional to their equivalent weights.* You will recall that the equivalent weight of an element is equal to its atomic weight divided by its valence. Thus 107.88/1 weights of silver (atomic weight = 107.88; valence = 1) are equivalent to 63.57/2 weights of divalent copper and to 197.2/3 weights of trivalent gold. An experiment which Faraday might have carried out in this connection will make the meaning of his law clear. Three electrolytic cells are connected in series to a source of direct current (Fig. 111). Connected in this way, the same amount of electricity must pass through each of the cells. In the first cell is a solution of silver nitrate; in the second, a solution of copper sulfate; and in the third, one of gold chloride. We have purposely chosen a salt of a monovalent, Ag, a divalent, Cu, and a trivalent, Au, metal the better to illustrate the law. The metal in each case will be deposited on the cathode; and its weight can be easily determined by weighing this electrode before and after electrolysis. The gain in weight will be equal to the

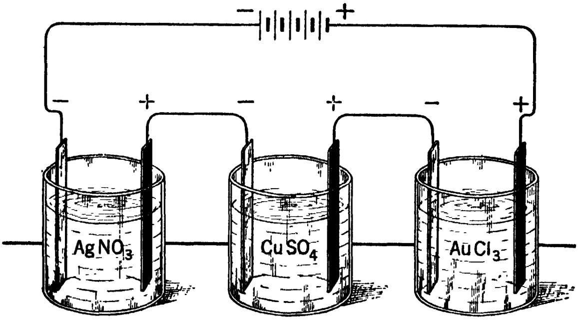

FIG. 111.—An experiment illustrating Faraday's law.

weight of the metal deposited on the electrode by the current during this electrolysis. As the result of one experiment, it was found that the passage of 4,825 coulombs of electricity through the three cells deposited 5.394 g. of silver, 1.589 g. of copper, and 3.29 g. of gold. These weights are chemically equivalent since they are in the same ratio as the equivalent weights of the metals as can be seen from Table 31.

TABLE 31

Metal	Metal deposited by 4,825 coulombs, g.	Chemical equivalents
Silver	5.394	107.88
Copper	1.589	31.785
Gold	3.290	65.73

Since

$$\frac{5.394}{1.589} = \frac{107.88}{31.785}$$
$$\frac{5.394}{3.29} = \frac{107.88}{65.73}$$
$$\frac{1.589}{3.29} = \frac{31.785}{65.73}$$

From this law it follows that there must be a certain quantity of electricity which will deposit a gram-equivalent weight of any element. This quantity we can calculate from the above results. If 4,825 coulombs deposit 5.394 g. of silver, how many will deposit 107.88 g.?

$$\frac{5.394\text{ g.}}{4{,}825\text{ coulombs}} = \frac{107.88\text{ g.}}{x\text{ coulombs}}$$

Solving, $x = 96{,}500$ coulombs $= 1$ faraday

This is the amount of electricity that will deposit a gram-equivalent weight of an element during electrolysis, and it is called, appropriately, a *faraday*.

Faraday's law gives us information as to the magnitude of the charge on an ion. It is evident that 96,500 coulombs, or 1 faraday, of electricity will deposit a gram-equivalent weight of an element by neutralizing the charge on its ions at the electrode at which the discharge occurs. One faraday, for example, will discharge 107.88 g. of silver ions, 31.785 g. of copper ions, and 65.7 g. of gold ions as shown in Table 32.

Keeping in mind that the gram-equivalent weight is equal to the gram-atomic weight divided by the valence, we can calculate that it takes 1 faraday to discharge a gram-atomic weight of a univalent metal like silver, 2 faradays for a gram-atomic weight of a divalent metal like copper, and 3 faradays for a gram-atomic weight of a trivalent metal like gold. The same relationship holds for the nonmetallic ions. Since gram-atomic weights of all elements contain the same number of atoms, it follows that it takes twice as much electricity to discharge a divalent ion and three times as much to discharge a trivalent ion as to discharge a univalent ion. *The magnitude of the charge on an ion, therefore, is proportional to its valence.* Hence we write the silver ion as Ag^+, the copper ion as Cu^{++}, the gold ion as Au^{+++}, the chloride ion as Cl^-, the sulfate ion as $SO_4^=$, etc.

TABLE 32

Metal	Valence	G.-eq. wt. = g.-at. wt. ÷ valence	Electricity necessary to deposit a g.-eq. wt., faradays	Gram-atomic weight	Electricity necessary to deposit a g.-at. wt., faradays
Silver.......	1	107.88	1	107.88	1
Copper......	2	31.785	1	63.57	2
Gold........	3	65.73	1	197.2	3

5. The Faraday and the Charge on an Electron.—One faraday, or 96,500 coulombs, must represent the amount of negative electricity needed to neutralize the positive charges on one gram-atomic weight of silver ions. A single silver ion is discharged by gaining an electron from the cathode:

$$Ag^+ + e^- \rightarrow Ag^0$$

A gram-atomic weight and, therefore, Avogadro's number of silver ions must gain Avogadro's number of electrons. The total charge on this number of electrons must, therefore, be equal to 96,500 coulombs. By dividing the charge on a single electron into 96,500 coulombs, Avogadro's number may be calculated. The electronic charge is equal to 4.80×10^{-10} electrostatic unit, or to 1.60×10^{-19} coulomb. Hence Avogadro's number

$$N = \frac{9.65 \times 10^4}{1.60 \times 10^{-19}} = 6.02 \times 10^{23}$$

This is one of the most accurate methods by which Avogadro's number can be determined.

6. Water as a Solvent for Salts.—Water is by all odds the best solvent for salts. The reasons why salts are so generally soluble in water but so sparingly soluble in solvents like benzene are fairly well known. Water is successful above all other solvents in breaking down the strong forces of electrical attraction that hold the ions so firmly in the crystal lattice of a salt. These Coulomb forces vary directly as the amount of charge on each ion and inversely as the square of the distance between them.

$$F_c \propto \frac{e^+e^-}{d^2}$$

We may convert the above variation into an equation by introducing the constant D

$$F_cD = \frac{e^+e^-}{d^2}$$

or

$$F_c = \frac{e^+e^-}{Dd^2}$$

The value assigned to this constant depends on the nature of the medium that separates the ions. When no such medium is present, as is the case in the crystals of a salt, the value of this constant is unity. When, however, a medium like water is between the ions as in aqueous salt solutions, D has a definite value characteristic of the medium. Since it occurs in the denominator, the greater its value, the smaller are the Coulomb forces between the dissolved ions. It is called the *dielectric constant* of the medium and is a direct measure of the ability of the medium to reduce the Coulomb forces between the ions of a salt. The dielectric constant of water is about 80, higher than that of any common solvent. Hence the force of attraction between oppositely charged ions, dissolved in water, is eighty-fold less for the same average distance apart than in the crystals of the salt. The ions, therefore, are readily detached by water from the surface of a salt crystal and in solution lead an independent existence showing little or no tendency to form ion pairs. On the other hand, the dielectric constant of benzene is only 2.3. Thus the Coulomb forces are not reduced sufficiently to enable this solvent to break down the crystal structure of a salt to any appreciable extent.

7. The Ionic Atmosphere.—Earlier in this chapter we have seen that the lowering of the freezing point for the 0.01m potassium chloride solution was *nearly* twice that of the sugar solution of the same molality. We were very careful not to italicize the "nearly" at that point. Now, however, we must return in the interests of accuracy. Twice as many ions in the salt solution as molecules in the sugar solution should reduce the freezing point of water twice as much unless factors exist that complicate the picture.

The forces of interionic attraction in aqueous solutions, though small compared with those in salt crystals, are still in operation. They interfere with the movements of the ions. Debye and Hückel have pointed out that each ion is surrounded on the average by more ions of opposite than of like charge. This *ionic atmosphere* of ions of opposite charge exerts a "drag" on the free movements of an ion. Hence the deviations from the solution laws, indicated by the "nearly" in the above statements, are due to interionic, or Coulomb, forces of attraction just as deviations from the gas laws are due to the van der Waals forces of intermolecular attraction.

Since diluting a salt solution by the addition of water increases the average interionic distance and so reduces the force of attraction, ions are more free to move. The more dilute the potassium chloride solution, the more nearly twice the lowering of the freezing point. Further, we should expect that the forces are greater, the more highly charged the ions. This is the case. Deviations are greater, the greater the valence of the ions of a salt.

8. The Properties of Ions.—One of the most puzzling implications of the theory of ionization to chemists at the time when the theory was first proposed was that metal and nonmetal "atoms" could exist in aqueous salt solutions. For example, if sodium and chlorine "atoms" exist in aqueous solutions of common salt as Arrhenius suggested, then why does not the sodium react violently with water to liberate hydrogen gas and form sodium hydroxide (10-3)? Further, why do not the toxic properties and disagreeable odor of chlorine (17-3) make our sea coasts uninhabitable? They failed to grasp what Arrhenius himself had carefully pointed out that *the properties of an ion are entirely different from those of the corresponding neutral atom.* To eat metallic sodium would cause dire consequences too horrible to contemplate. To season one's soup with salt is entirely safe. The properties of neutral sodium atoms in the free metal are quite different from those of the sodium ions in any sodium salt.

Each of the ions is characterized by its own set of properties. The properties of an aqueous solution of a given salt are those of the ions of which it is composed. A knowledge of this fact simplifies the study of aqueous salt solutions, since we need study the properties of the ions only and not those of the combination of ions found in a given salt. The properties of the copper ion, for example, are the same whether it is introduced into a solution by dissolving copper sulfate, copper nitrate, or any other copper salt.

One final word of caution. It is impossible to prepare a solution containing one kind of ion only. Positive ions are always paired with negative ions in salt crystals. The total positive charge on the cations is exactly balanced by that of the anions, and the salt as a whole is electrically neutral. To prepare a solution that contains copper ions, some copper salt must be dissolved in water and thus some negative ions introduced at the same time.

9. Summary of the Theory of Ionization as Applied to Salts.—We have assembled below in parallel columns the facts upon which the theory of ionization is based and the corresponding postulates of the theory.

Facts	*Theory*
1. Salts in aqueous solution lower the vapor pressure and the freezing point and raise the boiling point nearly a small whole number times as much as do nonelectrolytes in aqueous solutions of the same molality.	1. Salts exist in aqueous solutions as particles that are smaller than molecules.
2. Aqueous salt solutions are conductors of electricity.	2. The solute particles in aqueous solutions are electrically charged atoms or groups of atoms called ions.
3. Metals are liberated at the cathode and nonmetals at the anode when salt solutions are subjected to electrolysis.	3. Metal ions are positively and nonmetal ions are negatively charged.
4. The number of faradays of electricity required to liberate a gram-atom of an element is equal to the valence of the element.	4. The number of unit charges on an ion is equal to its valence.
5. The multiple referred to in 1 is nearly but not exactly a small whole number.	5. Forces of interionic attraction hamper the free movements of ions in solution.

In closing this chapter, you will be interested in the following quotation from an address of Arrhenius before the Chicago Section of the American Chemical Society in which he tells in his own highly entertaining way of the reception that was accorded his theory:[1]

> I came to my professor, Cleve, whom I admire very much, and I said: "I have a new theory of electrical conductivity as a cause of chemical reactions." He said: "That is very interesting," and then he said "Good-by." He explained to me later, when he had to pronounce the reason for my receiving the Nobel Prize for that work, that he knew very well that there are so many different theories formed, and that they are all almost certain to be wrong, for after a short time they disappear; and, therefore, by using the statistical method of forming his ideas, he concluded that my theory also would not exist very long. [Laughter]
>
> I was not very content with that opinion, and then I thought, in foreign countries there are such prominent scientists, they might look at it differently; it might appeal to them. Then I wrote to Clausius, and said: "What do you think of that?" I wrote to Ostwald—he worked on the same line. I wrote to Thomson. I received friendly answers from most of these scientists, and they were very glad to make my acquaintance, and so on, but it was not very much more. [Laughter] The only exception was Ostwald, and he describes himself, how it was that he got on the same day this dissertation, a toothache, and a nice daughter, and that was too much for one day, and the worst was the dissertation, for the others developed quite normally. But this bulky dissertation was very hard for him, and he said there were indications that some of its parts were not quite in order. There were some unfamiliar expressions and sanguine ideas, but, finally, he found it still might be good to look into, if it was true. . . . Then he came to see me personally, and spoke with me, and we had some very pleasant days together.
>
> Then Ostwald, of course, visited my dear friend and teacher, Cleve. Ostwald spoke to him one day in the laboratory. I came a little later. I was not expected, and then I heard Cleve say. "Do you believe sodium chloride is dissolved into sodium and chlorine?" "In this glass I have a solution of sodium chloride; do you believe there are sodium and chlorine in it?" "Do they look so?" "Oh, yes," Ostwald said, "there is some truth in that idea," and then I came and the discussion was at an end. I was very sorry for that.[2]

EXERCISES

1. What factual evidence leads to the conclusion that the dissolved particles of a salt are smaller than molecules?

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[1] *J. Am. Chem. Soc.*, **34**, 353 (1912).

[2] The remainder of this paper you will find intensely interesting. Look it up.

2. Why do melted salts and aqueous salt solutions conduct electricity?

3. Why is it assumed that the number of unit charges on an ion is equal to its valence?

4. How may Avogadro's number be determined?

5. What is the approximate lowering of the freezing point produced by dissolving 0.1 mole of calcium nitrate in 1,000 g. of water?

6. How many coulombs of electricity are required to plate out 10 g. of gold?

7. Why is not the lowering of the freezing point of water exactly twice 1.86°C. when 58.454 g. of sodium chloride is dissolved in 1,000 g. of water?

8. What are cations and anions?

9. Why do solutions of sodium nitrate, sodium acetate, and sodium chloride possess certain properties in common?

10. Why is water such an excellent solvent for salts?

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CHAPTER THIRTY-ONE

REACTION VELOCITY AND CHEMICAL EQUILIBRIA

Unlike salts, acids are molecular compounds. Nevertheless when acids are dissolved in water, their solutions conduct the electric current. Acids are, therefore, electrolytes. To understand what happens when acids dissolve in water, it will be necessary first to study chemical equilibria.

1. The Mechanism of a Chemical Reaction.—A chemical equation shows the smallest number of molecules of the reacting substances that enter into a reaction and of the products formed in a reaction. When weighable quantities of substances react, we are dealing with a process in which millions of molecules take part. The equation represents what one might call the unit reaction which is repeated over and over again when matter in the mass reacts. Before reaction can take place, it is obvious that the molecules which react must come into actual contact by collision. That reaction does not occur, whenever collision of the proper molecules takes place, we have ample proof. Certain kinds of molecule will not react with certain other kinds at all. In all other cases, only a certain percentage of the collisions result in interaction.

Some of the best evidence as to the mechanism of chemical reactions has been obtained by studies of the various factors that influence the speed at which they take place. These factors were discussed earlier (8-9) in connection with combustion. In this chapter, their effects will be treated in greater detail. The rate of a reaction under a given set of conditions may be expressed in terms of moles of a reactant which are converted into products in a unit of time. First of all, this rate depends on the inherent tendency of the substances, entering into a given reaction, to react. Under the same conditions, the explosion of a stick of dynamite and the rusting of iron are reactions that take place at widely different rates. The rate of a given reaction depends, in general, on *the frequency of collisions between the reacting molecules* and on what we may call *the collision efficiency, i.e.*, the percentage of the total number of collisions that actually result in interaction. Any change in conditions that increases the collision frequency or the collision efficiency or both will increase the reaction velocity. Let us consider some of the conditions that influence the rate of chemical reactions.

2. Concentration.—Consider a reaction between two gaseous substances that have been mixed together in a certain volume at a certain temperature and so allowed to react. At the same temperature, the average kinetic energy of each type of molecule will be the same. At room temperature, their velocity will be of the order of a few thousand feet per second. Collisions between the two types of molecules will occur a tremendous number of times in a second, but only a small fraction of these collisions will result in chemical interaction. As a result of these effective collisions, the reaction as a whole will proceed at a rate proportional to their number. If we start with definite concentrations of each substance at a definite temperature, the initial speed of the reaction is fixed by the number of collisions. Let us study what the effect of increasing the concentration of either or both types of molecule is on the collision frequency and, therefore, on the reaction velocity.

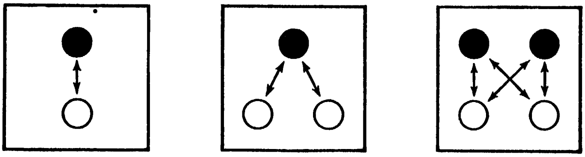

FIG. 112.—The rate of a chemical reaction is proportional to the concentration of each of the reacting substances.

Perhaps an analogy might help. Consider for a moment the absurd situation of 10 red and 10 blue automobiles in a space of one acre area, enclosed by strong fence, all going at the same speed and driven by perfectly crazy drivers. The number of times a red automobile collides with a blue one per unit of time would, on the average, remain the same for the concentration of each kind of car (10 cars per acre) and their speed remain constant—always assuming no damage to the machines in collision. Now if we double the concentration of the red automobiles by entering an additional 10 red cars in the field, but keep the concentration of the blue the same, then we double the number of red automobiles that can collide with a blue car per unit area. The number of collisions per unit time will be doubled. If we double the concentration of the blue cars also, the number of collisions will be quadrupled. In other words, the frequency of collisions is proportional to the concentration of each kind of car.

Now, coming back to our reaction between the two different kinds of molecule, which we shall call A and B to save words, if we start with a mole (6.02×10^{23} molecules) of each per liter, the collision frequency and, therefore, the reaction rate will be fixed by these concentrations. If we double the concentration to two moles per liter of either A or B, the collision frequency and reaction rate, at the start of the reaction, will be doubled. If we double the concentration of both, the reaction rate will be quadrupled. As the reaction proceeds, however, or in other words, as the reacting molecules are changed to those of the products, their concentration must grow smaller and the reaction rate must, therefore, diminish.

3. The Law of Mass Action.—In 1867, Guldberg and Waage, two Norwegian chemists, stated the law of mass action—the speed of a chemical reaction is proportional to the active mass of the reacting molecules. The use of the term "active mass" led to no little confusion until "concentration" was substituted, whereupon the meaning became clear. This law follows naturally from what we have been considering in the last paragraph.

Here is another chance to indulge in what to some of you may seem an annoying habit of stating a law mathematically. Let us start with a simple reaction in which one molecule of A combines with one of B to form the products C and D.

$$A + B \rightarrow C + D$$

The rate of this reaction R will be proportional at any time during its course to the molecular concentrations of A and of B present at that time. If we use brackets to indicate molecular concentration,

$$R \propto [A] \times [B]$$

or

$$R = k \times [A] \times [B]$$

The constant k, which we have used to convert a variation into an equation, is known as the velocity constant, or the *specific* *reaction-rate constant,* and has a value that is characteristic of this reaction at a given temperature. It is really a measure of the inherent tendency of the reaction to take place. If the substances show a great tendency to react, the constant is large, and vice versa.

Now let us consider another reaction in which two molecules of E react with one of F.

$$2E + F \rightarrow G$$

For this reaction to take place, a collision must occur in which two molecules of E and one of F collide simultaneously. The concentration of E must then appear twice in our equation for the reaction rate.

$$R = k'[E] \times [E] \times [F]$$

or

$$R = k'[E]^2[F]$$

In general, if n molecules of X react with m molecules of Y,

$$nX + mY \rightarrow Q$$

the reaction rate is expressed

$$R = k[X]^n[Y]^m$$

As a matter of fact, few reactions involving more than two molecules are known to take place. More complicated reactions take place in steps as a series of successive simple reactions.

In deriving such expressions for the velocity of a reaction, we must always remember that it is practically impossible to change the concentration of either a pure solid or a pure liquid since substances in these states of matter are so incompressible. The number of molecules per unit volume, therefore, remains constant. For example, the rate of combustion of carbon is proportional to the concentration of the oxygen only since carbon is a solid:

$$C + O_2 \rightarrow CO_2$$

$$R = k[O_2]$$

The concentration of gases and of substances in solution can be changed and must appear in the equations for reaction rates.

4. The Effect of Temperature.—Temperature, we have seen, is a measure of the average kinetic energy of molecules and so, also, of their velocity. An increase in temperature will increase molecular velocity. Hence, a temperature increase will increase the frequency with which molecules collide with each other if their concentration is kept constant. We have, then, in temperature another means of increasing reaction velocity. The magnitude of the effect that temperature has on the velocity of reactions in general is surprising. Although the effect in individual instances varies, on the average a rise of 10°C. in temperature doubles or triples the reaction rate. A reaction that takes 1 sec. to go to completion at 0°C. would be complete in about one-thousandth of a second at 100°C., and in about one-millionth of a second at 200°C. as shown in Table 33. On the other hand, a change that takes place in 1 sec. at 200°C. would require 10^6 sec. or a little over 11 days at 0°C. This is surprising because, as we know (12-6), the velocity at which molecules move is proportional to the square root of the absolute temperature. Such a small rise in temperature does not produce a sufficiently greater number of molecular collisions to account for the doubled or trebled velocity. The explanation lies in the fact that when molecules collide they must have sufficient kinetic energy for the reaction to take place. This is called the *energy of activation* and has a specific value for a given reaction. Although the absolute temperature determines the *average* kinetic energy, a single molecule may have any energy from zero to infinity. The ratio of collisions between molecules, which have the required energy of activation, to the total number of collisions determines the collision efficiency. As the temperature rises, this ratio increases and the collision efficiency as well as the collision frequency is increased.

TABLE 33.—THE INFLUENCE OF TEMPERATURE ON REACTION RATE

Temperature, °C.	Time, Seconds
0	1.0
10	0.5
20	0.25
30	0.125
40	0.0625
50	0.03125
60	0.015625
70	0.0078125
80	0.00390625
90	0.001953125
100	0.0009765625
200	10^{-6}

The spoilage of food involves chemical reactions. The lower the temperature, the slower the rate at which spoilage occurs.

Hence the importance of refrigeration in the preservation of foods. At the temperature of Dry-ice, approximately 90°C. below room temperature, foods spoil only $1/500$ as fast as at room temperature.

5. The Effect of Surface.—Reactions that take place between substances in different states of matter occur at the boundary, or interface, between the phases. When a solid reacts with a gas as, for example, in the case of the combustion of coal, the atoms and molecules in the surface layers only are in contact with the gas and so capable of reacting. Grinding a solid into smaller pieces exposes new surfaces and hence increases its reactivity. We have learned how combustible dusts in air explode violently. Stirring and shaking of immiscible liquids have the same result and also bring fresh layers of reactants into contact. Dissolving the reactants in some solvent in which they are mutually soluble breaks them down into single molecules or ions and so provides a maximum opportunity for contact. If crystals of mercuric chloride and sodium iodide are merely mixed together, no reaction is noticeable. When ground together in a mortar, the red color of mercuric iodide, one of the products, soon appears. If aqueous solutions of these substances are mixed, the reaction is practically instantaneous.

6. Catalysis.—Back at the beginning of the last century, when chemistry was little more than a lusty infant, chemists were gradually becoming conscious of a new phenomenon, which was destined to become a power in the chemical industry. Investigators were beginning to report instances of chemical reactions that could be made to take place much more rapidly in the presence of a third substance. The most surprising thing about it all was that these "third substances" seemed to take no active part in the reaction, for they remained unchanged at the end of the reaction. For example, in 1822, Döbereiner reported that the metal platinum induced a vigorous, spontaneous combustion of a mixture of hydrogen and oxygen at room temperature. Ingenious, he devised an apparatus in which hydrogen was generated by the action of zinc on sulfuric acid and allowed to impinge as a fine jet on a piece of spongy platinum. The platinum caused such a vigorous union of the hydrogen and the oxygen of the air to take place that a flame was produced. Here was the ancestor of our pocket lighters of today.

In 1835, Berzelius, of whom you have heard before as the father of chemical symbols, proposed the name *catalyst* for these substances. During the greater part of the nineteenth century, little was known of the way by which catalysts accelerate a chemical reaction; but new examples of catalysis, many of them of great practical importance, were discovered. During this period, there was a tendency to hide behind a pompous name to cover a profound ignorance of the nature of a phenomenon. Gradually, however, several facts about catalytic action became apparent. (1) Catalysts have been found for certain reactions only. (2) A substance that is a catalyst for one reaction need not be and usually is not a catalyst for another reaction. (3) A catalyst apparently can never start a reaction that will not go of itself. It can only accelerate a reaction. A catalyst has been compared with the oil on the machinery of a chemical reaction by the great German chemist Ostwald. Finally, *negative catalysts*, or inhibitors, have been discovered for certain reactions which retard the speed at which they take place. For example, if acetanilid, a fever-reducing drug derived from coal tar, is added to hydrogen peroxide, the well-known antiseptic, the speed at which the latter decomposes is greatly decreased.

Two types of catalysts were soon recognized. The *contact catalysts*, usually finely divided metals, adsorb molecules of the reacting substances on their surfaces and so bring them into intimate contact. Here the catalytic power is a function of the surface and, therefore, of the degree of subdivision of the catalyst. The other type, known as the *carrier catalysts*, forms an intermediate compound with one of the reacting substances, which in turn reacts with the molecules of the other substance, regenerating the catalyst. These theories of catalytic action will be discussed in greater detail later on.

Many examples of catalysis will be considered in the chapters that follow, among which may be mentioned the contact process for the preparation of sulfuric acid (36-9), the synthetic-ammonia process (38-8), the ammonia-oxidation process (38-12), synthetic methanol, acetic acid, and acetone (43-1), the hydrogenation of fats (45-7), and enzyme action (45-12).

7. Photochemical Action.—The relationship of radiant energy to certain chemical reactions is a very interesting one. The rate at which certain reactions take place is greatly influenced by illuminating the reactants. Hydrogen and chlorine, for example, react to form hydrochloric acid

$$H_2 + Cl_2 \rightarrow 2HCl$$

The rate at which this reaction takes place in the dark is very slow. Exposure to bright sunlight or to the light from a burning magnesium ribbon, however, will result in a violent, explosive reaction. Whenever the reaction is an exothermic one, the action of light seems to be purely catalytic—photocatalysis. Small quantities of light will produce relatively large amounts of chemical action. The reaction of hydrogen and chlorine is one of this type. When the reaction is endothermic, however, the radiant energy is actually stored up by the system as the chemical energy of its products. The photosynthesis of carbohydrates by plants from the carbon dioxide of the air and water is an example of this type, which is of tremendous importance to mankind (45-1). By this reaction alone, it has been calculated that some 1.32×10^{16} cal. of the radiant energy that comes to this earth from the sun are stored up annually as chemical energy by the plants. This is the energy that makes life possible on the earth and provides fuel for the power that modern civilization demands. One of the best known photochemical reactions is that of photography. Here silver bromide molecules in the emulsion on the photographic plate are decomposed into metallic silver and bromine (49-6).

8. Reversible Reactions and Equilibria.—Thus far, we have studied several examples of reversible changes. Such changes result in the establishment of an equilibrium if they take place in a closed system. Thus you will recall that when a liquid is confined in a vessel an equilibrium is established between the liquid and the vapor phases. Here we have two reactions, evaporation and condensation, of exactly opposite character taking place at equal rates. Another example is the equilibrium between a solid and its saturated solution in which the solid is dissolving at the same rate at which it crystallizes from solution (19-7).

Similarly, many chemical changes are reversible. Thus not only will hydrogen iodide decompose into hydrogen and iodine, but it will also be formed again by the recombination of its elements:

$$2HI \rightleftarrows H_2 + I_2$$

This reversible reaction is a simple one to study since, if it is carried out at about 400°C., all substances involved are gases. Placed in a closed tube at a constant temperature, molecules of pure hydrogen iodide start to decompose into molecules of hydrogen and iodine. The rate at which this change takes place is proportional to the square (Why?) of the molecular concentration of the hydrogen iodide. As the reaction proceeds, this concentration gradually decreases, since fewer undecomposed molecules remain. Hence the rate of decomposition diminishes also. On the other hand, at the beginning of the experiment the rate of the reverse reaction is zero, since no hydrogen and iodine molecules are present. As soon as any of these molecules are formed, the reverse reaction starts. Since the concentration of hydrogen and iodine increases as the decomposition of hydrogen iodide continues, the speed of the reverse reaction increases also. Eventually, the rate of the reverse reaction becomes equal to that of the direct and an equilibrium is established. Thereafter, the concentrations of all the substances remain the same; for each substance is being formed at the same rate at which it is reacting.

In general, *at equilibrium the rates of two reactions, each the opposite of the other, are equal.*

9. Equilibrium Constants.—The rate at which the hydrogen iodide decomposes is proportional to the square of the concentration of its molecules.

$$r = k[HI]^2$$

The rate at which hydrogen and iodine recombine,

$$r' = k'[H_2][I_2]$$

At equilibrium, these two rates are equal and

$$k'[H_2][I_2] = k[HI]^2$$

$$\frac{[H_2][I_2]}{[HI]^2} = \frac{k}{k'} = K$$

The constant K, the ratio of the two velocity constants, is called the *equilibrium constant* of the reaction. You will remember that each velocity constant is a measure of inherent tendency of the reaction to take place. From the above equation it will be seen that the concentrations of the products of a reaction in the equilibrium mixture are proportional to the velocity constant of the reaction

$$[H_2] \times [I_2] \propto k$$

and

$$[HI]^2 \propto k'$$

Hence if the tendency for hydrogen iodide to decompose (k) is greater than that of hydrogen and iodine to recombine (k'), the product of the hydrogen and iodine concentrations will be greater than the square of the concentration of hydrogen iodide in the equilibrium mixture, and vice versa.

The equilibrium constant K has a definite numerical value at a given temperature. In Table 34 the experimental work of Taylor and Crist[1] on this equilibrium is summarized. The equilibrium was established by starting with different concentrations of hydrogen iodide at a temperature of 393.7°C. The concentrations of HI, H_2, and I_2 at equilibrium were determined by analysis. From these results the equilibrium constant was determined. They started also with pure hydrogen and iodine and so approached the equilibrium from the other side. The value for the equilibrium constant was the same.

TABLE 34.—EQUILIBRIUM DATA FOR $2HI \rightleftarrows H_2 + I_2$ AT 393.7°C.

Concentrations, moles/l. × 10^2			$K = \frac{[H_2]\,[I_2]}{[HI]^2}$
H_2	I_2	HI	
0.32583	0.12949	1.5869	0.01676
0.46981	0.07014	1.3997	0.01682
0.07106	0.07106	0.5168	0.01689

In general, if n molecules of A react with m of B to form o molecules of C and p of D,

$$nA + mB \rightarrow oC + pD$$

then the expression for the equilibrium constant will be

$$\frac{[C]^o[D]^p}{[A]^n[B]^m} = K$$

It is customary to place the concentrations of the substances, appearing on the right of the arrows of the equation, in the numerator of the expression for the equilibrium constant.

A knowledge of the equilibrium constant of any reversible reaction is very useful. Since the concentrations of the products of the direct reaction appear in the numerator, the greater the equilibrium constant, the greater the percentage of these products

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[1] *J. Am. Chem. Soc.*, **63**, 1381 (1941).

at equilibrium. The size of the constant for a reaction, by which he is attempting to obtain certain products, means a great deal to a chemical engineer. If large, it may mean success; if small, failure.

10. The Theorem of Le Châtelier.—The law of van't Hoff has been applied (14-9) to predict the effect of a rise in temperature on the equilibrium between a liquid and its vapor. You will remember that this law states that a new equilibrium is established at the higher temperature and that the products of the reaction which absorbs heat will make up a greater percentage of the equilibrium mixture. Applied to an equilibrium between a liquid and its vapor

$$\text{Vapor} \rightleftarrows \text{liquid} + \text{heat}$$

the law predicts that the higher the temperature, the greater the relative amount of vapor at equilibrium because the reverse reaction is endothermic.

This law may be applied to chemical equilibria as well. For example, it is known that the synthesis of ammonia is accompanied by a liberation of heat:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + \text{heat}$$

Hence we know that the higher the temperature, the less will be the yield of ammonia in the equilibrium mixture.

The law of van't Hoff is a corollary to a more general law known as the theorem of Le Châtelier. An increase in temperature may be considered as a type of stress applied to an equilibrium. By absorbing heat, the system can in some measure relieve the stress of increased temperature. Hence the reaction that absorbs heat is favored. The *theorem of Le Châtelier* states: *If any stress is applied to a system in equilibrium, that one of the two opposing reactions is favored which relieves this stress.*

To illustrate its general applicability, let us consider the application of the stress of increased pressure to the ammonia-nitrogen-hydrogen equilibrium. That one of the two reactions will be favored which reduces the pressure when it takes place. Remember that the pressure exerted by a gas depends on its molecular concentration so that *any reaction that reduces the number of gas molecules will relieve the stress and so be favored.* The direct reaction, *i.e.*, the synthesis of ammonia, reduces the number of molecules from four to two each time it takes place, whereas the reverse reaction causes an increase. Hence an increased pressure will increase the yield of ammonia in the equilibrium mixture.

11. The presence of a catalyst does not seem to affect the equilibrium since it increases the velocity of both reactions in the same ratio. It does not, therefore, increase the yield of any desired substance by its presence, but it does *lessen the time necessary for the establishment of the equilibrium.* Hence it gives the same yield in a shorter time under the same conditions of temperature and pressure. Further, *it permits the employment of conditions that favor the formation of the desired product but would form this product too slowly without the catalyst.* Thus the yield of ammonia at equilibrium is greater, the lower the temperature. But reactions take place more slowly at lower temperatures and the establishment of equilibria takes longer. With the catalyst, the time is shortened at the otherwise more advantageous lower temperatures.

TABLE 35.—YIELD OF AMMONIA

Temperature, °C.	Pressure, atm.					
	1	100	200	300	600	1,000
200	15.3	80.6	85.5	89.9	95.4	98.3
300	2.2	52.1	62.8	71.0	84.2	92.6
400	0.44	25.1	36.3	47.0	65.2	79.8
500	0.129	10.4	17.6	26.4	42.15	57.5
600	0.049	4.5	8.25	13.8	23.1	31.4
700	0.022	2.14	4.10	7.25	12.6	12.9
800	0.012	1.15	2.24			
900	0.007	0.68	1.34			
1000	0.004	0.44	0.87			

From what we have said, it should be apparent that a knowledge of chemical equilibria and of the application of the theorem of Le Châtelier are of the greatest practical importance to the chemical industry. We shall have occasion to return to the material discussed in this chapter many times.

EXERCISES

1. Why, in general, does the reaction velocity depend on the collision frequency and efficiency?

2. Why does a rise in temperature increase both of these?

3. Why is the rate at which hydriodic acid molecules decompose proportional to the square of its concentration?

4. Why is the concentration of a solid constant?

5. Of what is the specific-reaction-rate constant a measure?

6. Why is a combustible dust suspended in air dangerous?

7. How does a contact catalyst increase reaction velocity?

8. Write the expression for the equilibrium constant for each of the following reversible reactions between gases:

$$N_2 + O_2 \rightleftarrows 2NO$$
$$2NO + O_2 \rightleftarrows 2NO_2$$
$$CO + Cl_2 \rightleftarrows COCl_2$$

9. Under what conditions would a high yield of sulfur trioxide be obtained in a short time.

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + \text{heat}$$

10. The equilibrium constant for the above reaction at 627°C. is 3.16×10^3. From this value, would you predict high or low yields of sulfur trioxide at equilibrium at this temperature?

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CHAPTER THIRTY-TWO

IONIZATION OF ACIDS

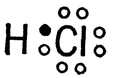
To the layman, acids are chemicals to be avoided. He thinks of them as horribly corrosive liquids. Yet he drinks carbonic acid in carbonated beverages, enjoys the sour taste of fruit juices, and his wife bathes the baby's eyes with boric acid. True, sulfuric acid is not to be handled casually, but many weaker acids are common constituents of our foods.

1. The Physical Properties of Acids.—*In general, acids are gases or liquids. Only those of relatively high molecular weight are solids.* Hydrochloric, hydrobromic, and hydriodic acids are gases, although these substances are usually used as reagents in aqueous solution. Sulfuric, nitric, phosphoric, and acetic acids are liquids. The acids that are solids are almost invariably organic substances like benzoic, lactic, and citric acids.

Pure acids in the liquid state are exceedingly poor conductors of electricity. These properties are distinctly different from those of salts. The latter, you will remember, are solids of relatively high melting point. Melted salts are good conductors. We must assume, therefore, that *acids are composed of neutral molecules in which the atoms are linked by covalent bonds.* Between such neutral molecules, the van der Waals forces are small as compared with the Coulomb forces operating between the ions of a salt. This explains the fact that acids are usually gases or liquids under ordinary conditions. The lack of ions in pure liquid acids explains the low conductivity.

2. The Proton Bond.—The neutral hydrogen atom consists of a single proton as the nucleus and one planetary electron. Even when uncombined, hydrogen atoms are never found alone, except under extraordinary conditions, but always exist in pairs in the hydrogen molecule. When combined with other atoms, the valence bond is invariably one of the covalence type (27-5). Furthermore, one shared pair of electrons is sufficient to complete the first level of this atom.

The molecule of hydrochloric acid, a compound of hydrogen and chlorine, has the following structure:



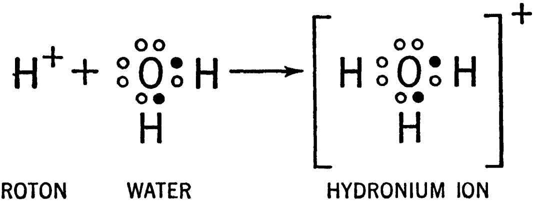
It is a gas under ordinary conditions and, when liquefied, shows little electrical conductivity. These are characteristic of a substance made up of covalent molecules.

3. Aqueous Solutions of Acids.—*When an acid is dissolved in water, however, the resulting solution is a conductor of electricity.* An aqueous solution of a strong acid has a conductivity comparable to that of a salt solution of the same concentration. Whereas all aqueous salt solutions are excellent conductors, the conductivity of aqueous solutions of acids varies widely and depends on the strength of the acids. Solutions of weak acids, like acetic acid, are relatively poor conductors. For this reason, salts and strong acids are called strong electrolytes whereas weak acids are weak electrolytes.

The fact that aqueous solutions of acids conduct electricity is definite evidence of the existence of ions in these solutions. Arrhenius assumed that ionization of its molecules occurs when an acid is dissolved in water, *e.g.*,

$$HCl \rightarrow H^+ + Cl^-$$

and that the common properties of all acid solutions are due to the hydrogen ion. This ion, however, is a single proton (Why?); and we now have excellent evidence that free protons cannot exist in a solvent like water. A water molecule adds onto a proton one of its lone pairs of electrons forming a dative bond:



This hydrated proton, or *hydronium ion*, is found in aqueous solutions of all acids and endows such solutions with their typical acid properties. In the general literature of chemistry, however, the hydronium ion is still being called the hydrogen ion.

The solution of an acid in water is accompanied by a reversible reaction in which molecules of the acid react with water to form hydronium ions and their characteristic anions. For example, hydrochloric acid reacts with water to form hydronium and chloride ions:

$$\mathrm{HCl + H_2O \rightleftarrows H_3O^+ + Cl^-}$$

Since this reaction is reversible an equilibrium is established. In this case as in the case of all strong acids, the tendency for the direct, or ionization, reaction to take place is so much greater than that of the reverse reaction that the direct reaction goes virtually to completion before equilibrium is established.

$$\mathrm{{\scriptstyle HCl + H_2O} \underset{\leftarrow}{\xrightarrow{\qquad\quad}} {\Large H_3O^+ + Cl^-}}$$

Hence the ion concentration in aqueous solutions of a strong acid like hydrochloric is comparable to that of salt solutions of the same concentration. For all practical purposes, we may consider strong acids to be completely ionized in dilute aqueous solutions. *The concentration of the hydronium ion determines the acidity of the solution.* Since in this case it is high, hydrochloric acid is a strong acid.

On the other hand, acetic acid is a weak acid. Its aqueous solutions are poor conductors. We must assume that they contain low concentrations of ions. Hence the tendency of acetic acid molecules to give protons to water molecules must be comparatively small. Thus at equilibrium the solution will contain mainly acetic acid molecules,

$$\mathrm{{\Large HC_2H_3O_2 + H_2O} \overset{\rightarrow}{\xleftarrow{\qquad\quad}} {\scriptstyle H_3O^+ + C_2H_3O_2^-}}$$

Since the hydronium-ion concentration is low, solutions of this acid are feebly acidic. Vinegar is an aqueous solution of this acid.

4. Definition.—An acid may be defined as a substance whose molecules react with water with the formation of hydronium ions. This definition is of course restricted to aqueous solutions. A more general one may be derived as follows. Since protons are given by the acid to the water molecules or, in general, to some other substance, acids may be defined as *proton donors.*

5. Ionization Constants.—The constant for such an equilibrium between molecules of the acid and its ions is called its ionization constant. The equilibrium constant for acetic acid may be obtained as follows:

$$\frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2][H_2O]} = K'$$

In dilute solutions, the concentration of the water is virtually constant. Hence we may include it with K' in the ionization constant K:

$$K = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = [H_2O] \times K' = 1.8 \times 10^{-5}$$

It is numerically equal to 1.8×10^{-5}.

It may help to consider how such a constant may be calculated. In a $0.1M$ acetic acid solution, 1.32 per cent of the acetic acid molecules are ionized. Hence the concentration of the hydronium and acetate ions is 0.1×0.0132, and that of the undissociated molecules of acetic acid, 0.1×0.9868. Substituting we obtain for the ionization constant

$$\frac{0.00132 \times 0.00132}{0.09868} = 0.000018 = 1.8 \times 10^{-5}$$

Dilution increases the extent of ionization. With more water between the ions in a more dilute solution, the rate at which they collide and hence the rate of the reverse reaction is lessened. Hence the ionization goes more nearly to completion before equilibrium is established.

In solutions of strong acids, the concentration of the ions is very great as compared with that of the undissociated molecules. Hence strong acids have large ionization constants—indeed too large to be determined accurately. That of hydrochloric acid is of the order of 10^7. Weak acids like acetic have small ionization constants since in their solutions the ratio of the ions to molecules is low.

Whereas the ionization constant of an acid at a given temperature has a definite value, it does change with a change in temperature—in general, increasing as the temperature rises.

6. pK.—The pK of an acid is defined as the logarithm of the reciprocal of its ionization constant:

$$pK = \log \frac{1}{K_{\text{ionization}}}$$

This definition sounds particularly terrifying, but its bark is worse than its bite. If, for example, the ionization constant of acetic acid is 10^{-5}, its pK is 5:

$$pK = \log \frac{1}{10^{-5}} = \log 10^5 = 5$$

If the ionization constant is expressed as a power of 10, the pK is that power with its sign changed. If an acid has an ionization constant of 10^{-7} (100 times smaller than that of acetic acid), its pK is 7. *Note that the smaller the ionization constant, the larger the* pK. Weak acids have large pK's; strong acids, small. Note also that a change of one unit of pK corresponds to a tenfold change in ionization constant. Hydrocyanic acid with a pK of 9 is 10,000 times weaker than acetic acid. (Why?)

7. Polyprotic Acids.—Acids whose molecules may donate more than one proton are called polyprotic acids. The old term polybasic acid, which has the same meaning, is still being used. Included in this class are such diprotic acids as sulfuric (H_2SO_4) and carbonic (H_2CO_3) and such triprotic acids as phosphoric (H_3PO_4). At first sight, the formula for acetic acid ($HC_2H_3O_2$) might indicate a tetraprotic acid. However, acetic acid never gives up more than one proton per molecule and is, therefore, monoprotic.

Polyprotic acids ionize in steps, *e.g.*,

$$H_2SO_4 + H_2O \rightleftarrows H_3O^+ + HSO_4^- \qquad (1)$$
$$HSO_4^- + H_2O \rightleftarrows H_3O^+ + SO_4^= \qquad (2)$$

The primary ionization (1) proceeds much further to completion than the secondary (2), since the escape of the first proton from the neutral sulfuric acid molecule is easier than that from the negatively charged bisulfate (HSO_4^-) ion.

For each step in the ionization, there is a corresponding ionization constant, *e.g.*,

$$\frac{[H_3O^+][HSO_4^-]}{[H_2SO_4]} = K_1$$

and

$$\frac{[H_3O^+][SO_4^=]}{[HSO_4^-]} = K_2$$

K_1 is very large, indicating that the primary ionization of sulfuric acid is virtually complete. K_2 is equal to 2×10^{-2}.

8. Ion Acids.—The bisulfate ion and similar ions, which may act as proton donors, are as truly acids as the neutral molecular acids. Negative ion acids, or anion acids, include the bicarbonate (HCO_3^-), bisulfite (HSO_3^-), and bisulfide (HS^-) ions and the two acid phosphate ions ($H_2PO_4^-$ and $HPO_4^=$). The commonest cation acid is the ammonium ion which reacts with water to form the hydronium ion and ammonia.

$$NH_4^+ + H_2O \rightleftarrows H_3O^+ + NH_3$$

Such ion acids are not complete substances (30-8) but may be obtained in solution by dissolving the appropriate salt. Thus sodium bicarbonate or any other soluble bicarbonate may be used as a source of the bicarbonate ion. Similarly, any ammonium salt will furnish ammonium ions. Sodium bisulfate crystals are composed of sodium and bisulfate ions and go into solution as these ions just as any salt would do. Thereafter the bisulfate ion shows its acid character by reacting with water.

$$HSO_4^- + H_2O \rightleftarrows H_3O^+ + SO_4^=$$

Salts that are the source of anion acids are called *acid salts*, *e.g.*, sodium bisulfate.

9. Common Ion Effect.—We have studied the ionization of acetic acid in some detail.

$$HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^-$$

If an acetate like the salt sodium acetate were dissolved in a solution that already contained acetic acid, the immediate result would be a great increase in the concentration of the acetate ion. This in turn would increase the speed of the reverse reaction, since hydronium ions would encounter acetate ions more frequently. Hence the equilibrium would shift in the direction that forms more acetic acid molecules and at the same time reduces the hydronium-ion concentration. *In general, the addition of a salt with a common ion to the solution of an acid will reduce the extent to which the acid is ionized.*

10. The Ionization of Water.—Pure water shows a slight but definitely measurable electrical conductivity which indicates that ions must be present. These are formed by the following reaction:

$$HOH + H_2O \rightleftarrows H_3O^+ + OH^-$$

In this reaction, one of the water molecules acts as a typical acid donating its proton to a second molecule. The ionization constant for this reaction takes the following form:

$$\frac{[H_3O^+][OH^-]}{[H_2O]^2} = K'$$

Again (32-5) we may include the constant concentration of the water molecules with K' and obtain

$$[H_3O^+][OH^-] = K' \times [H_2O]^2 = K_w$$

The concentrations of these ions in pure water may be determined from the observed electrical conductivity and by other methods. Since the two ions are formed in equal quantities, their concentrations must be equal. The calculated value for their equal concentrations at 25°C. is 10^{-7} gram-ionic weight per liter. Hence K_w, the ionization constant of water, must equal 10^{-14}

$$K_w = [H_3O^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

This product has this constant value not only in pure water, but also in all aqueous solutions.

To make the meaning of these numerical values clearer, let us examine them more closely. One liter of water weighs 1,000 g. and one mole of water, 18 g. Hence there are 1,000/18, or 55.5, moles of water in 1 liter. For every 55.5 moles there are 10^{-7} gram-ionic weight each of H_3O^+ and OH^- ions. Therefore, for every 55.5 molecules of water there are 10^{-7} H_3O^+ and 10^{-7} OH^- ions. Finally, there are one H_3O^+ and one OH^- for every 555,000,000 water molecules. To say that water is only slightly ionized is to put it mildly.

11. Acid, Basic, and Neutral Solutions.—The hydronium and the hydroxyl ions are unique among the ions found in aqueous solution, for molecules of the solvent are formed when they combine. Further, the definite relationship between their concentrations, pointed out above, always exists in all aqueous solutions. If the concentration of the hydronium ion is increased, the hydroxyl-ion concentration decreases correspondingly since the product must always equal 10^{-14}. The hydronium-ion concentration may be increased by dissolving an acid in water. For example, if 0.1 mole of hydrochloric acid is dissolved in a liter of water, the concentration of the hydronium ion will rise from 10^{-7} to 10^{-1}, since the ionization of this acid is virtually complete.

We may calculate the hydroxyl-ion concentration in this solution as follows:

$$[H_3O^+] \times [OH^-] = 10^{-14}$$
$$10^{-1} \times [OH^-] = 10^{-14}$$
$$[OH^-] = 10^{-13}$$

This millionfold reduction in the concentration of the hydroxyl ion from 10^{-7} to 10^{-13} takes place because these ions have combined with the more numerous hydronium ions and formed water molecules.

TABLE 36.—THE RELATIONSHIP BETWEEN $[H_3O^+]$ AND $[OH^-]$

Concentration of H_3O^+, moles/liter	Concentration of OH^-, moles/liter	$[H_3O^+] \times [OH^-]$	pH	Character
$1 = 10^0$	10^{-14}	10^{-14}	0	Acidic
10^{-1}	10^{-13}	10^{-14}	1	Acidic
10^{-2}	10^{-12}	10^{-14}	2	Acidic
10^{-3}	10^{-11}	10^{-14}	3	Acidic
10^{-4}	10^{-10}	10^{-14}	4	Acidic
10^{-5}	10^{-9}	10^{-14}	5	Acidic
10^{-6}	10^{-8}	10^{-14}	6	Acidic
10^{-7}	10^{-7}	10^{-14}	7	Neutral
10^{-8}	10^{-6}	10^{-14}	8	Basic
10^{-9}	10^{-5}	10^{-14}	9	Basic
10^{-10}	10^{-4}	10^{-14}	10	Basic
10^{-11}	10^{-3}	10^{-14}	11	Basic
10^{-12}	10^{-2}	10^{-14}	12	Basic
10^{-13}	10^{-1}	10^{-14}	13	Basic
10^{-14}	$1 = 10^0$	10^{-14}	14	Basic

The usual method of increasing the hydroxyl-ion concentration is to dissolve a metal hydroxide. Since the hydroxides of the alkali and alkaline-earth metals are soluble, these are commonly used. These metal hydroxides are solids with an ionic, saltlike crystal structure. Hence they dissolve in water as ions as do all salts. If 0.01 mole of sodium hydroxide is dissolved in a liter of water, the concentration of the hydroxyl ion will increase to 10^{-2}. That of the hydronium ion will be reduced to 10^{-12}. (Why?)

Solutions, in which the hydronium- and hydroxyl-ion concentrations are equal, i.e., each equal to 10^{-7}, *are called neutral solutions.*

If the hydronium-ion concentration exceeds that of the hydroxyl ion, the solution is acidic. If the hydroxyl-ion concentration is greater, the solution is basic. Thus:

Neutral: $[H_3O^+] = [OH^-] = 10^{-7}$
Acidic: $[H_3O^+] > OH^-$
$[H_3O^+] > 10^{-7}, \quad [OH^-] < 10^{-7}$
Basic: $[H_3O^+] < [OH^-]$
$[H_3O^+] < 10^{-7}, \quad [OH^-] > 10^{-7}$

As a summary of the relationship between these two ions you will find Table 36 useful.

12. Hydronium-ion Concentration and pH.—The fourth column of this table with its heading pH has no doubt puzzled you. This is a method of expressing hydronium-ion concentration which has come into great favor recently because of its simplicity and convenience. The acidity of a solution, expressed in pH, is equal to the logarithm of the reciprocal of the hydronium-ion concentration:

$$\text{pH} = \log \frac{1}{[H_3O^+]}$$

Thus a solution whose hydronium-ion concentration is 10^{-7}, has a pH value of 7 since

$$\text{pH} = \log \frac{1}{10^{-7}} = \log 10^{+7} = 7$$

This is the pH value of a neutral solution. By referring to Table 36, it will be clear that a solution whose pH is greater than 7 is basic and one whose pH is less than 7, acidic. Since we are dealing with a logarithmic scale, a solution of pH 6 has ten times the hydronium-ion concentration of one of pH 7. Further, if we know the hydronium-ion concentration, we can calculate the concentration of the OH ions so that the pH of a solution gives information of both the hydronium- and hydroxyl-ion concentrations. For example, in a solution of pH 5, the hydronium-ion concentration is 10^{-5} and that of the hydroxyl ions 10^{-9} ($10^{-14} \div 10^{-5}$), since $[H_3O^+] \times [OH^-] = 10^{-14}$ always.

The acidity of a solution is often of the utmost importance not only in chemical research, but also in many industrial operations. Today we find bacteriologists, biologists, physiologists, and pathologists, in addition to chemists, speaking of the pH of solutions in which they are interested. Even farmers, paper manufacturers, sugar refiners, sanitary engineers, electroplaters, and electrotypers glibly refer to pH, since they know that this factor plays an important part in determining the quality of their products, the growth of plants and bacteria, the diagnosis of diseases, etc.

TABLE 37.—TABLE OF INDICATORS

Name	Color change as pH increases	pH range of sensitivity
Acid cresol red	Red to yellow	0.2–1.8
Meta cresol purple	Red to yellow	1.2–2.8
Brom phenol blue	Yellow to blue	3.0–4.6
Brom cresol green	Yellow to blue	4.0–5.6
Chlor phenol red	Yellow to red	4.8–6.4
Brom thymol blue	Yellow to blue	6.0–7.6
Phenol red	Yellow to red	6.8–8.4
Cresol red	Yellow to red	7.2–8.8
Thymol blue	Yellow to blue	8.0–9.6
Cresol phthalein	Colorless to red	8.2–9.8

13. The Determination of pH—Indicators.—The pH of a solution may be determined in either of two ways—by electromotive-force determinations or by the use of indicators. The first method is more involved but also more accurate. It involves theoretical considerations that are beyond the scope of this book. The second method, however, is simple to apply and easy to understand. There are certain colored organic substances whose color not only varies in shade with the pH of the solution, but actually changes at a certain characteristic pH value. Such substances are called indicators. The commonest of these is litmus which is blue in color in solutions that are more basic than pH 7 and red in those more acid. Test papers, such as are so often used for testing roughly the acidity of a solution, are usually prepared by drying strips of filter paper that have been soaked in a concentrated litmus solution. Litmus paper will turn a faint pink in weakly acid solutions and a brighter red in those which are more strongly acidic. Similarly, a pale blue color indicates a weakly basic and a deep blue a strongly basic solution. Litmus paper, however, is at best only a roughly quantitative means of determining the pH of a solution. Other indicators are known which are more sensitive to slight differences in pH, although no one indicator is known which is equally sensitive over a wide range of pH values. A series of indicators, such as is given in Table 37, must, therefore, be used to cover a range of pH values from, say, 0.2 to 9.8.

Standard color samples are prepared of a given indicator at hydronium-ion concentrations corresponding to each two-tenth of a pH within its range of sensitivity. To a sample of the solution whose pH is to be determined is added enough of the indicator to make its concentration the same as in the standard samples. The color of this solution is then matched with that of one of the standard samples. Its pH will then be that of the sample.

EXERCISES

1. What properties of acids lead to the assumption that they are composed of molecules rather than ions?

2. Explain why acids in the liquid state have a very low conductivity whereas their aqueous solutions are relatively good conductors of electricity.

3. How does the theory explain the difference between strong and weak acids?

4. What is the ionization constant of an acid?

5. What is its pK, and how is this constant related to the strength of an acid?

6. Write equations for the ionization of carbonic and phosphoric acids.

7. Why is the secondary ionization constant of a polyprotic acid always less than its primary ionization constant?

8. Why are solutions of ammonium chloride and sodium bisulfate acidic?

9. What is the pH of a $0.1M$ solution of hydrochloric acid?

10. What is the pH of a solution of acetic acid in which the concentration of the acetic acid molecules is $0.1M$?

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CHAPTER THIRTY-THREE

PROTOLYSIS REACTIONS

About 20 years ago, Lowry and Brönsted suggested an extension of the classical definitions of an acid and a base. Their suggestions are gradually being adopted. Most chemists, who have been educated to use the classical definitions, acknowledge the gain in simplicity and usefulness of those of Lowry and Brönsted once familiarity with their use has been attained. Those of you who have never studied chemistry before will experience little difficulty in their use. On the other hand, others who have learned to use the classical definitions must approach the newer ones with an open mind and realize that the classical are incorporated in the newer definitions. The best way to learn a new language is to think in its terms as soon as possible and so to stop the time-wasting process of translating thoughts into words.

1. The Lowry-Brönsted Definitions.—We have already used the modern definition of an acid, *i.e.*, *a proton donor. A base* is defined as *a proton acceptor.* We have learned that acids may be molecules or ions. The same is true of bases. These definitions may be summarized by the equation:

$$\underset{\text{acid}}{HB} \rightleftarrows \underset{\text{proton}}{H^+} + \underset{\text{base}}{B^-}$$

Since the donation of a proton is reversible, every acid must change into its *conjugate base* when it gives its proton away. The base in turn is converted into its conjugate acid when it gains a proton—the reverse reaction in the above equation. Thus the chloride ion is the conjugate base of hydrochloric acid:

$$HCl \overset{\longrightarrow}{\leftarrow} H^+ + Cl^-$$

and the acetate ion is the conjugate base of acetic acid:

$$HC_2H_3O_2 \underset{\longleftarrow}{\rightarrow} H^+ + C_2H_3O_2^-$$

Similarly, the hydroxyl ion is the conjugate base of the acid, water:

$$HOH \underset{\longleftarrow}{\rightarrow} H^+ + OH^-$$

Ion acids similarly have conjugate bases. Thus ammonia is the conjugate base of the ammonium ion:

$$NH_4^+ \rightleftarrows H^+ + NH_3$$

The carbonate ion is the conjugate base of the bicarbonate ion:

$$HCO_3^- \rightleftarrows H^+ + CO_3^=$$

In general, if n is the number of charges on the acid, $n - 1$ will be the charge on the conjugate base

$$HB^n \rightleftarrows H^+ + B^{n-1}$$

The loss of a proton with its unit positive charge makes the charge on the conjugate base one less than that of the acid.

TABLE 38.—ACIDS AND THEIR CONJUGATE BASES

Acid	Conjugate base	Ionization constant		pK	
		Exact	Approximate	Exact	Approximate
HCl	Cl^-	....	10^7	......	−7
HNO_3	NO_3^-	....	Large	......	Small
H_2SO_4	HSO_4^-	....	Large	......	Small
H_3O^+	H_2O	55.5	10^2	−1.74	−2
HSO_4^-	$SO_4^=$	2×10^{-2}	10^{-2}	+1.70	+2
H_2SO_3	HSO_3^-	1.7×10^{-2}	10^{-2}	1.77	2
H_3PO_4	$H_2PO_4^-$	7×10^{-3}	10^{-2}	2.16	2
$HC_2H_3O_2$	$C_2H_3O_2^-$	1.8×10^{-5}	10^{-5}	4.74	5
HSO_3^-	$SO_3^=$	5.0×10^{-6}	10^{-5}	5.30	5
H_2CO_3	HCO_3^-	3.1×10^{-7}	10^{-7}	6.51	7
H_2S	HS^-	7.9×10^{-8}	10^{-7}	7.10	7
$H_2PO_4^-$	$HPO_4^=$	7.5×10^{-8}	10^{-7}	7.13	7
HClO	ClO^-	....	10^{-8}	......	8
HCN	CN^-	7×10^{-10}	10^{-9}	9.14	9
H_3BO_3	$H_2BO_3^-$	6.5×10^{-10}	10^{-9}	9.19	9
NH_4^+	NH_3	5.5×10^{-10}	10^{-9}	9.26	9
HCO_3^-	$CO_3^=$	4.5×10^{-11}	10^{-10}	10.35	10
$HPO_4^=$	$PO_4^{\equiv}$	5×10^{-13}	10^{-12}	12.30	12
HS^-	$S^=$	2×10^{-15}	10^{-15}	14.70	15
HOH	OH^-	1.78×10^{-16}	10^{-16}	15.75	16
OH^-	$O^=$	....	10^{-24}	......	24

2. The Strength of Acids and Bases.—The strength of an acid is determined primarily by the ease with which it loses a proton; this in turn determines the magnitude of its ionization constant and so also its pK. Conversely, the strength of a base is determined by its inherent tendency to gain a proton. Further, the greater the ease with which an acid loses a proton, the less the tendency of its conjugate base to gain one. Consider the case of acetic acid and its conjugate base the acetate ion:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

The ionization constant of the acid is small (10^{-5}) and its pK (5) correspondingly large. This means that the acid does not release protons readily and that it is a weak acid. Conversely, the acetate ion shows a great tendency to gain protons and is, therefore, a strong base. Hence, if the acid is weak, its conjugate base is strong, and vice versa. More exactly, *the smaller the ionization constant and the larger the pK of an acid, the stronger is its conjugate base.*

In Table 38 are listed the common acids, their conjugate bases, ionization constants, and pK's. This table need not be committed to memory, but we shall have occasion to refer to it many times in what follows.

3. Reactions of Strong Acids and Metal Hydroxides.—The hydroxyl ion (OH^-) is one of the strongest bases. Further, when it acts as a base by combining with a proton in aqueous solution, it is unique in that it forms a molecule of the solvent. We have learned that the alkali and alkaline-earth metal hydroxides are the best sources of hydroxyl ions. When aqueous solutions of an acid and a metal hydroxide are mixed, an important type of reaction known as neutralization takes place. As an example of this type, let us consider what happens when a solution of sodium hydroxide is added to one of hydrochloric acid. Since sodium hydroxide has an ionic, saltlike, crystal structure, its aqueous solution contains sodium and hydroxyl ions. Since hydrochloric acid is a strong acid, its ionization is virtually complete and its aqueous solution is made up of hydronium and chloride ions. Since the hydronium ions are a strong acid and the hydroxyl ions a strong base, protons will be given by the hydronium ions to the hydroxyl ions in the following reaction:

$$H_3O^+ + OH^- \rightleftarrows HOH + H_2O$$

The reaction is the exact opposite of the ionization of water, which we learned takes place to only an infinitesimal extent.

Hence, the reaction of hydronium and hydroxyl ions goes virtually to completion. The characteristic acid properties of the hydronium ion disappear as these ions combine with the hydroxyl ions. This neutralization of the properties of acids by the hydroxyl ion is responsible for the name of this type of reaction.

The sodium ions of the sodium hydroxide and the chloride ions of the hydrochloric acid take no active part in the reaction. They might be called "spectator ions." Nevertheless, these ions are in the same solution after the reactants have been mixed. Provided the acid and the hydroxide were in equivalent amounts, the solution after neutralization has taken place is in every respect identical with one obtained by dissolving sodium chloride in water. Hence neutralization reactions may be used to prepare salts by the proper choice of acid and metal hydroxide. When solutions of nitric acid and potassium hydroxide are mixed in equivalent amounts, exactly the same reaction takes place, that of hydronium and hydroxyl ions to form water. However, the spectator ions are different, and a solution of potassium nitrate is formed. The two examples of neutralization considered above have been between a strong acid and a metal hydroxide in each case. In these and all similar cases, the neutralization reaction is between hydronium and hydroxyl ions.

4. Reactions of Weak Acids and Metal Hydroxides.—When a weak acid, like acetic acid, is used, a slightly different type of neutralization takes place. Remember that in 0.1*M* acetic acid nearly 99 per cent of the solute is in the form of acetic acid molecules and only slightly more than 1 per cent is in the form of hydronium and acetate ions. When a metal hydroxide is added, these few hydronium ions will react with hydroxyl ions in the normal way. However, by far the more abundant reaction will be between the more numerous acetic acid molecules and the hydroxyl ions:

$$\underset{\text{acid}_1(\text{A}_1)}{HC_2H_3O_2} + \underset{\text{base}_2(\text{B}_2)}{OH^-} \underset{5}{\overset{16}{\rightleftarrows}} \underset{\text{acid}_2(\text{A}_2)}{HOH} \underset{+}{+} \underset{\text{base}_1(\text{B}_1)}{C_2H_3O_2^-}$$

This reaction needs careful study as it is typical of reactions that take place between acids and bases in general. Invariably, such a reaction involves a competition between two bases for the possession of protons. In the above change the two bases are the hydroxyl and the acetate ions. The strength of a base is determined by the weakness of the conjugate acid and, therefore, by the smallness of the ionization constant and the magnitude of the pK of the acid. The strength of the hydroxyl ion as a base is determined on a logarithmic scale (Why?) by the pK of water (16), its conjugate acid; that of the acetate ion, by the pK of acetic acid (5). The tendency for the direct reaction in the above equation to take place depends on the strength of the hydroxyl ion as a base, *i.e.*, on its ability to capture protons. Hence we place the number 16 above the arrow pointing to the right. Similarly, the tendency for the reverse reaction depends on the strength of the acetate ion as a base; and we place 5 below the arrow for the reverse reaction. Remember the pK's are really powers of 10 (32-6). Hence the relative tendencies of the direct and of the reverse reactions to take place are as 10^{16} is to 10^5. We should expect the direct reaction to proceed nearly to completion under these circumstances.

5. Protolysis Reactions Defined.—*All reactions between acids and bases which involve proton transfer are called protolysis reactions.* All the reactions considered in this chapter are of this type. The extent to which any protolysis reaction takes place may be determined by the method used to analyze the reaction between acetic acid and a metal hydroxide in the last paragraph.

Neutralization may be defined as a protolysis reaction between an acid and the hydroxyl ion. Thus the reactions considered in paragraphs 3 and 4 are of this type. To summarize, when a strong acid reacts with a metal hydroxide, the reaction is the same in each case:

$$\underset{A_1}{H_3O^+} + \underset{B_2}{OH^-} \overset{16}{\underset{-2}{\rightleftarrows}} \underset{A_2}{HOH} + \underset{B_1}{H_2O}$$

The spectator ions determine the salt formed. However, molecules of a weak acid react with the OH^- as follows:

$$\underset{A_1}{HB} + \underset{B_2}{OH^-} \overset{16}{\underset{pK\text{ of }A_1}{\rightleftarrows}} \underset{A_2}{HOH} + \underset{B_1}{B^-}$$

The following are specific examples:

$$HC_2H_3O_2 + OH^- \overset{16}{\underset{5}{\rightleftarrows}} HOH + C_2H_3O_2^-$$

$$HCN + OH^- \overset{16}{\underset{9}{\rightleftarrows}} HOH + CN^-$$

In these cases, again the positive ion of the metal hydroxide and the negative ion of the acid determine the salt formed.

Although the equations, which we have been writing, show the actual reaction and the extent to which it takes place, they do not indicate what salt has been formed. Hence it is frequently desirable to write the more complete equations of the familiar type given below:

$$\begin{aligned}
NaOH + HCl &\longrightarrow NaCl + HOH \\
KOH + HNO_3 &\longrightarrow KNO_3 + HOH \\
NaOH + HC_2H_3O_2 &\rightleftarrows NaC_2H_3O_2 + HOH \\
KOH + HCN &\rightleftarrows KCN + HOH
\end{aligned}$$

When the weights of the reacting substances and of the products are to be determined, such equations must be used. On the other hand, when the actual mechanism of the reaction must be explained, the ionic reactions are preferable.

Because of the importance of the OH^- as a base, it has long been the custom to refer to metal hydroxides like sodium hydroxide, NaOH, as bases. This custom is still common and should cause no confusion if it is remembered that such hydroxides are the source of the real base, the hydroxyl ion.

6. Polyprotic Acids in Neutralization Reactions.—When a diprotic acid, like sulfuric acid, is neutralized by sodium hydroxide, the neutralization takes place in two steps:

$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + HOH$$

and

$$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + HOH$$

It is evident that one mole of sulfuric acid requires two moles of sodium hydroxide for its complete neutralization. If only one mole of the hydroxide is used, the second step does not take place and the acid salt, sodium bisulfate, $NaHSO_4$, is the final product. If solid sodium bisulfate is dissolved in water and an equivalent amount of sodium hydroxide added, the second step of the neutralization takes place and normal sodium sulfate is formed.

Similarly, the neutralization of the triprotic phosphoric acid takes place in three steps:

$$\begin{aligned}
H_3PO_4 + KOH &\rightarrow KH_2PO_4 + HOH \\
KH_2PO_4 + KOH &\rightleftarrows K_2HPO_4 + HOH \\
K_2HPO_4 + KOH &\rightleftarrows K_3PO_4 + HOH
\end{aligned}$$

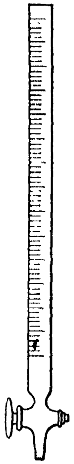

Fig. 113.—A burette.

7. Acid-base Titrations.—When it becomes necessary t determine the total amount of an acid or of a base in a solution this can be readily accomplished by means of a neutralizatio reaction. A certain volume of the solution of unknown concentration is measured out into a beaker together with a few drop of a suitable indicator. If the solution contains a base, then a acid solution of known concentration is dropped slowly into i from a graduated tube, called a burette (Fig. 113) until the indicator just begins to turn color, showin that the solution is neutral. This process is calle titration. The volume of the acid solution require to neutralize the base is then read off from the scal on the burette. From this and the known concentration of the acid, the unknown concentration c the base can be calculated. If the unknown solutio is acidic, then a standard solution of a base is added

The best way to express the concentration c standard solutions of acids and of bases used i titrations is in terms of normality. *A normal solutio is* defined as *one in which a gram-equivalent weight c an acid or base is dissolved in a liter of solution.* gram-equivalent weight of an acid is equal to on mole divided by the number of protons which molecule of the acid can donate to bases. Thus normal solution of hydrochloric acid (monoprotic would contain 1 mole (36.5 g.)/liter; and one of sulfuric acid ½ mole (49 g.)/liter. A gram-equivalent weight of a base is equa to one mole divided by the number of OH groups in its formula Here the term base is applied to the metal hydroxide. Thus normal solution of sodium hydroxide, NaOH, contains 1 mole liter and one of calcium hydroxide, $Ca(OH)_2$, ½ mole/liter. Fron the above it can be seen that there are as many protons in a give volume of a normal solution of any acid as there are hydroxy groups in the same volume of a normal solution of any base. Th *normality* N of a solution is a number which compares its concentration with that of a normal solution. Thus a $0.1N$ NaOH solution is one-tenth as concentrated as a $1N$ solution, *i.e.*, it contain 0.1 mole NaOH/liter. Finally, *equal volumes of solutions of an acid and any base of the same normality will neutralize eac other.*

Now for an example of an actual titration. Thirty milliliters of a $0.1N$ solution of sodium hydroxide is required to neutralize 25 ml. of a solution of sulfuric acid of unknown concentration. What weight of sulfuric acid is dissolved in these 25 ml. of its solution? The volumes of the two solutions will be in an inverse ratio to their normalities, since the less the normality, the greater the volume required for neutralization. Hence:

$$\frac{30\text{ ml.}}{25\text{ ml.}} = \frac{xN}{0.1N}$$
$$x = 0.12$$

which is the normality of the sulfuric acid. A normal sulfuric acid solution contains ½ mole (98/2 g.)/liter. A $0.12N$ solution contains $0.12 \times 98/2$ g., or 5.88 g./liter. Twenty-five milliliters would contain

$$\frac{25}{1{,}000} \times 5.88\text{ g.} = 0.147\text{ g.}$$

8. Protolysis Reactions in General.—When any acid is treated with any base, a protolysis reaction will take place. The extent to which the direct reaction will go toward completion may be predicted by the method outlined in paragraph 4. To make such predictions, we must constantly refer to the pK's given in Table 38. The examples given below will help you to understand the method.

a. Hydrochloric Acid and Sodium Acetate:

$$H_3O^+ + C_2H_3O_2^- \underset{-2}{\overset{5}{\rightleftarrows}} HC_2H_3O_2 + H_2O$$

This reaction will proceed nearly to completion, as the "drive" behind the direct reaction is 10,000,000 (10^7) times greater than that behind the reverse. Thus sodium acetate may be used to neutralize hydrochloric acid, and the salt sodium chloride may be prepared at the same time.

$$HCl + NaC_2H_3O_2 \rightleftarrows NaCl + HC_2H_3O_2$$

Here we have an example of a strong acid (HCl) reacting with a strong base ($C_2H_3O_2^-$). Such reactions go nearly to completion.

b. Ammonium Chloride and Sodium Hydroxide.—At first sight we have difficulty in finding the acid. Ammonium chloride is a salt consisting of ammonium and chloride ions. Referring to Table 38 we find that the ammonium ion is an acid though a weak one. The reaction is between the ammonium and the hydroxyl ions

$$\underset{A_1}{NH_4^+} + \underset{B_2}{OH^-} \xrightleftharpoons[9]{16} \underset{B_1}{NH_3} + \underset{A_2}{HOH}$$

Hence the reaction will proceed well toward completion. If at the same time the reaction mixture is heated to drive off the ammonia as a gas, the reverse reaction is prevented and the direct reaction goes to completion. Such a reaction is used to prepare ammonia from an ammonium salt.

$$NH_4Cl + NaOH \rightarrow NaCl + NH_3\uparrow + H_2O$$

One may wonder why we did not consider the chloride ion as a base, since it is so listed in Table 38. This is because the negative ions of strong acids are almost infinitesimally weak bases. This is brought out in the next example.

c. Acetic Acid and Sodium Chloride.—Here the only possible bases present are the chloride ion and the water molecule. Both are very weak, but of the two the water molecule is the stronger. Thus the reaction will be

$$\underset{A_1}{HC_2H_3O_2} + \underset{B_2}{H_2O} \xrightleftharpoons[5]{-2} \underset{A_2}{H_3O^+} + \underset{B_1}{C_2H_3O_2^-}$$

In other words, acetic acid will ionize as it does in pure water (32-3) despite the fact that sodium and chloride ions are present. If the chloride ion were to act as the base, the following reaction must be considered:

$$HC_2H_3O_2 + Cl^- \xrightleftharpoons[5]{-7} HCl + C_2H_3O_2^-$$

with a 10^{12}, or a million millionfold greater, drive behind the reverse reaction.

Therefore, such ions as Cl^-, NO_3^-, HSO_4^-, and $SO_4^=$ need never be considered as bases since they are the negative ions of strong acids.

9. Hydrolysis.—When sodium acetate is dissolved in water, the resulting solution is basic. The hydroxyl-ion concentration increases and that of the hydronium ion decreases, since the following reaction takes place:

$$\underset{A_1}{HOH} + \underset{B_2}{C_2H_3O_2^-} \xrightleftharpoons[16]{5} \underset{A_2}{HC_2H_3O_2} + \underset{B_1}{OH^-}$$

Such reactions are known as *hydrolysis, i.e., the reaction of an ion with water.* The hydrolysis of the acetate ion involves a competition between this base and the hydroxyl ion of which the latter is stronger. Therefore, the hydrolysis does not proceed very far before equilibrium. Nevertheless, the fact that it goes at all results in an increased hydroxyl-ion concentration and a basic solution.

Hydrolysis does not occur when sodium chloride is dissolved in water, because the chloride ion is an infinitesimally weak base:

$$\mathrm{HOH} + \mathrm{Cl}^- \underset{16}{\overset{-7}{\rightleftarrows}} \mathrm{HCl} + \mathrm{OH}^-$$

so that no increase in hydroxyl-ion concentration takes place and the solution remains neutral. Similarly, no hydrolysis of the nitrate ion or of any other conjugate base of a strong acid occurs. Only negative ions that are strong bases are hydrolyzed.

Hydrolysis of positive ions also takes place but not in all cases. Alkali and alkaline-earth metal ions are not hydrolyzed. In general, the greater the charge on an anion, the greater its hydrolysis. When aluminum chloride is dissolved in water, its solution is acidic, an indication of an increase in the hydronium-ion concentration. Ions of high positive charge like the aluminum ion are invariably hydrated in aqueous solution. Each aluminum ion is surrounded by six water molecules attached by dative bonds. We have seen that a water molecule is an acid though a very weak one, since its tendency to lose a proton is slight. Attached to a positively charged ion, however, this tendency is noticeably increased, since there is a force of repulsion between the proton and the ion both of which are positively charged. A hydrated positive ion is, therefore, an acid:

$$\mathrm{Al(H_2O)_6}^{+++} \rightleftarrows \mathrm{H}^+ + \mathrm{Al(H_2O)_5OH}^{++}$$

Such an ion reacts with water to form hydronium ions:

$$\mathrm{Al(H_2O)_6}^{+++} + \mathrm{H_2O} \rightleftarrows \mathrm{Al(H_2O)_5OH}^{++} + \mathrm{H_3O}^+$$

This is really the ionization of a weak acid, but it is commonly classed as a hydrolysis.

Many examples of hydrolysis will be studied in the chapters that follow. The above will serve merely as an introduction to this type of reaction.

10. Amphiprotic Substances and Ions.—In Table 38, certain substances are listed both as acids and as bases. Thus water may act as an acid, or proton donor,

$$HOH \rightleftarrows H^+ + OH^-$$

and as a base, or proton acceptor,

$$H_2O + H^+ \rightleftarrows H_3O^+$$

Certain ions, like the bisulfate and bicarbonate ions, are both acids and bases:

$$HSO_4^- \rightleftarrows H^+ + SO_4^=$$
$$HSO_4^- + H^+ \rightleftarrows H_2SO_4$$

Such substances and ions are *amphiprotic.*

EXERCISES

1. What is a base?

2. What are the formulas of two molecular, two anion, and one cation acids and their conjugate bases?

3. What are the relationships between the strength, the ionization constant, and the pK of an acid and the strength of its conjugate base?

4. Why are such substances as the hydroxides of sodium and calcium commonly called bases?

5. In what respect does the neutralization of a strong acid by the hydroxyl ion differ from one in which a weak acid takes part?

6. Define hydrolysis.

7. Upon what does the extent of hydrolysis of an anion depend?

8. A solution of sodium hydroxide requires 20 ml. of 0.2N hydrochloric acid for its neutralization. What weight of sodium hydroxide is present in the solution?

9. What is an amphiprotic substance? Write equations to show that water is amphiprotic.

10. Write equations for the following protolysis reactions, and predict qualitatively the extent of each reaction:

Sodium hydroxide + nitric acid
Potassium hydroxide + hypochlorous acid
Sodium hydroxide + sulfuric acid
Potassium hydroxide + potassium bisulfate
Ammonia-water + hydrochloric acid
Ammonium chloride + sodium hydroxide
Sodium carbonate + hydrochloric acid
Sodium bicarbonate + acetic acid
The hydrolysis of the bicarbonate ion

Ammonium chloride + sodium acetate
Ammonium carbonate dissolved in water

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CHAPTER THIRTY-FOUR

SULFUR AND THE SULFIDES

Sulfur is placed in Group VI of the periodic table along with oxygen and the less important elements selenium and tellurium. This element has been known since almost the beginning of recorded history. In 2000 B.C., its combustion product, sulfur dioxide, was used to bleach linen. To the alchemists, sulfur was symbolic of fire; the term brimstone by which sulfur is still commonly known emphasizes this relationship.

1. Occurrence of Sulfur.—Sulfur occurs free in nature wherever there has been volcanic activity, although rarely are deposits of this type of sufficient magnitude to be commercially important. Exceptions are those in Japan and in the crater of the volcano Popocatepetl, in Mexico. By far the most important occurrence of free sulfur is where it is associated with the mineral gypsum, calcium sulfate. The important sulfur deposits along the Gulf Coast of Louisiana and Texas, which produce 85 per cent of the world's supply, and the deposits in Sicily are of this type.

Many metals occur as sulfides, among which are sulfides of zinc, iron, lead, and copper. Of these iron pyrite, FeS_2, is the most important as a source of sulfur compounds. It is found in large deposits in Spain; in Virginia, Ohio, Indiana, Illinois, and California; and in Canada. The sulfides of zinc, lead, and copper are important ores of these metals; and sulfur compounds are obtained as a by-product when these ores are smelted. Important sulfates are gypsum, $CaSO_4.2H_2O$, and barite, $BaSO_4$.

2. Extraction of Sulfur.—The deposits of sulfur on the Gulf Coast were discovered in 1867 by geologists drilling for oil. They lie buried under some 500 ft. or more of quicksand through which there is a heavy flow of ground water charged with sulfur dioxide and hydrogen sulfide. Immediately the economic importance of this discovery was recognized, and an attempt was made to sink a shaft lined with large iron cylinders to keep out the poisonous ground water. This attempt met with disaster when five workmen were killed by the dangerous hydrogen sulfide gas.

About 1890 Herman Frasch, a chemist in charge of research and development work at the Standard Oil Company, conceived

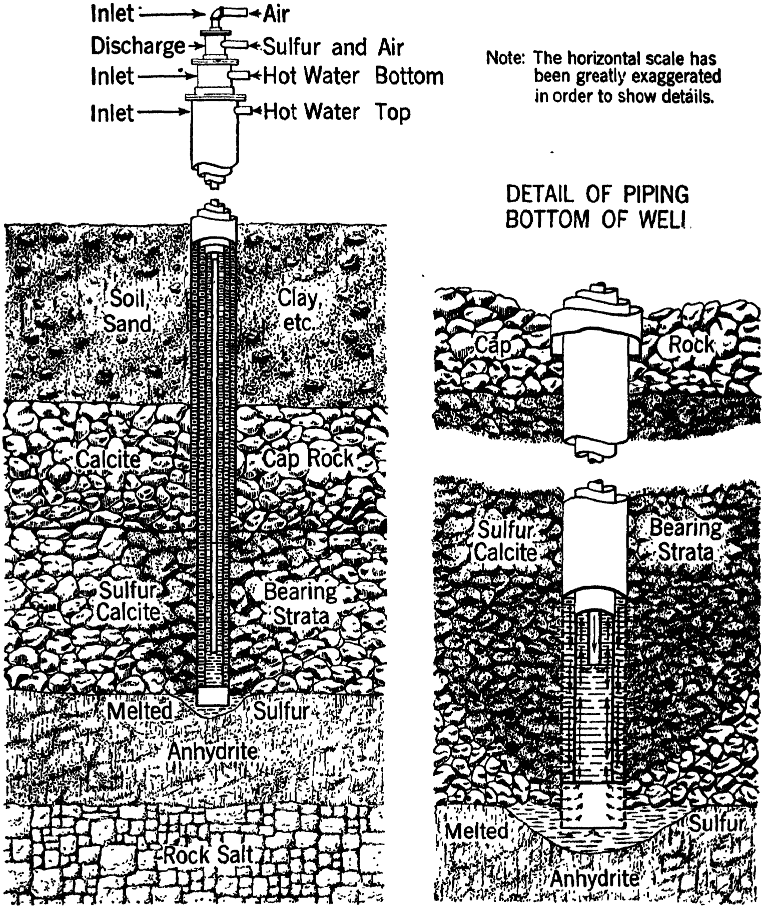

Fig. 114.—The Frasch process. (*Courtesy of Texas Gulf Sulphur Company.*)

the idea of drilling a well into the sulfur-containing strata, melting the sulfur in the ground by means of superheated water, and pumping the liquid sulfur to the surface. Since the melting point of sulfur (115°C.) is above the boiling point of water at atmospheric pressure (100°C.), the latter had to be heated under pressure in order to attain a temperature sufficient to melt sulfur. The first attempt made in 1894 was successful, and Frasch's own account makes interesting reading.[1] The original method had to be modified and other troubles overcome before the process became financially successful. By 1904, however, enough sulfur was being raised to supply the entire demand of the United States and to permit the first cargo to be exported.

Fig. 115.—Liquid sulfur pouring into a storage vat. (*Courtesy of Texas Gulf Sulphur Company.*)

The modern sulfur well is shown in cross section in Fig. 114. The outer 10-in. casing is cemented to the limestone cap rock which lies at depths varying from 1,000 to 1,600 ft. Within this casing and extending down farther into the sulfur-bearing strata are three concentric pipes of 8, 4, and 1½ in. diameters. The superheated water at 168°C. is pumped down into the well between the two outer pipes. Air at a pressure of 500 lb./sq. in. enters the well through the 1½-in. line and forces the liquid sulfur up through the space between the 4- and 1½-in. pipes. The sulfur is carried through steam-heated insulated pipe lines

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[1] Perkin Medal award to Herman Frasch, *Ind. Eng. Chem.*, 4, 131 (1912).

to gigantic bins in which it solidifies. When full, the walls of these bins are knocked down and the sulfur dynamited loose as needed for shipping. It is of remarkable purity, running constantly over 99½ per cent. The total production in 1940 in the United States was 2,732,088 tons. In all, the Frasch process had succeeded in raising nearly 50,000,000 tons of sulfur by 1940.

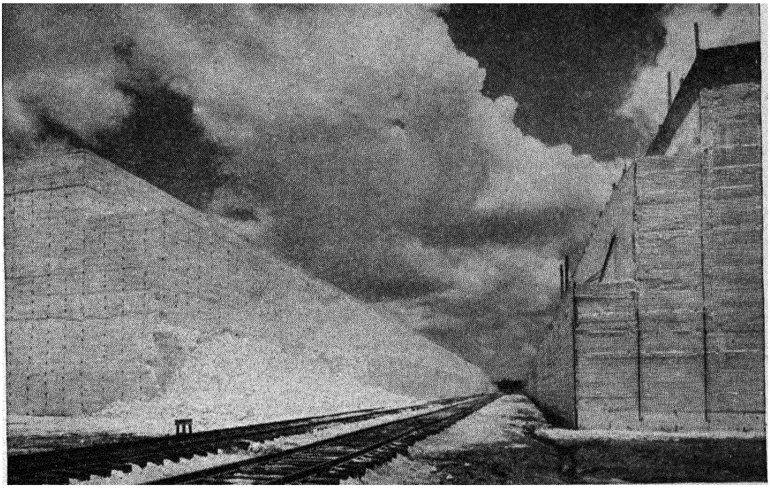

FIG. 116.—Mountains of sulfur brought to the surface by the Frasch process. Solid sulfur after the walls of the vat have been removed. Each vat is about 1,200 ft. long, 170 ft. wide and 50 ft. high and contains approximately one-half million tons of sulfur. (*Courtesy of Texas Gulf Sulphur Company.*)

3. Physical Properties.—Sulfur is a yellow solid at room temperature. It may exist in two allotropic modifications: rhombic crystals below 95.5°C. and monoclinic crystals above this transition temperature (Fig. 117). The rhombic form may be obtained by allowing sulfur to crystallize from its solution in carbon disulfide below the transition temperature. Monoclinic crystals are formed when melted sulfur freezes at 118.9°C.

When liquid sulfur is heated, the viscosity of the straw-colored liquid at first decreases normally. At this stage, the liquid consists of S_8 molecules in which the eight sulfur atoms are joined by covalent linkages in distorted rings. These molecules are also the structure units in sulfur crystals. As the temperature rises, there is a marked increase in viscosity to a maximum at 186°C. and a deepening in color. During this stage, the S_8 ring-type molecules break and long chains of atoms with as many as 36 atoms form. The increased viscosity is explained by assuming that such chains tangle with one another far more than do the more or less egg-shaped S_8 molecules. If the viscous liquid is chilled by pouring into water, a rubbery mass of plastic sulfur is the result. Further heating decreases the viscosity once again. The long chains break into shorter ones, until finally at the boiling point the molecules are diatomic. Sulfur vapor like oxygen is diatomic.

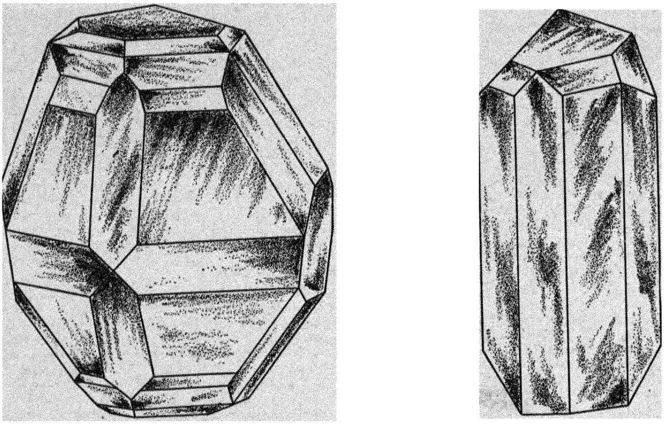
RHOMBIC MONOCLINIC

FIG. 117.—The two allotropic forms of sulfur.

Sulfur is soluble in carbon disulfide but insoluble in water.

4. The Reactions of Sulfur.—Sulfur burns readily with a blue flame to form sulfur dioxide, a gas with a characteristic sweetish but choking odor.

$$S + O_2 \rightarrow SO_2$$

At the same time, a relatively small amount is oxidized further to the trioxide, SO_3. Carbon disulfide is manufactured by the action of hot sulfur vapor on charcoal or coke:

$$C + 2S \rightarrow CS_2$$

This straw-colored liquid has an evil odor due to impurities in the commercial product. Its vapors are poisonous, and it is extremely inflammable. It is an important solvent and the raw material for the manufacture of carbon tetrachloride:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

At the same time the improperly named sulfur monochloride, S_2Cl_2, an important rubber vulcanizer, is formed.

When heated, sulfur combines directly with all metals except gold and platinum. In this respect it is very similar to oxygen. These reactions are, in general, strongly exothermic. Metal sulfides are formed, *e.g.*,

$$Fe + S \rightarrow FeS$$
$$2Cu + S \rightarrow Cu_2S$$

Hot sulfur combines directly with hydrogen to form hydrogen sulfide:

$$H_2 + S \rightarrow H_2S$$

5. Uses.—Nearly 85 per cent of the sulfur produced in this country is converted into sulfuric acid. This acid is one of the most important chemicals manufactured and is used in many diversified industries. In addition, the element itself is used in the vulcanization and compounding of rubber, in the manufacture of viscose rayon, in sprays and dusts to control insects and fungi, in the preparation of paper pulp from wood, and in many other ways. In fact, there is scarcely an article of commerce in the manufacture of which sulfur in some form has not been used.

6. Hydrogen Sulfide.—This gaseous compound is not only malodorous, but also *extremely poisonous.* Inhalation of as low a concentration as 1 part in 50,000 parts of air is rapidly fatal. Fortunately, its vile odor gives sufficient warning of its presence. It is found in nature wherever organic matter putrifies, *e.g.*, rotten eggs, and dissolved in certain natural waters. It is released when sulfur compounds in petroleum and in soft coal are decomposed by the commercial process of distillation.

Although hydrogen sulfide may be prepared by the direct union of its elements, the more convenient method is by the action of dilute acid on the insoluble ferrous sulfide:

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S\uparrow$$

It is only sparingly soluble in water. As in the cases of all such gases, its solubility depends on the temperature and on its partial pressure (19-11). At 25°C. and at a partial pressure of 1 atm., its saturated solution is 0.1*M*.

The dissolved gas is slowly oxidized by the oxygen in the air; in this reaction finely divided sulfur is formed:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

Hence the cloudy appearance of its aqueous solutions. The gas burns readily with the formation of water vapor and sulfur dioxide:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

The valence number of sulfur in hydrogen sulfide and in the metal sulfides is -2. Its conversion to free sulfur or to an oxygen compound of sulfur is an oxidation. Hence hydrogen sulfide is a reducing agent (23-3). When treated with a mild oxidizing agent like ferric chloride, the sulfur is oxidized to the free state:

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + S\downarrow + 2HCl$$

With a more active oxidizing agent, as for example nitric acid, oxidation to sulfuric acid results:

$$3H_2S + 8HNO_3 \rightarrow 3H_2SO_4 + 8NO + 4H_2O$$

This equation may be easily balanced by the valence changes involved (17-2c):

$$(S^{-2} \rightarrow S^{+6} + 8e^-) \times 3$$
$$(3e^- + N^{+5} \rightarrow N^{+2}) \times 8$$

An extremely weak acid, its primary ionization constant is 10^{-7} and its secondary, 10^{-15}. Thus it is not so weak an acid as water—remember oxygen and sulfur are in the same group. It will react with a strong base like the hydroxyl ion, but the reactions are reversible:

$$H_2S + OH^- \underset{7}{\overset{16}{\rightleftarrows}} HS^- + HOH$$

and

$$HS^- + OH^- \underset{15}{\overset{16}{\rightleftarrows}} S^= + HOH$$

If the metal hydroxide, used as the source of hydroxyl ions, is sodium hydroxide, sodium bisulfide will be formed first:

$$H_2S + NaOH \rightarrow NaHS + HOH$$

followed by the normal salt:

$$NaHS + NaOH \rightarrow Na_2S + HOH$$

Thus if an excess of sodium hydroxide is used, sodium sulfide is the product and both of the above equations may be combined in

$$H_2S + 2NaOH \rightarrow Na_2S + 2HOH$$

Hydrogen sulfide is used extensively in analytical chemistry to precipitate the insoluble metal sulfides.

7. Metal Sulfides.—Sulfides of all metals, except the alkali and the alkaline-earth metals, are insoluble in water. The soluble sulfides are most readily prepared by neutralization reactions. When hydrogen sulfide is passed into a solution containing the ion of a metal whose sulfide is insoluble, the latter precipitates (16-10). As an example, when hydrogen sulfide is passed into a solution of silver nitrate, a black precipitate of silver sulfide is formed:

$$2Ag^+ + S^= \rightarrow Ag_2S\downarrow$$

or

$$2AgNO_3 + H_2S \rightarrow Ag_2S\downarrow + 2HNO_3$$

The conditions for precipitation, so important in analytical chemistry, will be discussed in the next chapter.

When a sulfide, like sodium sulfide, dissolves in water, the resulting solution is strongly basic. This is because of the hydrolysis of the sulfide ion. The sulfide ion is the conjugate base of the exceedingly weak acid the HS^- ion. Hence it is a strong base and, therefore, extensively hydrolyzed:

$$S^= + HOH \underset{16}{\overset{15}{\rightleftharpoons}} HS^- + OH^-$$

The resulting increase in the hydroxyl-ion concentration makes the solution basic. The bisulfide ion is, as we have just said, an extremely weak acid.

$$HS^- \rightleftharpoons H^+ + S^=$$

It is also the conjugate base to the weak acid hydrogen sulfide

$$HS^- + H^+ \rightleftharpoons H_2S$$

and is, therefore, a strong base. When sodium bisulfide is dissolved in water, sodium and bisulfide ions are the solute particles. Since the bisulfide ion is both an acid and a base, *i.e.*, amphiprotic, it is interesting to note in which role it will react with water. As an acid, it will ionize as follows:

$$\underset{A_1}{HS^-} + \underset{B_2}{H_2O} \underset{15}{\overset{2}{\rightleftharpoons}} \underset{A_2}{H_3O^+} + \underset{B_1}{S^=}$$

Its ionization is slight since it is an exceedingly weak acid. As a strong base, it will be hydrolyzed:

$$\underset{B_1}{HS^-} + \underset{A_2}{HOH} \underset{16}{\overset{7}{\rightleftarrows}} \underset{A_1}{H_2S} + \underset{B_2}{OH^-}$$

Its hydrolysis is thus more extensive than its ionization, and the hydroxyl rather than the hydronium ion concentration should increase. Thus solutions of sodium bisulfide should be basic; and this is the case.

EXERCISES

1. Describe the Fasch process.

2. What happens to the molecular structure of sulfur when the liquid is heated and finally vaporized?

3. Write equations for the reactions by which sulfur may be converted into hydrogen sulfide.

4. Why are solutions of sodium sulfide basic?

5. Write the protolysis reaction that takes place when solutions of sodium bisulfide and hydrochloric acid are mixed.

6. Why do solutions of hydrogen sulfide turn milky-white on standing?

7. Write equations for two reactions in which hydrogen sulfide acts as a reducing agent.

8. Is hydrogen sulfide more or less dense than oxygen under the same conditions?

9. Are aqueous solutions of hydrogen sulfide good or poor conductors of electricity?

10. Why has not this substance been used as a poisonous gas in warfare?

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CHAPTER THIRTY-FIVE

PRECIPITATION

Whereas salts in general, especially those of the alkali and alkaline-earth metals, are readily soluble in water, there are many whose solubility is very small. These salts have been classed as insoluble, although this is, of course, an inexact use of the term. The precipitation of insoluble salts is of the greatest importance in both qualitative and quantitative analysis.

1. Saturated Solutions of Salts.—We have studied the mechanism of the establishment of the equilibrium which exists in a saturated solution between the dissolved and undissolved molecules of the solute. If, however, the solute is a salt, ions instead of molecules go into solution from the ionic crystals. In the saturated solution of a salt at a given temperature, there is an equilibrium between the ions in solution and those in the solid crystals of undissolved salt. In the case of barium sulfate, a sparingly soluble salt, the following equilibrium exists between the barium and sulfate ions in the undissolved crystals and those in the saturated solution:

$$\underset{\text{solid}}{BaSO_4} \rightleftarrows \underbrace{Ba^{++} + SO_4^{=}}_{\text{in solution}}$$

The constant for this equilibrium may be expressed in the usual way:

$$\frac{[Ba^{++}] \times [SO_4^{=}]}{\underset{\text{solid}}{[BaSO_4]}} = K$$

2. Solubility Product.—Since the concentration of a solid is constant (31-3), it may be included with the equilibrium constant in a new constant L, called the solubility product:

$$[Ba^{++}][SO_4^{=}] = K \times \underset{\text{solid}}{[BaSO_4]} = L_{BaSO_4}$$

If the example is lead chloride, the equilibrium associated with its saturated solution would be

$$\underset{\text{solid}}{PbCl_2} \rightleftarrows Pb^{++} + 2Cl^-$$

the equilibrium constant,

$$\frac{[Pb^{++}] \times [Cl^-]^2}{[PbCl_2]} = K$$

and the solubility product,

$$[Pb^{++}][Cl^-]^2 = L_{PbCl_2}$$

Therefore, *the solubility product of a salt at a given temperature is equal to the product of the concentrations of its ions in a saturated solution at that temperature, each concentration being raised to the appropriate power.*

The solubility product of a salt may be readily calculated if its solubility is known. For example, the solubility of barium sulfate at 25°C. is 0.00023 g. per 100 g. of water. Since concentrations in expressions for equilibrium constants and solubility products are expressed in moles per 1,000 g., we had best first convert the solubility of barium sulfate to these terms:

$$\frac{0.00023 \text{ g. } BaSO_4}{100 \text{ g. } H_2O} = \frac{0.0023 \text{ g.}}{1{,}000 \text{ g.}} = \frac{0.0023/233 \text{ mole}}{1{,}000 \text{ g.}} = \frac{1.03 \times 10^{-5} \text{ mole}}{1{,}000 \text{ g.}}$$

Since all salts are completely ionized, this is the concentration of both the barium and the sulfate ions. The solubility product is now easily calculated:

$$L_{BaSO_4} = [Ba^{++}][SO_4^{=}] = 1.03 \times 10^{-5} \times 1.03 \times 10^{-5} = 1.1 \times 10^{-10}$$

At a given temperature, the more insoluble a salt, the less is its solubility product. Since, in general, a salt becomes more soluble if the temperature is raised, its solubility product will likewise increase with the temperature. At 50°C. the solubility product of barium sulfate is 1.98×10^{-10}.

The solubility of a salt and so also its solubility product at a given temperature are changed slightly but definitely by the presence of other salts in the same solution. This effect is due to the Coulomb forces which operate between ions. For very accurate work, it must be taken into consideration, but for our present purposes it may be disregarded.

3. Precipitation Reactions.—When two solutions, each containing an ion of a certain insoluble salt, are mixed, precipitation of this salt occurs almost instantly. For example, if a solution of sodium sulfate is added to one of barium chloride, a white precipitate of barium sulfate is formed by the reaction

$$Ba^{++} + SO_4^{=} \rightarrow BaSO_4\downarrow$$

The sodium and chloride ions are spectator ions. Nevertheless, if the precipitate is removed from the solution by filtration, the remaining solution is one of sodium chloride. If this is evaporated, sodium chloride will crystallize. The equation

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2NaCl$$

shows this relationship.

As an aid to remembering which salts are insoluble, the following rules are helpful. These rules are for the more common salts.

SOLUBILITY RULES

1. All nitrates, acetates, and chlorates are soluble.
2. All potassium, sodium, and ammonium salts are soluble.
3. All chlorides are soluble except silver, lead, and mercurous chlorides.
4. All sulfates are soluble except those of barium, strontium, and lead.
5. All carbonates and phosphates are insoluble except those of sodium, potassium, and ammonium.
6. All sulfides are insoluble except those of the alkali and alkaline-earth metals and ammonium sulfide.

4. Conditions for Precipitation.—To obtain crystallization of a solute from solution, it is necessary to prepare a supersaturated solution (19-10). In terms of solubility product, a supersaturated solution of a salt is one in which the product of the concentrations of its ions, each raised to the appropriate power, is greater than its solubility product at that temperature. The more the solubility product is exceeded, the greater the degree of supersaturation, and the more rapid the crystallization. Since precipitation is rapid crystallization, it follows that *precipitation will occur when the ion-concentration product exceeds greatly the solubility product of a salt.*

As an example, consider what will happen when equal volumes of solutions of barium chloride and of sodium sulfate, each $0.2M$, are mixed. After mixing, each salt will be dissolved in twice as great a volume of solution and hence be half as concentrated. The concentrations of the barium and sodium ions will each be equal to $0.1M$. The ion-concentration product at mixing will be

$$[Ba^{++}] \times [SO_4^{=}] = 10^{-1} \times 10^{-1} = 10^{-2}$$

This is enormously greater than the solubility product of barium sulfate 10^{-10}:

$$[\mathrm{Ba}^{++}] \times [\mathrm{SO}_4^{=}] = 10^{-2} > L_{\mathrm{BaSO}_4} = 10^{-10}$$

Hence precipitation of barium sulfate will occur until the concentration product of the ions remaining in solution once again is equal to the solubility product. Then the solution will be no longer supersaturated but merely saturated.

5. The Solution of a Precipitate.—To dissolve a precipitate, its ion-concentration product in the solution in which it is suspended must be kept less than its solubility product. Under such conditions, the solution will not be saturated and the precipitate will dissolve. There are several methods by which this reduction of the concentration of the ions may be accomplished, but the solution of a given precipitate may not be possible by all the methods discussed below.

Theoretically, any precipitate may be dissolved by adding enough water and thus keeping the ion-concentration product less than the solubility product. Practically, however, it would take a tubful of water to dissolve even a small barium sulfate precipitate. This method is too inconvenient to be useful. Since the magnitude of the solubility product, in general, increases with the temperature, it seems possible to dissolve a precipitate by heating the solution. Practically, the increase in solubility product is in most cases so slight that this method is useless. In a few cases, *e.g.*, lead chloride, the solubility product increases rapidly with the temperature. Thus a lead chloride precipitate may be dissolved by heating the solution. This behavior is made use of in the separation of the chlorides of lead and silver in qualitative analysis.

6. Solution by the Formation of a Weak Acid.—If the anion of a precipitate is a strong base, as is the case with barium carbonate, ferric hydroxide or zinc sulfide, then the precipitate may usually be dissolved by the addition of an acid. Thus the addition of hydrochloric acid to these precipitates results in the following reactions:

$$\mathrm{CO}_3^{=} + \mathrm{H}_3\mathrm{O}^+ \rightleftarrows \mathrm{HCO}_3^- + \mathrm{H}_2\mathrm{O}$$
$$\mathrm{HCO}_3^- + \mathrm{H}_3\mathrm{O}^+ \rightleftarrows \mathrm{H}_2\mathrm{CO}_3 + \mathrm{H}_2\mathrm{O}$$
$$\mathrm{H}_2\mathrm{CO}_3 \rightarrow \mathrm{H}_2\mathrm{O} + \mathrm{CO}_2\uparrow$$

Any carbonate precipitate dissolves in an acid with the formation of carbonic acid which decomposes liberating the gas carbon dioxide. In the case of ferric hydroxide, the following reaction takes place:

$$OH^- + H_3O^+ \rightarrow HOH + H_2O$$

and in the case of zinc sulfide:

$$S^= + H_3O^+ \rightleftarrows HS^- + H_2O$$
$$HS^- + H_3O^+ \rightleftarrows H_2S + H_2O$$

The ion-concentration products are thus reduced to and kept below the solubility products

$$[Ba^{++}][CO_3^=] < L_{BaCO_3}$$
$$[Fe^{+++}][OH^-]^3 < L_{Fe(OH)_3}$$
$$[Zn^{++}][S^=] < L_{ZnS}$$

and the precipitates dissolve.

On the other hand, the anion of the precipitate, barium sulfate, is not a strong base. Hence the sulfate-ion concentration would not be appreciably reduced by the addition of hydrochloric acid. Sulfate precipitates are, therefore, insoluble in acids. The same would be true in the case of silver chloride. (Why?)

7. Solution by the Formation of a Complex Ion.—Complex ions are made up of a group of atoms. Technically the sulfate, nitrate, and even the hydronium and hydroxyl ions are complex. Usually, however, the simple oxygen-containing ions are not classified as complex ions. Among the common complex ions are $Ag(NH_3)_2^+$, $Fe(CN)_6^{\equiv}$, and $Ag(CN)_2^-$. Such complex ions may be formed in solution by reactions of simple ions with molecules, as in the case of the silver ion with ammonia

$$Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+$$

or with other ions,

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$$

In the first case, the charges on the simple and on the complex ions are the same, since the added molecules are neutral. In the second case, the charge on the complex ion is equal to the sum of the charges on the simple ions of which it is composed.

The formation of complex ions may be used to dissolve certain precipitates. Thus a precipitate of silver chloride dissolves when ammonia is added. Since ammonia combines with the silver ions as indicated above, the silver-ion concentration is reduced to such an extent that

$$[Ag^+][Cl^-] < L_{AgCl}$$

and the precipitate dissolves. Silver chloride may be reprecipitated from the resulting solution by adding nitric acid. Since ammonia is a base, the following reaction takes place:

$$Ag(NH_3)_2^+ + 2H_3O^+ \rightarrow Ag^+ + 2NH_4^+ + 2H_2O$$

Thus the silver-ion concentration is increased to such an extent that

$$[Ag^+][Cl^-] > L_{AgCl}$$

and precipitation results.

8. **The precipitation of sulfides** plays such an important role in qualitative analysis and is such an excellent illustration of the principles we have been considering that we shall consider such precipitations in some detail.

Hydrogen sulfide is the reagent used for their precipitation. This weak acid ionizes in two steps for each of which there is a corresponding ionization constant.

$$H_2S + H_2O \rightleftarrows H_3O^+ + HS^-$$

$$\frac{[H_3O^+][HS^-]}{[H_2S]} = 10^{-7}$$

$$HS^- + H_2O \rightleftarrows H_3O^+ + S^=$$

$$\frac{[H_3O^+][S^=]}{[HS^-]} = 10^{-15}$$

For convenience, the two equations may be added

$$H_2S + 2H_2O \rightleftarrows 2H_3O^+ + S^=$$

Similarly, the two ionization-constant equations may be multiplied to give an ionization constant for the combined equation:

$$\frac{[H_3O^+]^2[S^=]}{[H_2S]} = 10^{-22}$$

Hydrogen sulfide gas at a pressure of 1 atm. is bubbled into the solution of the ion to be precipitated as a sulfide. At this pressure, 0.1 mole of the gas dissolves in a liter of water. Hence the concentration of hydrogen sulfide molecules is $0.1M$.

$$\frac{[H_3O^+]^2[S^=]}{(10^{-1})} = 10^{-22}$$

and $$[H_3O^+]^2[S^=] = 10^{-23}$$

Thus in the solution, saturated with hydrogen sulfide, the product of the square of the hydronium-ion concentration and that of the sulfide ion is equal to a constant. Hence the sulfide-ion concentration is inversely proportional to the square of that of the hydronium ion:

$$[S^{=}] \propto \frac{1}{[H_3O^+]^2}$$

This relationship is very useful, for it shows how the sulfide-ion concentration may easily be varied by changing the acidity of the solution. In solutions of strong acids in which the hydronium-ion concentration is high, that of the sulfide ion is very low. Thus if 0.1*M* hydrochloric acid is saturated with hydrogen sulfide, the resulting sulfide-ion concentration may easily be calculated.

$$\begin{aligned}
&[S^{=}][H_3O^+]^2 = 10^{-23} \\
&[S^{=}] \times (10^{-1})^2 = 10^{-23} \\
&[S^{=}] \times 10^{-2} = 10^{-23} \\
&[S^{=}] = 10^{-21}
\end{aligned}$$

This is extremely low.

In neutral solutions

$$[H_3O^+] = 10^{-7}$$

Hence

$$\begin{aligned}
&[S^{=}] \times (10^{-7})^2 = 10^{-23} \\
&[S^{=}] = 10^{-9}
\end{aligned}$$

In basic solutions, the sulfide-ion concentration is relatively high. By adding sodium hydroxide to a solution of hydrogen sulfide, the following neutralization reaction takes place:

$$H_2S + 2OH^- \rightleftarrows S^{=} + 2HOH$$

which results in the increased sulfide-ion concentration.

The solubility products of the sulfides of copper, cadmium, and manganese are 8.5×10^{-45}, 3.6×10^{-29}, and 1.4×10^{-15}, respectively. Let us assume that we have a solution containing all three of these metals as ions and, further, that the concentration of each is 0.1*M*. If this solution is acidified to a hydronium-ion concentration of 0.1*M* and the solution saturated with hydrogen sulfide, which sulfides will precipitate? The sulfide-ion concentration will be 10^{-21}. In the case of copper sulfide

$$[Cu^{++}][S^{=}] = 10^{-1} \times 10^{-21} = 10^{-22} > 8.5 \times 10^{-45} = L_{\text{CuS}}$$

Therefore copper sulfide will precipitate.

$$[Cd^{++}][S^{=}] = 10^{-1} \times 10^{-21} = 10^{-22} > 3.6 \times 10^{-29} = L_{CdS}$$

Cadmium sulfide will precipitate. But

$$[Mn^{++}][S^{=}] = 10^{-1} \times 10^{-21} = 10^{-22} < 1.4 \times 10^{-15} = L_{MnS}$$

and, therefore, manganese sulfide will not precipitate.

Thus by choosing the proper acidity of the solution it is possible to precipitate certain metal sulfides and to prevent the precipitation of others. This is of great value in analytical chemistry.

EXERCISES

1. Define solubility product.

2. Explain the conditions for the formation of a precipitate in terms of solubility product.

3. What conditions must be maintained to dissolve a precipitate?

4. Why does barium carbonate dissolve in hydrochloric acid whereas barium sulfate does not?

5. The solubility product of silver chloride is 1.5×10^{-10}. Would this substance precipitate if 500 ml. of 0.0002*M* silver nitrate and the same volume of 0.0002*M* sodium chloride were mixed?

6. Write the expressions for the solubility products of lead iodide, silver sulfide, silver phosphate, and aluminum hydroxide.

7. A saturated solution of barium sulfate contains 10^{-5} mole of this salt per liter. Calculate its solubility product.

8. The solubility product of silver bromide is 7.7×10^{-13}. Calculate its solubility in moles per 1,000 g. and in grams per 100 g.

9. Can you suggest the reason why a precipitate of magnesium hydroxide dissolves in ammonium chloride?

10. Why does a precipitate of silver chloride dissolve when ammonia water is added?

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CHAPTER THIRTY-SIX

THE OXIDES AND OXYGEN ACIDS OF SULFUR

Sulfur may exist in two positive valences, +4 and +6, in its compounds with oxygen. Corresponding to these valences are the oxides, sulfur dioxide (SO_2) and sulfur trioxide (SO_3); the two acids, sulfurous (H_2SO_3) and sulfuric (H_2SO_4); and the sulfite, *e.g.*, (Na_2SO_3), and sulfate, *e.g.*, (Na_2SO_4), salts. In these compounds, sulfur is linked to oxygen by covalent linkages with the shared electron pairs nearer the oxygen atoms. Hence the valence numbers of the sulfur in such compounds are positive. Simple sulfur ions of positive charge do not exist.

1. Preparation of Sulfur Dioxide.—Sulfur dioxide may be prepared by the combustion of sulfur

$$S + O_2 \rightarrow SO_2$$

or by the combustion, or *roasting, of a metal sulfide*

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

These are the two largest commercial sources of sulfur dioxide. The combustion of sulfur yields the purest product, that of iron pyrite, FeS_2, the cheapest. The roasting of zinc and copper sulfides is the first step in the extraction of the free metals from these important ores. Hence the sulfur dioxide formed is considered a by-product. Within recent years, the petroleum industry has recovered so much hydrogen sulfide gas as a by-product of their cracking and hydrogenation operations that they have burned this gas in the first step of its conversion into sulfuric acid:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

In the laboratory, sulfur dioxide may be prepared *by the action of a dilute acid on a sulfite, e.g.,*

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2SO_3$$
$$H_2SO_3 \rightarrow H_2O + SO_2\uparrow$$

In this reaction the unstable sulfurous acid decomposes as it is formed into water and sulfur dioxide.

Sulfur dioxide is formed *when hot, concentrated sulfuric acid reacts with a reducing agent, e.g.,*

$$2H_2SO_4 + Cu \rightarrow CuSO_4 + SO_2\uparrow + 2H_2O$$

2. Physical Properties of Sulfur Dioxide.—Sulfur dioxide is a colorless gas with the familiar odor associated with burning sulfur. Since its critical temperature 157.2°C. is above room temperature, it can be readily liquefied either by cooling to below -10°C. at a partial pressure of 1 atm.—a salt-ice mixture will suffice—or by compressing to a little over 3 atm. at room temperature. At -72.7°C. it freezes to a white solid. It is available commercially as a liquid in steel cylinders from which the gas may be removed as desired. The pressure in such cylinders remains constant. (Why?)

3. Reactions of Sulfur Dioxide.—Sulfur dioxide is an acidic oxide which reacts with water to form sulfurous acid:

$$SO_2 + H_2O \rightleftarrows H_2SO_3$$

Since this reaction is reversible, it will come to an equilibrium in a closed system, *e.g.*, in a stoppered bottle. In open vessels, sulfur dioxide escapes from solution; and the decomposition of sulfurous acid, the reverse reaction, goes to completion. Eventually nothing but water remains.

Since the sulfur in sulfur dioxide is in its lower positive valence (+4), this substance is *a reducing agent.* In the presence of a suitable catalyst, it is oxidized to sulfur trioxide by atmospheric oxygen:

$$2SO_2 + O_2 \overset{\longrightarrow}{\longleftarrow} 2SO_3$$

This reaction will be discussed in greater detail in a later paragraph. An oxidizing agent, like nitric acid or bromine, converts it to sulfuric acid:

$$2H_2O + 3SO_2 + 2HNO_3 \rightarrow 3H_2SO_4 + 2NO$$
$$(S^{+4} \rightarrow S^{+6} + 2e^-) \times 3$$
$$(N^{+5} + 3e^- \rightarrow N^{+2}) \times 2$$
$$Br_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr$$
$$(S^{+4} \rightarrow S^{+6} + 2e^-)$$
$$(Br_2^0 + 2e^- \rightarrow 2Br^-)$$

4. Uses of Sulfur Dioxide.—By far the greater part of the sulfur dioxide formed is converted into sulfuric acid. A lesser amount is used in the manufacture of paper pulp in the form of calcium sulfite. The gas is used as a refrigerant and as a bleaching agent.

5. Sulfurous Acid.—This unstable acid exists only in aqueous solution in equilibrium with water and sulfur dioxide. It ionizes as a diprotic acid:

$$\begin{gathered} H_2SO_3 + H_2O \rightleftarrows H_3O^+ + HSO_3^- \\ HSO_3^- + H_2O \overset{\rightarrow}{\longleftarrow} H_3O^+ + SO_3^{=} \end{gathered}$$

The primary ionization constant of 10^{-2} indicates that it is a moderately strong acid and that the bisulfite ion is a weak base. This is an exception to the general rule that "ous" acids are weak. The secondary ionization constant of 10^{-5} shows that the bisulfite ion is a weak acid and that the sulfite ion is a strong base.

The reactions of sulfurous acid are essentially the same as those of sulfur dioxide. After all, the difference between them is only a molecule of water. Thus with nitric acid and bromine water the products are the same:

$$\begin{gathered} 3H_2SO_3 + 2HNO_3 \rightarrow 3H_2SO_4 + 2NO + H_2O \\ H_2SO_3 + Br_2 + H_2O \rightarrow H_2SO_4 + 2HBr \end{gathered}$$

With metal hydroxides, sulfurous acid enters into neutralization reactions:

$$\begin{gathered} H_2SO_3 + NaOH \rightarrow NaHSO_3 + HOH \\ NaHSO_3 + NaOH \rightarrow Na_2SO_3 + HOH \\ 2H_2SO_3 + Ca(OH)_2 \rightarrow Ca(HSO_3)_2 + 2HOH \\ Ca(HSO_3)_2 + Ca(OH)_2 \rightarrow 2CaSO_3 + 2HOH \end{gathered}$$

6. Sulfites and Bisulfites.—Both sulfites and bisulfites are prepared by passing sulfur dioxide into a solution of the appropriate metal hydroxide:

$$\begin{gathered} 2NaOH + SO_2 \rightarrow Na_2SO_3 + HOH \\ NaOH + SO_2 \rightarrow NaHSO_3 \end{gathered}$$

Since sulfites are the salts of the weak acid, the bisulfite ion, they are hydrolyzed and their aqueous solutions are basic:

$$SO_3^{=} + HOH \overset{\rightarrow}{\longleftarrow} HSO_3^- + OH^-$$

The bisulfites are salts of the stronger sulfurous acid and are hydrolyzed to a far lesser extent. Both sulfites and bisulfites react with strong acids, liberating sulfur dioxide:

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$$
$$NaHSO_3 + HCl \rightarrow NaCl + H_2O + SO_2$$

Calcium bisulfite is used extensively in the manufacture of paper pulp from wood to dissolve the lignin that binds cellulose fibers together.

7. Importance of Sulfuric Acid.—An industry that produces over 7,000,000 tons of its product valued at some $75,000,000 in this country alone is important. An industry whose product ensures to the farmer the fertility of his fields and gives to the mining and civil engineer the explosives without which metal ores could not be mined, nor bridges, roads, tunnels, and canals built, is essential. Without sulfuric acid, our modern civilization with its automobiles, railroads, airplanes, telephones, and radios would be no more. Without explosives, coal mining would be seriously crippled. Other ways of purifying gasoline and the lubricating oils would have to be devised. Without paint or without the protection of tin or zinc coating, our iron and steel would rust much more quickly than it does today. Finally, a variety of substances that we have come to consider more or less essential would be taken from us. Among these are celluloid, artificial silk and leather, lacquers, and many of our dyestuffs and drugs.

Since sulfuric acid enters into so many different processes in such large amounts, and since little of it is stored, its market is considered to be a better barometer of the economic prosperity of the nation than that of iron and steel.

8. The Lead-chamber Process.—The first step in the manufacture of sulfuric acid by either the chamber or the contact process involves the preparation of sulfur dioxide by the combustion of elementary sulfur or the roasting of a sulfide. The second step involves the oxidation of the dioxide to sulfuric acid.

In the older of the two commercial methods, the chamber process, an oxide of nitrogen is used as an oxidizing agent to increase the valence of the sulfur atom from its value of +4 in the dioxide to +6 in the trioxide and sulfuric acid. The actual reactions that take place in the process are somewhat in doubt but probably involve the formation of a complex intermediate product. For our present purpose, however, the following simplified version of the reactions that take place in this process is sufficient:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

In the presence of an excess of air, the nitric oxide, NO, is converted back to the dioxide again:

$$2NO + O_2 \rightarrow 2NO_2$$

In this way the oxides of nitrogen can be used over and over again and serve as a carrier catalyst for oxygen (31-6). These reactions take place simultaneously so that no sulfur trioxide can be isolated in the process. They are carried out in large lead chambers, which run 50 to 150 ft. long, 16 to 26 ft. high, and 20 to 30 ft. wide, three to six of which are arranged in series. The enormous volume of these chambers is necessary to provide space and time enough for the reactions between the gases to take place before these leave the system. They are built of lead because this metal is not attacked by dilute sulfuric acid. In front of the series of chambers is placed the Glover tower, and in back of them, the Gay-Lussac tower (Fig. 118). The oxides of nitrogen are brought

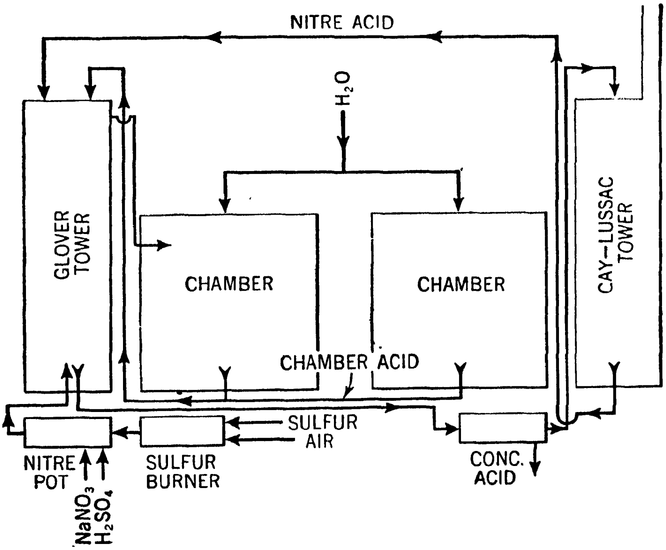

Fig. 118.—Diagram of the lead chamber process.

back from the end (the Gay-Lussac tower) to the beginning (the Glover tower) of the process in the form of a compound with concentrated sulfuric acid, the so-called nitrosyl sulfuric, or more simply, niter acid, $H(NO)SO_4$. The niter acid is mixed with the dilute sulfuric acid from the chambers at the top of the Glover tower, whereupon two birds fall with one stone. The water, which dilutes the chamber acid, serves to release the oxides of nitrogen from the niter acid

$$H_2O + 2H(NO)SO_4 \rightarrow 2H_2SO_4 + NO_2 + NO$$

thus concentrating the chamber acid and releasing the oxides of nitrogen at the beginning of the process. The sulfur dioxide from sulfur or iron pyrite burners enters the bottom of the Glover tower mixed with enough nitrogen dioxide to make up for the small loss of oxides of nitrogen which occurs during the process. This nitrogen dioxide is generated in a niter pot by the action of sulfuric acid on Chile saltpeter ($NaNO_3$)

$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$$
$$2HNO_3 + SO_2 \rightarrow H_2SO_4 + 2NO_2$$

or by oxidizing ammonia gas by passing it with air over a heated platinum catalyst (39-2):

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$

Some sulfuric acid is formed in the Glover tower, since sulfur dioxide, nitrogen dioxide, and water are present. Most of the sulfur dioxide and oxides of nitrogen, however, leave the Glover tower at the top and enter the chambers. Here they meet either steam or a fine mist of water droplets sprayed into the chambers. Dilute sulfuric acid (chamber acid) is formed and collects at the bottom of the chambers. It is about 62 per cent sulfuric acid. This dilute acid can be used directly by fertilizer manufacturers in the preparation of superphosphates (41-9), or it can be concentrated further. A portion of this acid is returned to the top of the Glover tower where reactions that result in its concentration take place as we have learned.

The unoxidized sulfur dioxide, of which there should be a minimum, together with all the oxides of nitrogen, leaves the last chamber and enters the Gay-Lussac tower. The purpose of this tower is to absorb the oxides of nitrogen so that they can be returned to the Glover tower to enter into a new cycle. This is accomplished by pumping some of the concentrated acid from the bottom of the Glover to the top of the Gay-Lussac. This acid reacts with the oxides of nitrogen to form niter acid:

$$2H_2SO_4 + NO + NO_2 \rightarrow 2H(NO)SO_4 + H_2O$$

As we have explained above, this acid is returned to the Glover tower to release the oxides of nitrogen when it reacts with the water that dilutes the chamber acid.

9. The Contact Process.—Since 1765, when sulfuric acid was first prepared commercially in large glass globes, the chamber process has supplied the world with a cheap dilute acid of moderate purity. When nitroglycerin and nitrocellulose high explosives created a demand for very strong sulfuric acid, a costly process of concentrating chamber acid had to be employed. About 1900, the contact process was first put into commercial operation. This process makes possible the preparation of sulfuric acid of any strength and of a high degree of purity. Its name is derived from the fact that platinum is used as a contact catalyst in the process.

The reaction between sulfur dioxide and oxygen to form sulfur trioxide is reversible and, hence, does not go to completion but arrives at an equilibrium:

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + \text{heat}$$

Since the direct reaction is exothermic, we have another example (31-10) of a reversible reaction in which the higher the temperature, the less the yield of the desired product but the shorter the time needed to establish equilibrium. You will remember that a catalyst permits the use of a more advantageous, lower temperature by shortening the time needed to establish equilibrium.

When a mixture of air and sulfur dioxide is passed over finely divided platinum or vanadium oxide, equilibrium conditions are reached within a few seconds at about 400°C. At this temperature conversions of 98 per cent or better of sulfur dioxide to sulfur trioxide are obtained in actual practice. Since the catalyst is very easily poisoned by impurities in the sulfur dioxide, this gas is prepared preferably from free sulfur rather than iron pyrite. In any case, the gas is purified before being passed into the catalyst chamber. The gases that leave the catalyst consist mainly of sulfur trioxide vapor and an excess of air. These are passed into

97 per cent sulfuric acid, in which the sulfur trioxide reacts with the 3 per cent of water present to form more sulfuric acid

$$SO_3 + H_2O \rightarrow H_2SO_4$$

so that the result is practically 100 per cent sulfuric acid. Part of this is withdrawn to be sold; the remainder is diluted to 97 per cent with water and again sent to the sulfur trioxide absorption towers. You are probably wondering why the sulfur trioxide cannot be passed directly into water which would seem far more simple than into 97 per cent acid. The reason for the commercial procedure is that sulfur trioxide vapors are only very incompletely absorbed by pure water, but their absorption is complete in the strong acid.

Sulfur trioxide is soluble in pure sulfuric acid. Such solutions are called fuming sulfuric acid, or oleum, and are extensively used in nitrating organic compounds (54-2).

The advantage of the contact process over the chamber process lies in the fact that a very pure acid of any strength can be prepared directly without expensive concentration. However, the expense of the initial installation of platinum makes this acid more expensive. For fertilizer manufacture, chamber acid is good enough. For nitration purposes, contact acid is essential.

10. Sulfur trioxide is a liquid that solidifies into transparent crystals at its freezing point 14.8°C. On standing, the liquid form polymerizes, *i.e.*, the single molecules combine with one another to a dimolecular form, or a dimer, with the formula S_2O_6. This is a solid whose long, silky crystals resemble those of asbestos. Both the monomer, SO_3, and the dimer, S_2O_6, react violently but incompletely with water to form sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$S_2O_6 + 2H_2O \rightarrow 2H_2SO_4$$

11. Properties of Sulfuric Acid.—The concentrated acid is an oily liquid—its older name was oil of vitriol—of relatively high density, 1.834. This acid contains 98 per cent sulfuric acid and is mainly a monohydrate, $H_2SO_4.H_2O$. It boils at 338°C. with some decomposition into sulfur trioxide and water. This boiling point is the highest of any of the common acids. The acid is soluble in all proportions in water. When these liquids are mixed, a large amount of heat is liberated. For this reason, extreme caution should be used. *Water should never be added to the hot, concentrated acid.* In any case the acid should be poured slowly into water when dilution is necessary.

12. Reactions and Uses of Sulfuric Acid.—Sulfuric acid is a strong diprotic acid.

$$\begin{array}{lcll} H_2SO_4 + H_2O & \underset{\leftarrow}{\longrightarrow} & H_3O^+ + HSO_4^- & K_1 = 10^7 \\ HSO_4^- + H_2O & \rightleftarrows & H_3O^+ + SO_4^{--} & K_2 = 10^{-2} \end{array}$$

As such, *it enters into all the reactions typical of strong acids, e.g.,*

$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + HOH$$
$$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + HOH$$
$$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + H_2O + CO_2$$
$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$$
$$3H_2SO_4 + Fe_2O_3 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$
$$H_2SO_4 + Zn \rightarrow ZnSO_4 + H_2$$

The reaction of sulfuric acid with the basic oxide, ferric oxide, represents an important industrial use, called somewhat quaintly the pickling of steel. When iron is to be coated with tin or zinc in the manufacture of tin plate or galvanized iron, its surface must be free from rust for the metal coating to adhere properly. Rust is essentially ferric oxide. Sheets of steel are, therefore, dipped first into a pickling bath of dilute sulfuric acid before they receive the metal coating.

Its reaction with ammonia converts this gas into the water-soluble salt ammonium sulfate. Over 200,000 tons of ammonia is produced annually from by-product coke ovens (42-8) and as synthetic ammonia from atmospheric nitrogen (38-5). Ammonium sulfate is one of our most important fertilizers.

Since the boiling point of sulfuric acid is higher than that of any other common acid, it is used in the commercial preparation of these acids. The dry salt of the desired acid is heated with concentrated sulfuric acid at a temperature above the boiling point of the former but below that of the latter. Thus the desired acid volatilizes away from the reaction mixture, but the sulfuric remains as a liquid to react completely with the salt. The following equations are reactions of this type:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$
$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3\uparrow$$
$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4\uparrow$$

Soluble phosphates are a necessary constituent of all mixed fertilizers. When the insoluble calcium phosphate, which occurs in nature as phosphate rock, is treated with dilute sulfuric acid, a soluble acid phosphate is formed:

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow 2CaSO_4 + Ca(H_2PO_4)_2$$

This is known as "superphosphate" in the fertilizer trade.

Hot, concentrated sulfuric acid is an *oxidizing agent.* In oxidation-reduction reactions involving this acid, the sulfur atoms are usually reduced to the valence number of +4 and appear as sulfur dioxide among the products. Examples of such reactions were discussed in this chapter under the preparation of sulfur dioxide.

We have pointed out the affinity of concentrated sulfuric acid for water. It is an excellent *dehydrating agent* not only drying substances that are wet, but actually pulling out the elements of water from compounds. Organic substances are charred by this acid, *e.g.*, sugar.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

This reaction is similar to that which occurs when the concentrated acid is spilled on the skin or on clothes.

When glycerin, cellulose, or certain hydrocarbons are treated with concentrated nitric acid, reactions take place in which the elements of water are removed from the reacting substances; and high explosives and other useful materials result. The following reactions are typical:

$$\underset{\text{glycerin}}{C_3H_5(OH)_3} + 3HNO_3 \rightarrow \underset{\substack{\text{glycerin}\\ \text{trinitrate}}}{C_3H_5(NO_3)_3} + 3HOH$$

$$C_7H_8 + 3HNO_3 \rightarrow \underset{\substack{\text{trinitrotoluene,}\\ \text{"TNT"}}}{C_7H_5(NO_2)_3} + 3HOH$$

Unlike reactions between electrolytes, these go very slowly indeed. The addition of concentrated sulfuric acid, however, serves to accelerate the reaction enormously, since it assists in the removal of water from the reactants due to its dehydrating action. Not only do high explosives result from these reactions, but also the materials from which celluloid, artificial ivory and leather, and the modern quick-drying lacquers are made (55-5).

13. Sulfates and Bisulfates.—Since sulfuric acid is diprotic, its neutralization takes place in two steps:

$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + HOH$$
$$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + HOH$$

Since both sulfuric acid and the bisulfate ion are strong acids, the conjugate bases the bisulfate and the sulfate ions, respectively, are extremely weak bases. For this reason, neither sulfates nor bisulfates are hydrolyzed. All sulfates of the common metals are soluble except those of barium, strontium, and lead.

14. Sodium Thiosulfate.—When a suspension of sulfur in a solution of sodium sulfite is boiled, sodium thiosulfate, or photographer's hypo, is formed.

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

The formula for this salt may be considered as derived from sodium sulfate by replacing one oxygen atom by sulfur—hence the prefix *thio*. When this salt is treated with an acid, the unstable thiosulfuric acid, which is first formed, decomposes:

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2S_2O_3$$
$$H_2S_2O_3 \rightarrow H_2O + SO_2 + S\downarrow$$

EXERCISES

1. What is the valence number of sulfur in each of the following compounds: Ag_2S, H_2SO_3, SO_2, Na_2SO_4, $NaHSO_3$, and $Na_2S_2O_3$?

2. What compound is formed when an excess of sulfur dioxide is bubbled into a solution of sodium hydroxide?

3. Why are aqueous solutions of sodium sulfite basic?

4. Why do sulfites react with strong acids whereas sulfates do not?

5. How is the sulfur in zinc sulfide converted into sulfuric acid commercially? How would you accomplish the same conversion in the laboratory? Write equations for all the reactions involved.

6. Write equations for reactions by which the following conversions could be accomplished in the laboratory:

$$SO_2 \rightarrow CaSO_4$$
$$Na_2SO_3 \rightarrow Na_2S_2O_3$$
$$BaCl_2 \rightarrow BaSO_4$$
$$BaSO_4 \rightarrow BaCl_2$$
$$ZnCO_3 \rightarrow ZnSO_4$$

7. How many tons of sulfur would be required to form 49 tons of sulfuric acid?

8. Write equations for the reactions of sulfuric acid with each of the following: copper, ferrous hydroxide, sodium carbonate, ammonia, and sugar, $C_{12}H_{22}O_{11}$.

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CHAPTER THIRTY-SEVEN

THE ATMOSPHERE

The ancient and medieval world considered the earth to be made of the four elements, fire, air, earth, and water, out of which matter in all its manifold ramifications was composed. This concept had its beginnings in the teachings of the ancient Hindu. We find it again in the teachings of the Greek philosophers Thales, Anaximenes, Heraclitus, and Empedocles. Their philosophy was championed by Aristotle (384–322 B.C.), whose authority kept it alive for some two thousand years. In the domain of natural philosophy, the ancients satisfied themselves with abstract generalizations. Experimental research, as we know it today, did not have its real beginning until Galileo performed his classic experiment from the gallery of the Leaning Tower of Pisa in 1591.

Boyle's experiments, which resulted in the famous law that bears his name, were carried out about 1660, before the composition of the atmosphere was known. In 1674, the English physician Mayow showed that when combustible substances were burned in air, contained in a vessel over a water seal, the volume diminished and a gaseous residue remained that would not support further combustion. In 1772, Priestley proved that the part of the atmosphere which supported combustion made up about a fifth part of the air and that it was identical with a gas which he had previously prepared. Lavoisier later gave the name "oxygen" to this gas.

1. The Composition of the Atmosphere.—Today we know that the atmosphere is a *mixture* of gaseous components, most of which are uncombined elements. Further, since the volume of the atmosphere is so great, the relative amounts of nitrogen, oxygen, and of the inert gases (argon, etc.) remain constant. However, the proportions of water vapor, carbon dioxide, and dust vary with the conditions in a given locality. If the variable components are removed from a given sample of air, the proportions of the fixed ones are as given in Table 39.

We have already discussed the importance of oxygen and shall consider the properties of nitrogen in the next two chapters. The discovery of the inert gases, however, makes an interesting story.

TABLE 39.—THE COMPOSITION OF THE FIXED COMPONENTS OF THE ATMOSPHERE

Components	By weight	By volume
Nitrogen	75.5	78.06
Oxygen	23.2	21.00
Argon, etc	1.3	0.94

2. The Inert, or Noble, Gases of the Atmosphere.—In 1799, there lived in England a nobleman of immense wealth, yet of so retiring and modest a disposition that his portrait was never painted—Lord Henry Cavendish. Cavendish carried out some surprisingly simple experiments, which proved to be of great importance, in the crudest sort of apparatus. This consisted of two wineglasses and a piece of bent glass tubing (Fig. 119). The glasses and the tube were filled with water; and air or any desired mixture of gases could be introduced into the tube by the displacement of some of the water. Wire terminals, connected with an electrostatic machine, were then inserted in the two ends of the tube and brought together as near as might be desired so that electric sparks could be generated between them. With this apparatus, Cavendish was the first to prove that two volumes of hydrogen combine with one of oxygen to form water. He was also the first to cause the nitrogen and the oxygen of the air to combine by means of an electric spark. This experiment was to grow some one hundred years later into the nitrogen-fixation in-

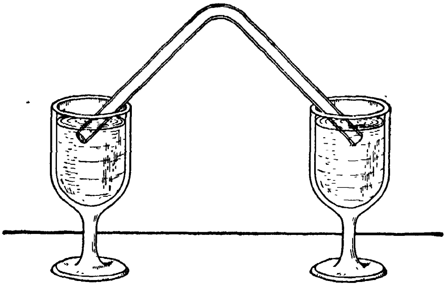

FIG. 119.

dustry which has solved the problem of man's food supply for all time. Yet another experiment was to result in the discovery of the inert gases of the atmosphere. In this experiment, we are especially interested. We can find it recorded in *Number* 3 of the *Alembic Club Reprints.* Cavendish, together with most scientists of his day, had accepted the phlogiston theory. He refers to oxygen, therefore, as dephlogisticated air and to nitrogen as phlogisticated air.

> I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest which would refuse to undergo that change. The foregoing experiments indeed, in some measure, decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet, as some remained unabsorbed, it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompound as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it and continued to spark until no further diminution took place. Having by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulfur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the dephlogisticated air let up into the tube; so that, if there be any part of the dephlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole.

The nature of this $\frac{1}{120}$ part residuum was to remain unknown until 1894, some one hundred years later. In 1887, John William Strutt (later Lord Rayleigh) became professor of natural philosophy at the Royal Institution. Lord Rayleigh had been determining with very great accuracy the densities and molecular weights of certain gases, among which was nitrogen. To his amazement he found that the density of nitrogen prepared from ammonium nitrite was always slightly less than that of nitrogen prepared by the removal of the other then-known constituents of air. The difference was slight, but greater than the limits of accuracy of his experiments. Disgusted, he confided his troubles to Sir James

Dewar, Fullerian professor of chemistry at the Royal Institution, and suggested that there might exist a component of the air which had not been discovered and which was responsible for his difficulty. If it did exist, it must have been surprisingly inert to have escaped detection. Together they went into an adjoining room to consult Cavendish's original memoirs and read the lines that we have quoted above. Immediately the residuum that Cavendish had so faithfully reported took on a new meaning. The aid of Sir William Ramsay, professor of chemistry at the University College, London, was enlisted, and in 1894 the discovery of the first of the family of inert gases of the atmosphere—argon—was reported by Rayleigh and Ramsay to the British Association.

3. **Argon** was isolated by Ramsay by removing the oxygen from the air by passing it over hot copper. The nitrogen was then removed in a similar manner by red-hot magnesium, with which it combines to form a solid nitride.

Argon is present in the air to the extent of a little over 1 per cent by weight. It has a higher density than either nitrogen or oxygen, which accounts for the results of Rayleigh. Its most surprising characteristic is its chemical inertness. It cannot be made to combine with other elements. This is because of the extraordinary symmetry of its atomic structure. Its name, derived from the Greek, means "the lazy one." It is produced in some quantity today as a by-product of air liquefaction, for it remains as a gas after oxygen and nitrogen have liquefied. Because of its inertness and its availability, it is useful as a filler for electric-light bulbs. All incandescent lights between 50 and 1,000 watts are now filled with this gas.

4. **The Discovery of Helium.**—The story of the discovery of helium and of the uses to which it has been put is one of the most interesting of all the elements. In the year 1868, Prof. Janssen discovered a yellow line in the chromosphere of the sun which belonged to the spectrum of no known terrestrial element. The same year Frankland and Lockyer made the same discovery and named the element "helium" (from the Greek for the sun). Nearly thirty years later, in 1890, the American chemist Hillebrand observed a slow and long-continued evolution of tiny bubbles when a sample of a mineral cliocite was treated with hydrochloric acid in a test tube. Because of its chemical inertness,

he erroneously concluded that it was nitrogen. Ramsay immediately bought all the samples of this and similar minerals which he could obtain in London after hearing of Hillebrand's experiments. From these he isolated a new inert gas helium. In a letter to his wife, he said:

> Let's take the biggest piece of news first. I bottled the new gas in a vacuum tube and arranged so that I could see its spectrum and that of argon in the same spectroscope at the same time. There is argon in the gas; but there was a magnificent yellow line, brilliantly bright, not coincident with but very close to the sodium yellow line. I was puzzled but began to smell a rat. I told Crookes (25-1), and on Saturday morning when Harley, Shields, and I were looking at the spectrum in the dark room a telegram came from Crookes. He had sent a copy here and I enclose that copy. You may wonder what it means. Helium is the name given to a line in the solar spectrum, known to belong to an element, but that element has hitherto been unknown on the earth.

In 1895, the announcement of the discovery of helium was made public on the occasion of the presentation of the Faraday medal to Lord Rayleigh at the annual meeting of the Chemical Society.

Soon Kayser established the fact that this gas also occurred in the air in an exceedingly small amount. It is found also in all minerals of radioactive elements, since the α-particles, which many radioactive elements emit, are positively charged helium atoms (28-6), and in natural gas. It is a gas of atomic weight 4, and, therefore, the lightest gas next to hydrogen. It is also chemically nonreactive. Helium is the most difficult gas to liquefy because of its critical temperature of −268°C.

5. The Use of Helium in Airships.—Shortly after the outbreak of the First World War, Dr. R. B. Moore of New York received the following telegram from his former teacher Sir William Ramsay: "I have been investigating blower, *i.e.*, coal damp, rushes of gas for helium for our government. There does not appear to be any in our English blowers, but I am getting samples from Canada and the States. The idea is to use helium in airships."

A German Zeppelin, bombing British cities in 1914, was attacked by Allied airplanes and, although filled with highly inflammable hydrogen gas and pierced by many incendiary bullets, it did not catch fire. Now helium has 92 per cent of the buoyant effect of hydrogen, and, at the same time, because of its lack of chemical reactivity, is absolutely noninflammable. Hence the British conceived the idea that the Germans had found some new source of helium and had filled the Zeppelin with this gas. Up to that time, the only way in which helium had been prepared was by the action of acids on radioactive minerals; and probably no more than 10 cu. ft. in all had been isolated from this source. The problem of filling airships of some 2,000,000 cu. ft. capacity seemed to be an impossible task at that time. At the Disarmament Conference in Washington after the war, Prof. Moureu of Paris declared that "if any one had told him five years before that helium would be put in airships he would have considered it in the same light as if someone in his audience told him that the Washington Monument was going to be covered with diamonds."

6. Helium in Natural Gas.—However, the presence of this gas in certain natural-gas wells in this country was to prove the source of sufficient helium for this purpose. In 1907, Cady and McFarland of the University of Kansas had discovered a natural gas that contained 1 per cent of helium. Previous to this, in 1903, a well had been drilled in Dexter, Kans., which resulted in a great flow of natural gas. Its owner had invited a large crowd to celebrate the discovery of the source of power. A burning fagot was applied to the gas, but, to the dismay of its owner and the amusement of his neighbors, the gas would not burn. It contained too high a percentage of nitrogen and helium. In 1914 to 1915, Burrell of the United States Bureau of Mines made a survey of the natural-gas resources of the country and found that the gas of Petrolia Field near Fort Worth, Tex., contained 35 per cent nitrogen and 0.97 per cent helium.

In June, 1917, Moore and Burrell presented the matter of the production of helium from natural gas for use in airships to the War Department with the result that by July money was appropriated to carry out the project. It was proposed to liquefy all the other components of the natural gas and, in this way, separate them from the difficultly liquefiable helium. The cost of helium from radioactive minerals was in excess of $1,700 per cubic foot. The small experimental plants that were first set up produced it for $300 per 1,000 cu. ft. In 1925, a plant at Petrolia Field was able to isolate it at a cost of $30 per 1,000 cu. ft.

The importance of the use of helium to airships cannot be overestimated. Hydrogen-filled airships have frequently met with disasters that could have been prevented had they been filled with helium. What happened to the *Hindenburg* at Lakehurst,

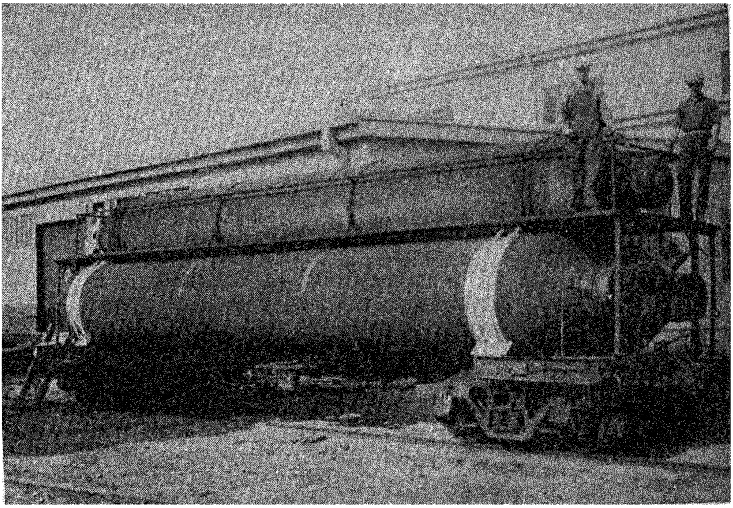

FIG. 120.—Tank car for the transportation of helium gas. Under a pressure of 2,000 lb./sq. in. in these cylinders, the gas will occupy about 200,000 cu. ft. when expanded to atmospheric pressure. (*Courtesy of U.S. Department of Commerce.*)

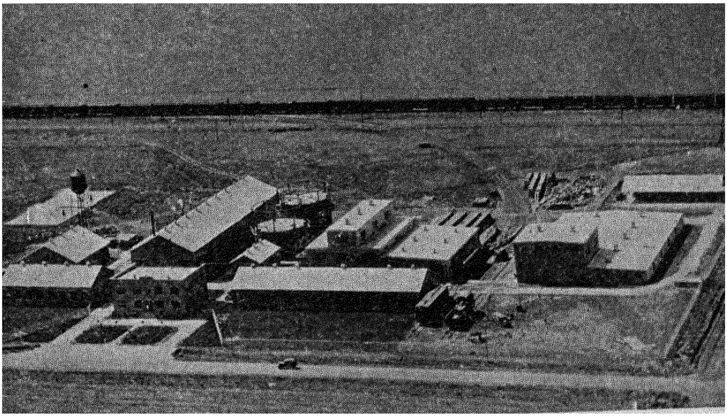

FIG. 121.—View of U.S. Bureau of Mines, Amarillo helium plant. (*Courtesy of U.S. Department of Commerce and the Edwards Studio, Amarillo, Texas.*)

N. J., is still fresh in our minds. We may have forgotten, however, the destruction of the *R-38* at Hull, England, of the *Roma* at Hampton Roads, Virginia, and of the *R-101* in France. Dr. Moore tells of a conversation that he had with Col. E. C. Hall of the Army Air Service, a survivor of the *Shenandoah* disaster. Colonel Hall said, "If the control car had been attached in a different way and the framework had not broken away, only three or four men out of the total crew would have been lost."

He was asked, "What did you say when you and the other survivors got on terra firma?"

"What did we say?" he replied. "Why, we turned to each other and said, "Thank God for helium.'"

7. Krypton, Xenon, Neon, and Radon.—The discovery of argon and helium led Ramsay to seek other gases of like nature in the air. In 1898, a method devised by Dewar, involving fractional absorption on charcoal at low temperature of the gases mixed with argon after the oxygen and nitrogen of the air had been removed, resulted in the discovery of three new elements—krypton, xenon, and neon. The fourth element radon is formed as a gaseous emanation when radium disintegrates. Of these four gases, uses have been found for radon and neon—radon in the treatment of cancer (28-14) and neon in a new type of illuminated sign (26-3) and in the so-called Pintsch neon-glow lamp.

8. Water Vapor.—We shall now consider the variable components of the atmosphere, of which the more important ones are water vapor, carbon dioxide, and dust. Water vapor gets into the atmosphere by evaporation from bodies of water. We have had occasion to say something of the conditions that govern its precipitation, as rain, and also of what is meant by "humidity" in an earlier chapter. When water vapor precipitates, it may remain suspended in the form of very tiny droplets which we recognize as a cloud if it is above us, or as a fog if we are so unfortunate as to be surrounded by it. These tiny droplets may coalesce into larger ones which then fall through the air as rain. If these drops fall through a very cold region before they reach the earth, hail is formed. If the precipitation is at a temperature below 0°C., ice crystals are formed and snow results.

9. Carbon Dioxide.—The combustion of fuels, all of which are either free carbon or its compounds, results in the liberation into the atmosphere of literally hundreds of thousands of tons of carbon dioxide gas annually. Every ton of carbon burned produces nearly four tons of this gas. It also gets into the air in the exhalation of animals and plants. The atmosphere over cities, quite naturally, contains more of this gas than the country air. The latter contains only about 3.5 parts per 10,000, whereas in crowded, ill-ventilated rooms the carbon dioxide sometimes rises above 1 per cent.

10. Ventilation.—The discomfort that persons in a crowded, ill-ventilated room feel has long been attributed to the accumulation of the products of respiration and the lowering of the oxygen content of the air. You all know of the way by which the oxygen of the air is absorbed by the hemoglobin of the blood in the lungs and carried by the circulation of the blood to the tissues in all parts of the body. Here chemical reactions take place in which oxygen combines with the various organic compounds that result from the digestion of food in the stomach and intestines and are carried in the blood stream to the tissues. These are the fuel for the living engine. The result of this chemical interaction is the production of mechanical work by the muscles, of heat to maintain the body temperature, and of carbon dioxide. The latter is carried through the veins back to the lungs, whence it is exhaled. The content of oxygen and carbon dioxide in inspired and expired air is given in Table 40.

TABLE 40.—COMPOSITION OF INSPIRED AND EXPIRED AIR

Components	Inspired, per cent	Expired, per cent
Oxygen	20.94	15.9
Carbon dioxide	0.03	3.7

It was believed for a long time that here was the explanation of the discomfort of the crowded room. The oxygen content in such rooms grew less, making the inspiration of a sufficient quantity for the needs of the body more difficult. Carbon dioxide, on the other hand, accumulated and acted as a toxic substance. It was one of the waste products of metabolism and was, therefore, necessarily poisonous. This reasoning proved fallacious when once it was tested by experiment. It was found that the oxygen content could be cut down to as low as 17 per cent before any harmful effects could be observed. This percentage is too small to support combustion. In one experiment, a group of students were confined in a small airtight room and noticed no ill effects, even when the oxygen content had fallen below 17 per cent, although they were unable to light their cigarettes. In crowded rooms, the oxygen content rarely goes below 20 per cent. Carbon dioxide was shown to be nonpoisonous in concentrations of 1 per cent or less. It rarely exceeds 0.4 per cent in badly overcrowded rooms. Oxygen and carbon dioxide, therefore, cease to be factors that have to be considered in ventilation.

Another belief which is widespread is that some subtile organic substances, toxic to living organisms, are present in expired air. No one, however, has been able to detect their presence, so that we have every reason to suppose that they do not exist.

Nearly fifty years ago, Hermanns first suggested that the cause of the discomfort in poorly ventilated rooms was to be sought in a disturbance of the factors that control the way in which the body eliminates its surplus heat. This is done by radiation of heat (infrared rays) from the skin and by the evaporation of water from the sweat glands of the skin. As Prof. Lee puts it:

> In considering ventilation from the latest standpoint, we are obliged to turn from chemistry to physics. At the same time, we turn also from the lungs to the skin. The physiological problems of ordinary ventilation have ceased to be chemical and pulmonary, and have become physical and cutaneous . . . .
>
> The normal loss of heat or, as the Germans call it, the "unwarming" of the body, may be interfered with by making the surrounding air too warm, thus preventing radiation and conduction; or by making the air too moist, thus preventing the evaporation of sweat; or most effectually by blocking both of these channels. This last mentioned procedure is that which happens to human beings confined in improperly ventilated rooms. From their bodies the temperature of the air rises and the humidity of the air increases. As these events happen each body finds it not so easy as at first to rid itself of its superfluous heat, and this becomes increasingly more difficult. Heat-laden blood must be sent in larger quantity to dilated cutaneous arteries, flushing and warming the skin; sweat glands must be stimulated to visible activity; breathing must be deepened; and every method of which the body is physiologically capable is unconsciously brought into action to protect it. At first the sensations are merely those of general uneasiness, manifesting itself in restlessness; then progressively appear sleepiness, an oppressive sense of heat, headache, thirst, and still more severe sensations which,

if relief is not obtained, may give place to the delirium of the Black Hole of Calcutta or the prison at Austerlitz—these sensations keeping pace with the development of the fever within and the other pathological events accompanying it.

The problem of ventilation, therefore, is one of supplying moving air to sweep away the hot envelope of air that surrounds the body and to supply the proper content of water vapor. If the latter is too high, evaporation is interfered with and body temperature increases, whereas, if it is too low, evaporation is excessive and the resulting cooling effect uncomfortable. In the winter the humidity should be kept high in our homes. The water pans of our hot-air furnaces and in back of our steam radiators should be kept full. In the summer the drier the air, the better.

11. Air Conditioning.—The problems of air conditioning have been discussed in an interesting paper by Midgley, which you are urged to read. He states:

> Air conditioning implies the creation of an atmospheric condition which is comfortable; comfort, in turn, implies a psychological condition closely associated with physiology. This environment is referred to as the comfort zone, which has been aptly described as being not too hot, not too cold, not too dry, and not too damp. Add to this a pleasing motion of the air and the absence of dust, dirt, pollen, disease organisms, and unpleasant odors, and the definition is about complete.

The essential functions performed by air-conditioning equipment include apparatus for cooling and dehumidification for summer weather, for heating and humidification in winter, for cleaning, for deodorizing, and for circulation of the conditioned air. Cooling and dehumidification are accomplished simultaneously by refrigeration, usually by mechanical means although ice is still being used for this purpose. Methods of heating by coal, oil, or gas are too well known to need discussion here. Humidification is accomplished by spraying water into the heated air. Water sprays also clean the air by removing suspended particles. The conditioned air is circulated by fans through ducts that vent into the rooms. Since hot air rises because of its lower density, it is released through outlets near the floor. Cooled air, however, comes through duct outlets near the ceiling.

The problem of heat-insulating walls and windows must be faced when air-conditioning equipment is installed. When the humidified warm air comes in contact with windowpanes, chilled by the outside winter air, moisture is deposited in quantity. Hence double glass windowpanes, hermetically sealed, must be used.

EXERCISES

1. What led Lord Rayleigh to suspect the presence of other gases in nitrogen extracted from the air?
2. Explain how the rare gases are separated from the oxygen and nitrogen of the air.
3. What differences in properties make possible the separation of helium from natural gas?
4. How does the fact that the rare gases form no compounds help in determining the arrangement of the planetary electrons about the nuclei of the atoms of the elements?
5. In terms of its atomic structure, why is radon chemically inert but radioactive?
6. What properties make helium the best gas to use in lighter than air ships?

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CHAPTER THIRTY-EIGHT

NITROGEN AND AMMONIA

The late Edwin E. Slosson in writing a chapter on nitrogen for his ever popular book "Creative Chemistry" characterized it as "a most unreliable and unsociable element" and again as the "preserver and destroyer of life." How true his characterization is can be judged from the following facts. The free element is inert, *i.e.*, it is difficult to get it to combine with other elements. On the other hand its compounds, especially certain organic compounds that contain nitro or nitrate groups, are energy rich and, therefore, very reactive. Practically all explosives are compounds of these types. Again quoting Slosson, modern warfare is "essentially a series of explosive reactions resulting in the liberation of nitrogen." On the other hand, nitrogen is an essential constituent in the proteins of all living organisms. It must be present in their food.

It was discovered in 1772 by Dr. Rutherford, a professor of botany at Edinburgh, who isolated the element from the air. He removed oxygen by burning such substances as phosphorus and carbon and removing their oxides by some suitable means.

1. Occurrence.—Nitrogen makes up about four-fifths of the air by volume. Over every square mile of the earth's surface there are some 20,000,000 tons of nitrogen, an inexhaustible natural resource. When we consider that the earth's atmosphere contains roughly 4×10^{16} tons of nitrogen, it may seem odd that Sir William Crookes, in an address before the British Association in 1898, saw the necessity of pointing out that unless some means were discovered of developing an industry that would supply nitrogen in a form available to plants as food the wheat fields of the world would soon be barren and the wheat eaters "squeezed out of existence by the races to whom wheaten bread is not the staff of life." We might paraphrase an old saying—"nitrogen, nitrogen everywhere, nor any bite to eat." For the nitrogen of the air is the free element, and plants must take their food in solution through their roots. The problem, therefore, of supplying nitrogen in an available form to plants was one of finding sources of soluble nitrogen compounds, or of "fixing" in some way atmospheric nitrogen, *i.e.*, combining it with other elements. Thanks to chemistry, this problem has been solved.

The world's most important natural resource of inorganic nitrogen is found in a long narrow strip on an arid plateau along the coastal range of Chile. In beds 4 to 12 ft. thick and some 200 miles long lie the valuable sodium nitrate deposits of Chile saltpeter. The sodium nitrate is leached from the ore, or caliche, with water and the solution evaporated. Shipments of this material, which began in 1809, have amounted to over 50,000,000 tons.

Nitrogen occurs in a class of organic substances called the proteins. In this form it gets back into the soil through the natural process of organic decay and when animal manures, fish scrap, dried blood, meat-packer's scrap, cottonseed meal, etc., are used as fertilizers. Since coal had its origin in vegetal matter (42-3), it contains nitrogenous compounds from which ammonia is obtained as a by-product when soft coal is baked in by-product coke ovens (42-7). Most of this ammonia is converted to ammonium sulfate, an important fertilizer. About 600,000 tons of this salt are produced annually in the United States.

2. Preparation.—The commercial preparation of nitrogen involves the fractional distillation of liquid air by a process we have already discussed (15-7). It is available in steel cylinders under high pressure. This source is so convenient that only on those rare occasions when a very pure sample is needed is it necessary to prepare nitrogen in the laboratory.

It may be prepared by passing air over heated copper which removes oxygen

$$2Cu + O_2 \rightarrow 2CuO$$

but the product contains the inert gases of Group 0 (37-2); and in pure form by passing ammonia over hot cupric oxide:

$$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$$

Small quantities of pure nitrogen may be obtained by heating an aqueous solution of sodium nitrite and ammonium chloride.

The unstable ammonium nitrite decomposes as it forms.

$$NaNO_2 + NH_4Cl \rightarrow NaCl + NH_4NO_2$$
$$NH_4NO_2 \rightarrow N_2\uparrow + 2H_2O$$

Perhaps it would be more accurate to say that the reaction is between ammonium and nitrite ions.

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

3. Properties.—Nitrogen is a colorless, odorless gas. Its critical temperature of -147.1°C. indicates that its liquefaction is relatively difficult. The liquid boils at -195.7°C. It is sparingly soluble in water.

Nitrogen is at the top of Group V in the periodic table. Its atom has, therefore, five electrons in the valency level. Its valence numbers are -3, $+3$, $+5$. Unlike sulfur, which in its valence of -2 can exist as the sulfide ion, nitrogen cannot exist as the nitride ion in aqueous solution. The simplest nitrogen-containing ions are the ammonium ion (NH_4^+), the nitrite ion (NO_2^-), and the nitrate ion (NO_3^-), in which its valence numbers are -3, $+3$, and $+5$, respectively.

Molecules of the free element are diatomic (N_2). The relatively large amount of energy (274,000 cal./mole) required to break down this molecule into single atoms is responsible for the inertness of the element.

4. Reactions of Nitrogen.—Because of the great economic importance of nitrogen fixation, any reaction of this element is interesting. Of these reactions, that with hydrogen has developed into the outstanding method of fixation. Before considering this reaction, we shall consider those of lesser importance.

Nitrogen will combine *with oxygen* when air is passed through an electric arc.

$$N_2 + O_2 \rightarrow 2NO$$

This reaction, first studied by Cavendish in 1790, was the basis of the first commercially successful nitrogen-fixation process. The nitric oxide is obtained in small yields but can be converted readily into nitric acid by the following reactions:

$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Wasteful of electric power, the *arc process* succeeded for a time in Norway but has been displaced by the more efficient synthetic-ammonia process.

Nitrogen will combine *with certain metals* (lithium, magnesium, calcium, and aluminum) and nonmetals (boron and silicon) to form nitrides

$$3Mg + N_2 \rightarrow Mg_3N_2$$

in which its valence number is -3. These nitrides react with water to form ammonia.

$$Mg_3N_2 + 6HOH \rightarrow 3Mg(OH)_2 + 2NH_3$$

They are not salts and obviously do not form the nitride ion $N^{\equiv}$ in aqueous solution.

When *calcium carbide* is brought into contact with nitrogen in electrically heated ovens, a reaction takes place in which *calcium cyanamide* is formed.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

This substance is converted into ammonia by treatment with steam under pressure

$$CaCN_2 + 3H_2O \rightarrow 2NH_3 + CaCO_3$$

which in turn can be converted readily into ammonium sulfate (38-11) or nitric acid (38-12). The rugged, dependable *cyanamid process* was chosen as the best source in this country of nitrogen compounds during the First World War. Although it has gradually been displaced by the synthetic-ammonia process as a source of fertilizers and nitric acid, calcium cyanamide is being prepared in larger quantities than ever, since industrially important cyanides and organic compounds are prepared from it.

5. The Haber, or Synthetic-ammonia, Process.—It has long been known that small amounts of ammonia are formed when a mixture of nitrogen and hydrogen gases is passed through heated tubes. However, it was not until about 1905 that Nernst and Haber, two German physical chemists, began to study systematically the following equilibrium:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + \text{heat}$$

and especially the influence of catalysts on the rate at which it is established. Thereafter, this reaction began to be considered as a possible basis of a process for fixing atmospheric nitrogen. The application of the theorem of Le Châtelier to this equilibrium has been discussed in detail (31-10).

In actual practice, the reaction is carried out at about 500°C. and at pressures that vary from 100 up to as high as 1,000 atm. The higher pressures demand more costly apparatus but produce greater yields of ammonia. A catalyst of iron, together with the oxides of aluminum and potassium which serve as promoters, is most widely used.

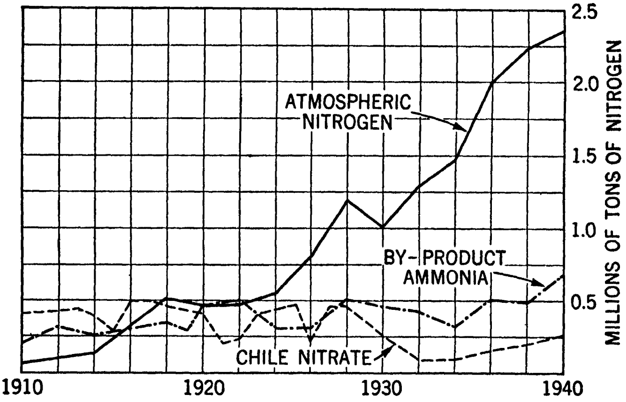


FIG. 122.—World production of fixed nitrogen.

The synthetic-ammonia process has proved the best of all the methods of fixing atmospheric nitrogen. Its energy consumption is the lowest of all. The way in which the distribution of the nitrogen production of the world has varied since 1910 is shown graphically in Fig. 122 and also in Table 41.

TABLE 41.—NITROGEN PRODUCTION

Source of nitrogen	1913, per cent	1924, per cent	1940, per cent
Fixed	7.1	38.8	70.9
Coke ovens	36.7	26.5	21.5
Chile saltpeter	56.2	34.7	7.6

The synthetic-ammonia process is now at such an advanced stage in its development that it can produce ammonia at a cost at least as low if not lower than that of ammonia from by-product coke ovens, and nitric acid by the oxidation of ammonia by the

Ostwald process (38-12) at a price that can compete with that from Chile saltpeter. We can with confidence consider the nitrogen problem as solved.

6. Nitrogen-fixing Bacteria.—If chemical engineers could only have followed the example of certain lowly organisms that are present in the soil and in nodules on the roots of certain plants, the solution of the problem would have been simple. These nitrogen-fixing bacteria can accomplish at atmospheric temperature and pressure without any great fuss that for which man requires electrical arcs or high pressures and complex apparatus. Certain of these bacteria thrive in nodules on the roots of such plants as clover, pea, or alfalfa. By growing such plants and then plowing them under the ground, the farmer can enrich his soil with fixed nitrogen. These bacteria have really made plant and animal life possible, for they supply what

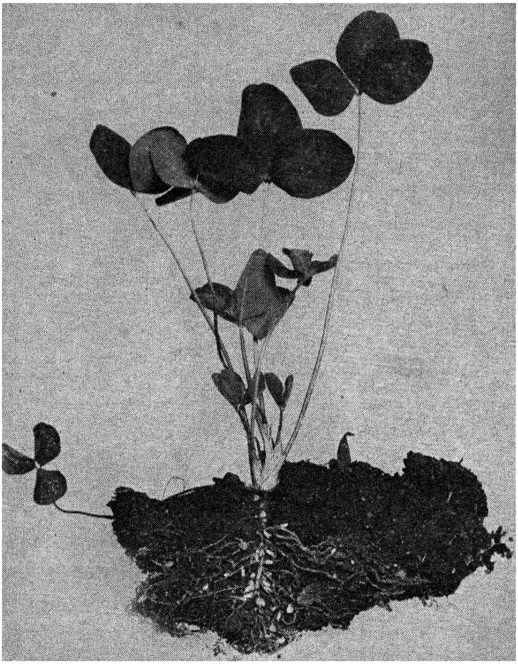


FIG. 123.—Nodules, containing nitrogen-fixing bacteria, on the roots of a red clover plant. (*Courtesy of the Bureau of Plant Industry, Soils, and Agricultural Engineering, U.S. Department of Agriculture.*)

amounts to the only link between the nitrogen of the atmosphere and the nitrogen in the proteins of plant and animal tissue. How they accomplish the fixation of nitrogen is as yet a mystery, but it need not forever remain unknown.

7. Uses of Nitrogen.—Because of its inertness, the free element is used to fill electric-light bulbs, the space above the mercury in high-grade thermometers, and wherever an inert atmosphere is needed.

8. Preparation of Ammonia.—By far the greatest amount of ammonia is prepared *by the synthetic-ammonia process.* Here the product is anhydrous and can be shipped as a liquid under pressure in steel cylinders and tank cars. A second commercial source is as one of the products of the coking of bituminous coal in by-product coke ovens. Here the ammonia is in aqueous solution since water is used to dissolve it from the coal gas formed at the same time. Most of the ammonia, obtained in this way, is converted into ammonium sulfate. We have learned that ammonia may also be produced *by the action of steam on calcium cyanamide.*

In the laboratory, when relatively small amounts are needed, it may be prepared *by the action of a soluble metal hydroxide on an ammonium salt.* The reaction is between the ammonium and hydroxyl ions:

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + HOH$$

or, *e.g.,*

$$NH_4Cl + NaOH \rightarrow NH_3\uparrow + HOH + NaCl$$

or

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2NH_3\uparrow + 2HOH + CaSO_4$$

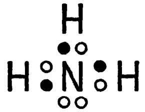
The reagents should be moist to give some mobility to the reacting ions, but the amount of water should be kept at a minimum owing to the great solubility of ammonia.

Metallic nitrides, in general, react quantitatively with water.

$$Mg_3N_2 + 6HOH \rightarrow 3Mg(OH)_2 + 2NH_3$$

9. Physical Properties of Ammonia.—The critical temperature of ammonia is 132.9°C., and its vapor pressure at room temperature (20°C.) is 8.46 atm. Hence at 20°C. it is a vapor unless confined in a vessel at a pressure equal to or greater than 8.46 atm. It is colorless and has a characteristic pungent odor. The ease with which it can be liquefied and its high heat of vaporization (5,560 cal./mole) make it a desirable commercial refrigerant. In many respects, liquid ammonia resembles water as a solvent. Its high dielectric constant makes it a good solvent for salts.

The atoms in the ammonia molecule are linked by covalent linkages.



The relatively small van der Waals forces between these neutral molecules account for the fact that ammonia is a vapor under ordinary conditions. Its low molecular weight (17) makes its density less than that of the air. Hence it may be collected in inverted bottles by the displacement of air.

Ammonia is very soluble in water; 200 volumes of the gas dissolve in one of water at 20°C. Hence it cannot be collected by the displacement of water. Priestley collected the pure gas, probably for the first time, in 1774 by the displacement of mercury in which it is insoluble.

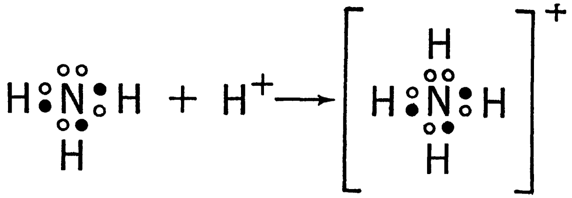
10. The Relationship between Ammonia and the Ammonium Ion.—Ammonia is the conjugate base to the cation acid, the ammonium ion, as shown by the following relationship:

$$\underset{\textbf{acid}}{NH_4^+} \rightleftarrows \underset{\textbf{base}}{NH_3} + \underset{\textbf{proton}}{H^+}$$

This is the same relationship that exists between the hydronium ion and water.

$$H_3O^+ \rightleftarrows H_2O + H^+$$

The union of the proton with ammonia, upon which the character of the latter as a base depends, is accomplished by the formation of a dative bond.



The ionization constant of the ammonium ion is 10^{-9}, which indicates that this acid is far weaker than the hydronium ion (10^{-2}) or acetic acid (10^{-5}) but that it is a stronger acid than water (10^{-16}). Hence ammonia is a stronger base than water or the acetate ion but a far weaker base than the hydroxyl ion.

When ammonia dissolves in water, the following protolysis reaction takes place:

$$NH_3 + HOH \underset{16}{\overset{9}{\rightleftarrows}} NH_4^+ + OH^-$$

The relative tendencies for the direct and the reverse reactions to take place are such that an equilibrium is established when the concentrations of the ammonium and hydroxyl ions are still quite small. For example the concentration of the hydroxyl ion in $0.1M$ ammonia solution is about 10^{-3}. In such solutions, ammonia molecules are about one hundred times as concentrated as hydroxyl ions.

Ammonia-water solutions may be considered as containing the substance ammonium hydroxide. If the water is evaporated from such solutions, ammonia gas escapes also. Hence the reverse reaction between ammonium and hydroxyl ions goes to completion. For this reason pure ammonium hydroxide has never been isolated.

11. The Reactions of Ammonia with Acids.—When ammonia reacts with an acid in the absence of water, a proton-transfer reaction takes place with the formation of the ammonium salt of the acid. Thus if ammonia and hydrochloric acid, both as gases, are mixed, a dense white smoke of small crystals of solid ammonium chloride forms very rapidly.

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

These ions form the crystal structure of the salt.

If aqueous solutions of these substances are mixed, the reaction is different but the salt formed, the same. The base in greatest concentration is again ammonia; but the acid in the hydrochloric acid solution is the hydronium ion. Hence the reaction that takes place is

$$NH_3 + H_3O^+ \rightleftarrows H_2O + NH_4^+$$

Since the chloride ion is present, the resulting solution is one of ammonium chloride. Both the reaction between the anhydrous substances and that which occurs in water may be summarized by

$$NH_3 + HCl \rightarrow NH_4Cl$$

Similarly with other acids, other ammonium salts may be prepared.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$
$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

12. Oxidation of Ammonia.—The valence number of the nitrogen atom in the ammonia molecule is −3. Hence it may be oxidized to a valence of 0 in free nitrogen or further to some positive valence. This is not too easily accomplished, and, therefore, ammonia is a rather poor reducing agent. Ammonia will burn in oxygen with the liberation of nitrogen.

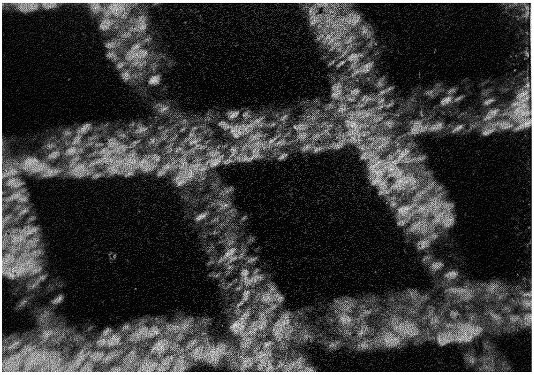


FIG. 124.—Activated platinum gauze for ammonia oxidation. (*Courtesy of U.S. Department of Agriculture.*)

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

The same oxidation is accomplished by passing dry ammonia over red-hot cupric oxide.

$$2NH_3 + 3CuO \rightarrow 3Cu + N_2 + 3H_2O$$

Such reactions would never interest an industrial chemist. The conversion of ammonia to nitric acid, however, is of great commercial importance, for it involves the preparation of the essential reagent in the manufacture of high explosives from the primary product of nitrogen fixation. The first step in this preparation is accomplished by the Ostwald process. When a mixture of ammonia and air is passed over a suitable catalyst at about 500 to 600°C., nitric oxide is formed by the following reaction:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The catalyst consists of platinum in the form of a cylinder of several layers of platinum gauze (Fig. 124). The remaining steps in the preparation of nitric acid are easily carried out by the following reactions:

$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

13. Inorganic Amides.—Ammonia will react with an alkali metal to form an amide.

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$

Sodium amide is really a salt. When dissolved in liquid ammonia, its crystals go into solution as sodium and amide (NH_2^-) ions. The amide ion is the conjugate base to the acid, ammonia.

$$NH_3 \rightleftarrows NH_2^- + H^+$$

We have learned that ammonia is a base so that this substance must be amphiprotic. As an acid, it is extremely weak, as a matter of fact, weaker than water. Hence the amide ion is a stronger base than the hydroxyl ion. When sodium amide is dissolved in water, hydrolysis of the amide ion goes to completion.

$$NH_2^- + HOH \rightarrow NH_3 + OH^-$$

Hence the amide ion is unknown in aqueous solution.

14. Complex Ions Containing Ammonia.—We have mentioned the formation of the complex silver-ammonia ion, $Ag(NH_3)_2^+$. Ions of metals in the Arabic-numbered groups of the periodic table in general tend to form such ions. The following are typical: $Cu(NH_3)_4^{++}$, $Zn(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$, $Ni(NH_3)_6^{++}$, $Co(NH_3)_4^{++}$.

15. Uses of Ammonia in Analytical Chemistry.—A detailed discussion of the usefulness of ammonia water in chemical analysis is beyond the scope of this text. We have pointed out how the formation of the complex silver-ammonia ion may be used to dissolve a precipitate of silver chloride. Similarly, precipitates containing other metals, which form ammonia complexes, may be dissolved or prevented from forming by the use of ammonia water.

This reagent is also a source of low concentrations of hydroxyl ions.

$$NH_3 + HOH \rightleftarrows NH_4^+ + OH^-$$

If an ammonium salt, *e.g.*, ammonium chloride, is dissolved in an ammonia-water solution, the concentration of the ammonium ion is greatly increased. This increases the speed of the reverse reaction and hence reduces the hydroxyl-ion concentration. This is another example of the common ion effect (32-9). To estimate the magnitude of this effect, let us consider the following example. In an ammonia-water solution, in which the concentration of the ammonia molecules is $0.1M$, the concentration of the hydroxyl ion can be obtained from the expression for the equilibrium constant.

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 10^{-5}$$

$$\frac{[NH_4^+][OH^-]}{10^{-1}} = 10^{-5}$$

Since the concentrations of the ammonium and hydroxyl ions must be equal in pure ammonia water, it follows that

$$[OH^-]^2 = 10^{-5} \times 10^{-1} = 10^{-6}$$

$$[OH^-] = 10^{-3}$$

Now if 0.1 mole of ammonium chloride is added to a liter of ammonia water, the concentration of the ammonium ion will increase to $0.1M$ since any salt is completely ionic. Hence

$$\frac{10^{-1} \times [OH^-]}{10^{-1}} = 10^{-5}$$

$$[OH^-] = 10^{-5}$$

The hydroxyl-ion concentration has been reduced a hundredfold.

By thus controlling the concentration of the hydroxyl ion, it is possible to precipitate preferentially metal hydroxides with smaller solubility products while preventing the precipitation of others whose solubility products are larger. This is a great help in analytical separations.

16. Properties of Ammonium Salts.—With two exceptions, ammonium salts decompose when heated into ammonia and the corresponding acid, *e.g.*,

$$NH_4Cl \rightarrow NH_3 + HCl$$

$$(NH_4)_2SO_4 \rightarrow 2NH_3 + H_2SO_4$$

The exceptions, ammonium nitrite and ammonium nitrate, yield nitrogen and nitrous oxide, respectively, on decomposition.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

The aqueous solution of an ammonium salt, whose negative ion is a weak base, *e.g.*, NH_4Cl, is weakly acidic since the ammonium ion is a weak acid.

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

If the anion of the ammonium salt is a strong base, *e.g.*, $NH_4C_2H_3O_2$, the two ions will react when dissolved in water.

$$NH_4^+ + C_2H_3O_2^- \rightleftarrows NH_3 + HC_2H_3O_2$$

Ammonium carbonate, commonly known as smelling salts, is of this type.

$$NH_4^+ + CO_3^{--} \rightleftarrows NH_3 + HCO_3^-$$

Hence the smell of ammonia.

We have mentioned the reaction of the ammonium and hydroxyl ions that results in the formation of ammonia (38-8).

17. Uses of Ammonia and Ammonium Salts.—The greater part of the ammonia manufactured is converted into ammonium salts or into nitric acid. It is one of the reagents in the Solvay process for the manufacture of soda (48-5). We have mentioned the use of anhydrous ammonia in refrigeration and in the manufacture of artificial ice. In solution it is familiar as household ammonia. Ammonium salts are used as fertilizers. Their mildly acid reaction must be taken into consideration when they are used for this purpose. When mixed with high explosives, the less expensive ammonium nitrate explodes with equal violence. Alone, it is relatively safe.

EXERCISES

1. Why is free nitrogen so relatively useless but its compounds so valuable?

2. Discuss the choice of pressure and temperature conditions and of the catalyst to ensure the success of the synthetic-ammonia process.

3. Write five equations that illustrate the basic character of ammonia.

4. Calculate the pH of a solution that contains 0.1 mole of ammonia per liter.

5. Write two equations that illustrate the action of ammonia as a reducing agent.

6. Why is silver chloride soluble in ammonia?

7. Write an ionic equation for the reaction by which ammonia is prepared from an ammonium salt. Why does not a farmer spread ammonium sulfate fertilizer and slaked lime on his field simultaneously?

8. Why does an ammonium salt prevent the precipitation of magnesium hydroxide when ammonia water is added to a solution containing the magnesium ion?

9. Why are aqueous solutions of ammonium salts acidic?

10. Smelling salts are essentially perfumed crystals of ammonium carbonate. Explain the strong odor of ammonia when these crystals are moistened.

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CHAPTER THIRTY-NINE

OXIDES AND OXYGEN ACIDS OF NITROGEN

Since nitrogen is in Group V of the periodic table, its maximum valence number is +5. However, five oxides exist corresponding to each of the positive valence numbers from +1 to +5. Only two of these valence numbers, +3 and +5, are to be found in important acids and salts. Oddly enough, the oxides corresponding to these valences, N_2O_3 and N_2O_5 are unstable. This information is summarized in Table 42.

TABLE 42.—SUMMARY OF THE CHEMISTRY OF NITROGEN

Valence Number	Hydride, Oxide or Free Element		Hydroxide or Acid		Ion in Salts
-3	NH_3 ammonia	$\xrightarrow{HOH}$	$NH_4^+OH^-$ ammonium hydroxide	$\xrightarrow{H_3O^+}$	NH_4^+ ammonium ion
0	N_2 nitrogen				
$+1$	N_2O nitrous oxide				
$+2$	NO nitric oxide				
$+3$	(N_2O_3)* nitrogen trioxide	$\xrightarrow{H_2O}$	(HNO_2)* nitrous acid	$\xrightarrow{OH^-}$	NO_2^- nitrite ion
$+4$	NO_2 nitrogen dioxide				
$+5$	(N_2O_5)* nitrogen pentoxide	$\xrightarrow{H_2O}$	HNO_3 nitric acid	$\xrightarrow{OH^-}$	NO_3^- nitrate ion

* Unstable.

1. Nitrous oxide is the general anesthetic commonly known as laughing gas. A colorless, odorless gas, it is moderately soluble in cold water but may be collected by the displacement of hot water. It may be prepared by cautious heating of ammonium nitrate.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

It is a splendid oxidizing agent, supporting combustion almost as well as pure oxygen. A glowing splint bursts into flame when lowered into the gas.

2. **Nitric oxide** may be prepared by three methods, two of which have been discussed: by passing air through an electric arc (38-4),

$$N_2 + O_2 + 43{,}000 \text{ cal.} \rightleftarrows 2NO$$

and by the Ostwald process (38-12),

$$4NH_3 + 5O_2 \xrightarrow[500°C.]{Pt} 4NO + 6H_2O$$

In the laboratory, it is prepared by the reduction of dilute nitric acid usually by a metal like copper.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

This colorless gas is only sparingly soluble in water.

If the temperature is not too high, nitric oxide reacts with atmospheric oxygen to form nitrogen dioxide.

$$2NO + O_2 \rightleftarrows 2NO_2 + \text{heat}$$

Since the direct reaction is exothermic, the percentage of the dioxide in the equilibrium mixture decreases as the temperature is raised. Hence the dioxide is not formed when nitrogen and oxygen combine at the temperature of an electric arc.

3. **Nitrogen dioxide** is a red-brown poisonous gas with a characteristic odor. It tends to polymerize (36-10) to the colorless tetroxide.

$$\underset{\text{red}}{2NO_2} \rightleftarrows \underset{\text{colorless}}{N_2O_4}$$

In general, low temperatures favor polymerization. Hence when the equilibrium mixture is heated in a closed tube, its red color becomes more pronounced.

The dioxide is usually prepared from nitric oxide. It is formed when concentrated nitric acid is reduced by copper and when nitrates, other than alkali metal and ammonium nitrates, are heated, *e.g.*,

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

Nitrogen dioxide reacts differently with hot water than it does with cold.

With hot water:

$$\begin{gathered} 3NO_2 + H_2O \rightarrow 2HNO_3 + NO \\ (N^{+4} \rightarrow N^{+5} + e^-) \times 2 \\ (2e^- + N^{+4} \rightarrow N^{+2}) \times 1 \end{gathered}$$

This is an oxidation-reduction reaction in which the dioxide is both the oxidizing and the reducing agent. (Why?)

With cold water:

$$\begin{gathered} 2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \\ N^{+4} \rightarrow N^{+5} + e^- \\ N^{+4} + e^- \rightarrow N^{+3} \end{gathered}$$

These reactions may be used as a means of preparing nitrite and nitrate salts from the dioxide by passing the gas into an aqueous solution of a metal hydroxide.

4. **Nitrogen trioxide and nitrogen pentoxide** are of no practical importance because of their instability.

$$N_2O_3 \rightleftarrows NO_2 + NO$$

and

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

They are the anhydrides of nitrous and nitric acids, respectively

$$\begin{gathered} N_2O_3 + H_2O \rightarrow 2HNO_2 \\ N_2O_5 + H_2O \rightarrow 2HNO_3 \end{gathered}$$

5. **Nitrous Acid and the Nitrites.**—Nitrites of the alkali metals are prepared by heating the corresponding nitrates.

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

As this method of preparation indicates, they are stable compounds. They may also be prepared by passing a mixture of nitric oxide and nitrogen dioxide into an aqueous solution of a metal hydroxide.

$$NO + NO_2 + Ca(OH)_2 \rightarrow Ca(NO_2)_2 + H_2O$$

Nitrous acid is a weak, unstable acid. Hence the nitrite ion is a strong base. The acid is formed and exists for a short time when an ice-cold solution of a nitrite is acidified.

$$NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_2$$

The free acid decomposes into the blue-colored nitrogen trioxide

$$2HNO_2 \rightarrow H_2O + N_2O_3$$

which in turn breaks down.

$$N_2O_3 \rightarrow NO + NO_2$$

Nitrites are important reagents in the manufacture of a class of dyestuffs called azo dyes.

6. Preparation of Nitric Acid.—About one-tenth of the nitric acid manufactured in this country is made by treating Chile saltpeter with concentrated sulfuric acid.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3\uparrow$$

The acid distills away from the reaction mixture and is condensed by a system of air- and water-cooled condensers. This method may also be carried out in the laboratory. Most of this acid is prepared from atmospheric nitrogen via reactions that we have already studied.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

synthetic-ammonia process

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

Ostwald process

$$2NO + O_2 \rightarrow 2NO_2$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The nitric oxide left over in the final reaction is mixed with more so that it may reenter the process at the third step.

7. Properties of Nitric Acid.—Pure nitric acid is a colorless liquid that freezes at −42°C. and boils at 86°C. It forms a constant-boiling (120.5°C.) mixture with water which contains 68 per cent of the acid; and this is the concentrated reagent of the laboratory. This reagent gradually becomes yellow since light causes a slight decomposition that results in the formation of the brown dioxide. Fuming nitric acid is a solution of the dioxide in the concentrated acid.

8. The reactions of nitric acid may be classified into three types: those in which it acts as an acid, as an oxidizing agent, and its reactions with organic substances.

a. As an Acid.—Nitric acid is a strong acid. In all but concentrated solutions its ionization is virtually complete.

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

The nitrate ion is, therefore, a negligibly weak base. The following reactions are typical:

$$KOH + HNO_3 \rightarrow KNO_3 + HOH$$

or

$$OH^- + H_3O^+ \rightarrow HOH + H_2O$$

$$Na_2CO_3 + 2HNO_3 \rightarrow 2NaNO_3 + H_2O + CO_2$$

or

$$CO_3^= + 2H_3O^+ \rightarrow CO_2 + 3H_2O$$

$$Al_2O_3 + 6HNO_3 \rightarrow 2Al(NO_3)_3 + 3H_2O$$

In writing the equations for its reactions as an acid, it must always be kept in mind that it is an oxidizing agent. Any substance which contains an element that can be easily oxidized will enter into an oxidation-reduction reaction with nitric acid. Thus a free metal or a basic oxide in which the metal is in its lower valence, *e.g.*, FeO, will not react with nitric acid in the normal manner of such substances with an acid.

b. As an Oxidizing Agent.—The nitrogen atom in nitric acid is in its maximum valence of +5. Since its reduction is relatively easy, the acid is an excellent oxidizing agent. The concentrated acid is in general reduced to the dioxide

$$HNO_3 \rightarrow NO_2$$

$$N^{+5} + e^- \rightarrow N^{+4}$$

whereas the dilute acid is reduced to nitric oxide, NO. Since oxidation-reduction reactions will be discussed in detail in the next chapter, we shall simply list the following reactions as typical and consider the problems connected with their balancing later:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$$

$$3P + 5HNO_3 + 2H_2O \rightarrow 3H_3PO_4 + 5NO$$

$$3FeO + 10HNO_3 \rightarrow 3Fe(NO_3)_3 + NO + 5H_2O$$

Nitric acid attacks all the common metals except gold and platinum. The latter are too difficult to oxidize. A solution of 1 part nitric acid and 3 parts hydrochloric acid will, however, "dissolve" gold. Hence the name *aqua regia* was applied to this solution by the alchemists. The two acids react as follows:

$$HNO_3 + 3HCl \rightarrow 2H_2O + Cl_2 + NOCl$$

The nitrosyl chloride formed in this reaction is an orange-yellow gas that slowly reacts with water in a series of reactions that finally produce hydrochloric acid and oxides of nitrogen. It is the free chlorine formed in the initial reaction which reacts with the gold.

c. Reactions with Organic Substances.—These reactions use most of the nitric acid manufactured. All our modern high explosives are prepared by such reactions, *e.g.*, nitroglycerin, the explosive constituent of dynamite, nitrocellulose, or guncotton, and trinitrotoluene, or T.N.T. Explosives are, of course, essential in war, but they are also important in mining and construction operations in peace.

9. The nitrates are typical salts of a strong acid. Since the nitrate ion is an infinitesmally weak base, it is not hydrolyzed nor will it react as a base with any acid. Nitrates may be prepared by neutralization reactions and by the action of nitric acid on metals, basic oxides, and carbonates. Since the solubility products of all nitrates are relatively large, these salts are soluble and cannot be prepared by precipitation.

Nitrates decompose on heating. Alkali-metal nitrates are reduced to the corresponding nitrites.

$$2KNO_3 \rightarrow 2KNO_2 + O_2$$

Nitrates of other metals decompose into the oxide of the metal, nitrogen dioxide and oxygen.

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

However, if the oxide of the metal is unstable when heated, as are the oxides of the metals below copper in the electromotive series, the free metal is obtained when the nitrate is heated.

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$$

Ammonium nitrate forms nitrous oxide when its solution is warmed.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Nitrates also are oxidizing agents. Powdered charcoal takes fire when dropped into melted sodium nitrate. Gunpowder is a mixture of powdered potassium nitrate, sulfur, and wood charcoal. The rapid combustion of gunpowder involves several different reactions. The principal reactions may be summarized by the equation

$$2KNO_3 + 3C + S \rightarrow K_2S + N_2 + 3CO_2$$

The rapid liberation of the gaseous nitrogen and carbon dioxide from solid reactants produces the sudden expansion needed to speed the bullet on its way. The solid potassium sulfide together with unburned particles of charcoal explains the smoke.

10. Test for Nitrates.—Since nitrates are soluble, it has been impossible to devise a simple test for the nitrate ion based on a precipitation reaction. The following test is sufficiently delicate. To a few drops of the solution to be tested are added approximately twice as much concentrated sulfuric acid. Several drops of a dilute ferrous sulfate solution are carefully added so as to avoid mixing. After several minutes, a brown ring develops at the boundary between the two liquid layers if the nitrate ion is present.

EXERCISES

1. How is nitrous oxide prepared, and for what is it used?

2. Write equations for methods by which nitric oxide may be prepared by the oxidation of nitrogen and by its reduction.

3. Why does a brown gas appear when nitric oxide is exposed to the air?

4. Write equations for reactions by which the following conversions may be accomplished:

$$NH_3 \rightarrow HNO_3$$
$$NO \rightarrow NaNO_2$$
$$HNO_3 \rightarrow NO$$
$$NaNO_2 \rightarrow NO_2$$
$$Pb(NO_3)_2 \rightarrow NO_2$$

5. Write equations for the reaction of nitric acid with each of the following substances: KOH, $CaCO_3$, NH_3, Fe_2O_3, $NaHCO_3$.

6. When nitric acid reacts with such substances as P, FeO, Zn, and H_2S what type of reaction is to be expected?

7. What weight of nitric acid would be required to form 10 l. of carbon dioxide at standard temperature and pressure from limestone, $CaCO_3$?

8. Account for the brown color of concentrated nitric acid.

9. What is the effect of an increased pressure on the following equilibria:

$$N_2 + O_2 \rightleftarrows 2NO$$
$$2NO + O_2 \rightleftarrows 2NO_2$$

10. Write equations showing four different ways in which nitrates decompose on heating.

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CHAPTER FORTY

OXIDATION-REDUCTION REACTIONS

At various places in the foregoing pages we have discussed oxidation-reduction reactions. It will be helpful to gather this material together before considering it more fully.

1. Oxidation-reduction reactions are those in which valence changes are involved. *Oxidation is an algebraic increase in* the *valence number* of an element *and,* therefore, *involves a loss of electrons* by the atoms of the element oxidized. Conversely, *an element is reduced when its valence number is decreased and,* therefore, *its atoms gain electrons.* Oxidation-reduction reactions are ones of electron transfer, the electrons passing from atoms of the element oxidized to atoms of the element reduced. It is well to recognize the parallelism between oxidation-reduction and protolysis reactions. The former involve electron transfer and the latter a transfer of protons, *e.g.*,

Oxidation-reduction: $2Na + Cl_2 \rightarrow 2Na^+ + 2Cl^-$
Oxidation: $2Na \rightarrow 2Na^+ + 2e^-$
Reduction: $Cl_2 + 2e^- \rightarrow 2Cl^-$
Protolysis: $HCl + NH_3 \rightarrow NH_4^+ + Cl^-$
Acid: $HCl \rightarrow Cl^- + H^+$
Base: $NH_3 + H^+ \rightarrow NH_4^+$

Since an element in being oxidized gives electrons to and thus accomplishes the reduction of another element, the *reducing agent is the substance that contains the element oxidized.* Similarly, *the oxidizing agent is the substance that contains the element reduced.*

As we have seen before, many oxidation-reduction equations are difficult to balance. If salts or acids in aqueous solution are involved, ions rather than molecules are among the reactants and products. Further, a balanced equation that involves more than a very small number of molecules and ions must be the sum of a series of simpler reactions rather than a single complex one, since the chance of a relatively large number of particles colliding simultaneously is exceedingly small. Since the intermediate steps involved in a given oxidation-reduction reaction are probably unknown, we write an equation that shows the initial reactants and the final products.

2. Predicting the Products.—In the last analysis, the only sure method of knowing what is formed, when a given oxidizing agent reacts with a given reducing agent, is to carry out the reaction in the laboratory, to isolate the products, and finally to identify them. However, a knowledge of the chemistry of the elements involved in the reaction will, in most cases, enable us to predict what the products will be. Consider the reaction between dilute nitric acid and silver as an example. We know that when dilute nitric acid acts as an oxidizing agent the reduced nitrogen atoms appear among the products in molecules of nitric oxide. The atoms of silver must be oxidized in this reaction. Since silver has but one positive valence number (+1), the compound, in which silver is found among the products, must contain silver atoms in this valence. What might this compound be? Possibly silver oxide, Ag_2O, but this is a basic oxide and hence will react further with nitric acid to form silver nitrate. This salt then is the probable product. We may now write tentatively

$$Ag + HNO_3 \rightarrow AgNO_3 + NO$$

The hydrogen will appear as water in the products and not as free hydrogen, since the latter would be oxidized by nitric acid to water. Hence the unbalanced equation would appear as

$$Ag + HNO_3 \rightarrow AgNO_3 + NO + H_2O$$

In short, the problem of setting up oxidation-reduction equations is solved by knowing to what the oxidizing agent is reduced and the reducing agent is oxidized.

3. Nitric Acid as an Oxidizing Agent.—Since nitric acid is one of the most commonly used oxidizing agents, we shall use this reagent in the discussion that follows. In concentrated aqueous solution, the nitrogen in nitric acid is reduced to the red-brown gas nitrogen dioxide. In this case, the valence change is from +5 to +4. In dilute solution the reduction goes further from +5 to +2 in the colorless nitric oxide. However, as soon as this gas escapes from the reaction mixture into the air, the familiar red-brown fumes appear. It is possible to reduce the nitrogen to its lowest valence number of -3 if the dilute acid is treated with zinc, which is a strong reducing agent. The final product in this case will not be ammonia but ammonium nitrate. (Why?)

4. **Reducing Agents.**—The other half of the problem of predicting the products is solved by knowing to what the reducing agent is oxidized. The following classes of reducing agents are suitable for nitric acid oxidation.

a. **Free Metals.**—All common metals except gold and platinum are oxidized to their highest positive valence number. As such, they will appear among the products as positively charged ions.

b. **Metals in lower valences** are to be found in solutions of "ous" salts and in basic oxides, *e.g.*, ferrous nitrate and ferrous oxide, respectively. Nitric acid oxidizes them to their higher valence ions.

c. **Nonmetals.**—In general nonmetals, except the halogens, are oxidized to their highest positive valence by nitric acid. Since nonmetals do not exist as simple positively charged ions, we must expect to find the nonmetal in a compound with oxygen. Further, since higher valence nonmetal oxides almost invariably react with water to form stable *-ic* acids, we should expect these to be the products. Thus sulfur is oxidized to sulfuric acid, phosphorus to phosphoric acid, etc.

d. **Nonmetal Anions.**—Simple negative ions are oxidized to the free nonmetal if the conditions are mild or, under more severe conditions, to the *-ic* acid except in the case of the halogens. Thus the chloride ion is oxidized to free chlorine under any conditions, but the sulfide ion may be oxidized to free sulfur or further to sulfuric acid.

e. **Nonmetals in lower positive valences** exist as lower acidic oxides and as *-ous* acids, *e.g.*, sulfur dioxide and sulfurous acid. These are oxidized by nitric acid to the corresponding *-ic* acid.

These rules may seem formidable at first glance, but they are the result of the common sense application of an elementary knowledge of chemistry. After the proper choice of products has been made and the skeleton equation written, there remains the problem of balancing. This is sufficiently difficult to require special methods of which the valence-change and the ion-electron methods are typical.

5. The Valence-change Method.—Equations that are balanced by this method are those in which formulas for complete substances are used rather than for the ions directly involved in the reaction. We shall use as an example the reaction between sulfur and dilute nitric acid. The skeleton equation is

$$HNO_3 + S \rightarrow H_2SO_4 + NO$$

We next consider the valence changes.

$$\begin{gathered} 3e^- + N^{+5} \rightarrow N^{+2} \\ S^0 \rightarrow S^{+6} + 6e^- \end{gathered}$$

Since the electrons lost by the atoms oxidized are those gained by the atoms reduced, we multiply by the smallest whole numbers needed to balance the electrons.

$$\begin{array}{c} 6e^- + 2N^{+5} \rightarrow 2N^{+2} \\ S^0 \rightarrow S^{+6} + 6e^- \\ \hline 2N^{+5} + S^0 \rightarrow 2N^{+2} + S^{+6} \end{array}$$

Upon adding, we find that two nitrogen atoms will oxidize one of sulfur. We proceed in the balancing of the skeleton equation by using this knowledge

$$2HNO_3 + S \rightarrow H_2SO_4 + 2NO$$

and in this case the reaction balances. In others it may be necessary to add water, *e.g.*,

$$\begin{gathered} 5HNO_3 + 3P \rightarrow 5NO + 3H_3PO_4 \\ (3e^- + N^{+5} \rightarrow N^{+2}) \times 5 \\ (P^0 \rightarrow P^{+5} + 5e^-) \times 3 \end{gathered}$$

Since neither the hydrogen nor the oxygen atoms balance, we must add the proper number of water molecules.

$$5HNO_3 + 3P + 2H_2O \rightarrow 5NO + 3H_3PO_4$$

The reactions of metals with nitric acid result in the formation of metal nitrates. Thus the acid not only oxidizes the metal, but also furnishes nitrate groups for the salt formed. Since the valence of nitrogen in any nitrate including nitric acid is +5, the nitrogen in these nitrate groups will not have been reduced and hence will not be included in the balancing by the valence change. Take the example of the oxidation of iron by nitric acid:

$$\begin{gathered} Fe + HNO_3 \rightarrow Fe(NO_3)_3 + NO + H_2O \\ (3e^- + N^{+5} \rightarrow N^{+2}) \times 1 \\ (Fe^0 \rightarrow Fe^{+++} + 3e^-) \times 1 \end{gathered}$$

The one nitrogen atom indicated in the above is reduced to a valence of +2 in the nitric oxide formed. However, the three nitrogen atoms in ferric nitrate have not been reduced and must come from three molecules of nitric acid in addition to the one molecule that acts as an oxidizing agent. The balanced equation is, therefore,

$$Fe + 4HNO_3 \rightarrow Fe(NO_3)_3 + NO + 2H_2O$$

6. Ion-electron Method.—The above reaction takes place in aqueous solution in which nitric acid, as a strong acid, and ferric nitrate, as a salt, are completely ionized. Thus we may write the equation in this manner

$$Fe + 4H^+ + 4NO_3^- \rightarrow Fe^{+++} + 3NO_3^- + NO + 2H_2O$$

and discover that three nitrate ions take no part in the reaction The equation may be simplified to

$$Fe + 4H^+ + NO_3^- \rightarrow Fe^{+++} + NO + 2H_2O$$

Such ionic equations may be obtained more directly by the ion-electron method. Two half reactions are written, one of reduction and one of oxidation. In the reaction between iron and dilute nitric acid, the reduction of nitric acid would be written

$$3e^- + NO_3^- + 4H^+ \rightarrow NO + 2H_2O$$

The fact that nitric acid exists as hydrogen (hydronium) and nitrate ions is taken into consideration. On the other hand, both nitric oxide and water are written as molecules since they are unionized. In this half equation, the four hydrogen ions are needed to take care of the two oxygen atoms removed from the nitrate ion when the latter is changed to nitric oxide. Not only must the number of atoms balance in an equation, but the charges must also. Hence three electrons are added on the left. The half reaction for the oxidation of the iron is written

$$Fe \rightarrow Fe^{+++} + 3e^-$$

In this case the number of electrons is the same in each half reaction. So these are added to give the final equation for this oxidation-reduction reaction.

$$Fe + NO_3^- + 4H^+ \rightarrow Fe^{+++} + NO + 2H_2O$$

A slightly more difficult equation to balance is that of the reaction between phosphorus and concentrated nitric acid.

$$1e^- + NO_3^- + 2H^+ \rightarrow NO_2 + H_2O$$

$$P + 4H_2O \rightarrow H_3PO_4 + 5H^+ + 5e^-$$

Note that concentrated nitric acid is reduced to the dioxide. The second half reaction needs explaining. We know that phosphorus will be oxidized to phosphoric acid; but the latter needs four oxygen and three hydrogen atoms to complete its formula. These we obtain by using four water molecules. The five remaining hydrogen atoms appear as hydrogen ions on the right. It would have been improper to have placed free hydrogen as a product, since none is liberated in the reaction.

To balance the electrons, the first half reaction must be multiplied by 5.

$$5e^- + 5NO_3^- + 10H^+ \rightarrow 5NO_2 + 5H_2O$$

$$P + 4H_2O \rightarrow H_3PO_4 + 5H^+ + 5e^-$$

The two half reactions are now added, taking account of the presence of both hydrogen ions and water molecules on each side of the arrows.

$$P + 5NO_3^- + 5H^+ \rightarrow H_3PO_4 + 5NO_2 + H_2O$$

As a final example, consider the reduction of dilute nitric acid by zinc. This reaction reduces the nitrogen atom to its lowest valence of −3 in the ammonium ion.

$$(8e^- + NO_3^- + 10H^+ \rightarrow NH_4^+ + 3H_2O) \times 1$$

$$(Zn \rightarrow Zn^{++} + 2e^-) \times 4$$

$$\begin{array}{r} 8e^- + NO_3^- + 10H^+ \rightarrow NH_4^+ + 3H_2O \\ 4Zn \rightarrow 4Zn^{++} + 8e^- \\ \hline 4Zn + NO_3^- + 10H^+ \rightarrow 4Zn^{++} + NH_4^+ + 3H_2O \end{array}$$

7. The Theory of Oxidation-reduction.—Thus far we have been considering the mechanical details involved in writing equations for oxidation-reduction reactions. The question of whether or not a given oxidizing agent will react with a given reducing agent under given conditions has not been discussed. An approach to the answer to this question may be found by returning to a consideration of replacement reactions and of the electromotive series of metals.

8. The Electromotive Series Again.—In an earlier chapter (10-9), we pointed out how the metals can be arranged in the order of their relative activity by a study of replacement reactions such as the following:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

Such a reaction would be carried out by immersing a piece of metallic zinc in an aqueous solution of copper sulfate. From the theory of ionization we know that copper sulfate in aqueous solution is completely ionized, so that the reaction which takes place must be between neutral atoms of zinc and either the copper or the sulfate ions. Further, the above equation shows the formation of zinc sulfate. Yet we know that this substance is a salt and exists as ions in solution. Hence the reaction can be more accurately stated as follows:

$$Zn^0 + Cu^{++} + SO_4^{=} \rightarrow Zn^{++} + SO_4^{=} + Cu^0$$

Since the sulfate ion appears on both sides of the equation, it must take no part in the reaction, so that the essential change which takes place simplifies to the following:

$$Zn^0 + Cu^{++} \rightarrow Zn^{++} + Cu^0$$

This reaction is obviously one of oxidation-reduction involving the transfer of two electrons from a zinc atom to a copper ion.

$$Zn^0 \rightarrow Zn^{++} + 2e^-$$
$$Cu^{++} + 2e^- \rightarrow Cu^0$$

The electrons are lost by the neutral atoms of the more active metal to the ions of the less active metal. The more active the metal, the greater the tendency of its neutral atoms to give up electrons and become ions and the less the tendency of its ions to take up electrons and become neutral atoms. The relative tendencies of the metals of the electromotive series to lose electrons and become ions and of their ions to gain electrons in the reverse process are indicated by the relative length of the corresponding arrows in Table 43.

When a metal atom loses electrons and becomes an ion, it acts as a reducing agent. (Why?) Hence the higher its position in the series, the stronger is the free metal as a reducing agent. Conversely, when its ion gains electrons and becomes a neutral atom of a free metal, it acts as an oxidizing agent. The lower the position of a metal in the series, the more powerful is its ion as an oxidizing agent. Thus zinc is a better reducing agent than silver, but the silver ion is a better oxidizing agent than the zinc ion. Consider the reaction between metallic zinc and silver nitrate as a reversible reaction

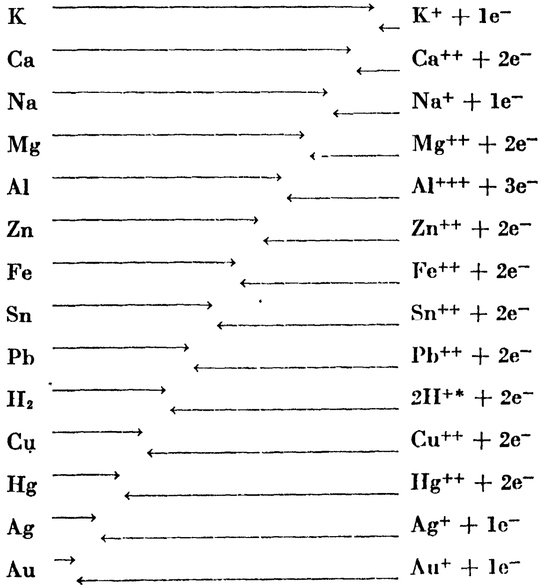
$$\mathrm{Zn} + 2\mathrm{Ag}^+ \rightleftharpoons \mathrm{Zn}^{++} + 2\mathrm{Ag}$$

It is obvious that the direct reaction will be almost complete, since the better reducing and oxidizing agents are on the left. On the other hand, the reaction between silver and ferrous sulfate would not take place to any extent

$$2\mathrm{Ag} + \mathrm{Fe}^{++} \rightleftharpoons 2\mathrm{Ag}^+ + \mathrm{Fe}$$

as the better oxidizing and reducing agents are on the right.

TABLE 43.—THE ELECTROMOTIVE SERIES OF METALS



$$\mathrm{K} \rightleftharpoons \mathrm{K}^+ + 1e^-$$
$$\mathrm{Ca} \rightleftharpoons \mathrm{Ca}^{++} + 2e^-$$
$$\mathrm{Na} \rightleftharpoons \mathrm{Na}^+ + 1e^-$$
$$\mathrm{Mg} \rightleftharpoons \mathrm{Mg}^{++} + 2e^-$$
$$\mathrm{Al} \rightleftharpoons \mathrm{Al}^{+++} + 3e^-$$
$$\mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{++} + 2e^-$$
$$\mathrm{Fe} \rightleftharpoons \mathrm{Fe}^{++} + 2e^-$$
$$\mathrm{Sn} \rightleftharpoons \mathrm{Sn}^{++} + 2e^-$$
$$\mathrm{Pb} \rightleftharpoons \mathrm{Pb}^{++} + 2e^-$$
$$\mathrm{H}_2 \rightleftharpoons 2\mathrm{H}^{+*} + 2e^-$$
$$\mathrm{Cu} \rightleftharpoons \mathrm{Cu}^{++} + 2e^-$$
$$\mathrm{Hg} \rightleftharpoons \mathrm{Hg}^{++} + 2e^-$$
$$\mathrm{Ag} \rightleftharpoons \mathrm{Ag}^+ + 1e^-$$
$$\mathrm{Au} \rightleftharpoons \mathrm{Au}^+ + 1e^-$$

* These hydrogen ions will be, of course, in the form of hydronium ions.

9. Electrochemical Cells.—Any oxidation-reduction reaction that takes place spontaneously may be used as a source of electrical energy. Let us consider as a typical reaction that one that takes place between zinc and chlorine and results in the formation of zinc chloride

$$Zn + Cl_2 \rightarrow ZnCl_2$$

The valence changes, together with the electron transfer which is responsible for them, are as follows:

$$Zn^0 \rightarrow Zn^{++} + 2e^-$$
$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

The zinc atoms are oxidized and the chlorine atoms reduced. Let us try to picture the mechanism of such a reaction in terms of the atoms that take part in it. We have immersed a strip of metallic zinc in a solution of chlorine gas in water. This is a reaction between two phases and will, therefore, take place at the interface between them, *i.e.*, at the surface of the zinc. We can imagine the chlorine molecules, each with its two atoms, colliding with the surface of the zinc. Frequently during such a collision, two electrons pass from a neutral zinc atom to the pair of atoms of the chlorine molecule. These atoms become chloride ions (Cl^-), and the zinc atom likewise goes into solution as an ion (Zn^{++}). All that is necessary for this reaction to take place is the passage of electrons from the zinc to the chlorine atoms. If the atoms are in physical contact when the electron transfer occurs, the energy given out is in the form of heat. However, this transfer can be accomplished in another way. An electrochemical cell can be designed in which the reacting atoms are not in physical contact but are connected by a metallic conductor through which the electrons can be sent from the zinc to the chlorine.

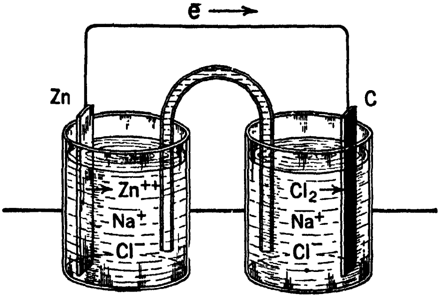


Fig. 125.—A simple electrochemical cell.

Such a cell can be constructed as follows. Two beakers are filled with a solution of some electrolyte that will not react with zinc or chlorine; sodium chloride will do very well. The solutions in the beakers are connected by means of an inverted U tube filled with the same solution (Fig. 125). One of the two solutions is then saturated with chlorine gas, and a zinc electrode is immersed in the other. A carbon electrode in the solution saturated with chlorine completes the cell. The zinc bar and the chlorine are separated from each other, but they will, nevertheless, react if the two electrodes are connected by means of a wire, the fundamental principle behind the generation of a current of electricity by any electrochemical cell.

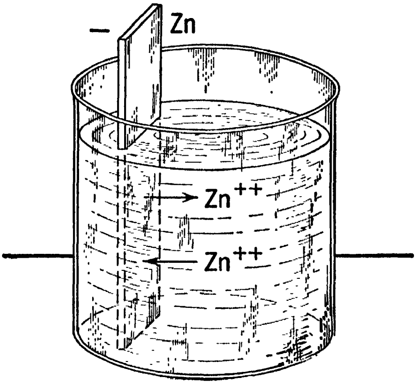


FIG. 126.

The function of the inverted U tube may have puzzled you. Its purpose is to prevent the diffusion of chlorine molecules into the solution surrounding the zinc electrode and yet to permit the migration of the ions of the salt in the electrical field of the electrodes. Since electrons are flowing out of the zinc pole, the negative pole of the cell, this pole is becoming more positive. Hence chloride ions in the solution will migrate toward this pole. On the other hand, the carbon pole is becoming more negative since electrons are flowing into it through the wire, and, therefore, the sodium ions in the solution will migrate in its direction.

10. The Equilibrium between a Metal and Its Ions.—A replacement reaction is one of oxidation-reduction and, therefore, can be used as a source of electrical energy. The reaction between metallic zinc and copper ions is the basis of an important cell, the Daniell cell. The dry cell is also one of this type. To understand the mechanism of such cells, we must first consider what takes place when a metal, *e.g.*, zinc, is immersed in a solution that contains its ions (Fig. 126). Here there are two opposing tendencies: that of neutral atoms of metallic zinc to go into solution as zinc ions, leaving electrons behind on the metal,

$$Zn^0 \rightarrow Zn^{++} + 2e^-$$

and that of zinc ions to take up electrons from the metal strip and become neutral atoms of the free metal,

$$Zn^{++} + 2e^- \rightarrow Zn^0$$

The first reaction, that of the neutral zinc atoms becoming ions, is due to an inherent tendency of the zinc atoms which has been called by Nernst the electrolytic-solution tension. Each metal has its own characteristic tendency of this kind. The more active the metal, the greater is this tendency. In the electromotive series of metals, those with the greatest electrolytic-solution tensions are at the top and those with the least at the bottom. When neutral metallic atoms go into solution as positively charged ions, they leave electrons on metal from which they dissolve. Hence the metal is made more negative and the solution more positive. This tends to attract any positive ions in the solution to the metal and exerts an important influence on the equilibrium, as we shall point out in the next paragraph.

We have assumed that the strip of metallic zinc is immersed in a solution that contains zinc ions, *e.g.*, a zinc chloride solution. These ions are moving about at random owing to their thermal motion which is, in turn, a function of the temperature. At a given temperature, the rate at which they bombard a neutral zinc strip is proportional to their concentration. Whenever a zinc ion comes in contact with the metallic zinc surface, it is in a position to take up electrons and become a neutral atom of zinc, thus reversing the reaction that we have been considering above.

$$Zn^{++} + 2e^- \rightarrow Zn^0$$

The rate at which this occurs is not only proportional to the concentration of the ions, but also to the electrostatic force of attraction between the zinc ions and the zinc pole which has become negatively charged owing to the solution of zinc atoms as ions from the pole. Thus, to sum up, the rate at which metallic zinc atoms become ions

$$Zn^0 \rightarrow Zn^{++} + 2e^-$$

is proportional to the electrolytic-solution tension of zinc, whereas the rate at which zinc ions deposit on the metal as neutral atoms

$$Zn^{++} + 2e^- \rightarrow Zn^0$$

is proportional to the concentration of the zinc ions and to the strength of the electrostatic forces between the ions and the negatively charged pole. When these effects balance, the two rates will be equal and an equilibrium set up.

$$Zn^0 \rightleftarrows Zn^{++} + 2e^-$$

The electrolytic-solution tension of metallic zinc is so high that no solution of zinc ions in water can be prepared whose concentration is enough to deposit ions as fast as they leave the pole. Therefore, when metallic zinc is immersed in a Zn^{++} solution, neutral zinc atoms will always ionize at a greater rate than zinc ions will discharge on the metal. Hence the metal will grow gradually more negative with respect to the solution, until the force of electrical attraction between the negatively charged metal and the positively charged zinc ions in solution is so great that the rates become equal. At equilibrium, in the case of zinc and other active metals, the metal is negative with respect to the solution.

On the other hand, when an inactive metal, like copper, is put into a solution containing a moderate concentration of copper ions, the electrolytic-solution tension of this inactive metal is so small that the rate at which copper atoms become ions is less than that of the reverse reaction. Hence copper ions start to deposit at a greater rate on the metal

$$Cu^{++} + 2e^- \rightarrow Cu^0$$

than neutral copper atoms become ions

$$Cu^0 \rightarrow Cu^{++} + 2e^-$$

This tends to make the metal positively charged with respect to the solution so that it tends to repel the ions. At equilibrium

$$Cu^0 \rightleftarrows Cu^{++} + 2e^-$$

the metal is positively charged with respect to the solution.

In any case, the electrostatic force becomes great so soon after the metal is immersed in a solution of its ions that an equilibrium is established before weighable amounts have left the metal as ions, or vice versa.

11. Electrode Potentials and the Electromotive Series.—We have pointed out in a qualitative way that at an equilibrium between metallic zinc and zinc ions the metal is negatively charged with respect to the solution. The problem of measuring this difference in potential quantitatively is complicated by the practical impossibility of connecting the solution to a voltmeter electrically without putting a metallic wire into it. A potential difference will, therefore, be set up between this wire and the ions in solution, so that the voltage indicated on the voltmeter will be due to two differences in potential: that of the metallic zinc in contact with zinc ions, and that of the metallic wire in contact with the same solution.

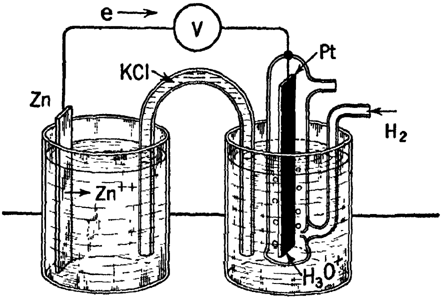


FIG. 127.—Use of the hydrogen electrode for measuring electrode potentials.

To avoid this difficulty, the electrode potentials of the metals are measured by the use of the so-called hydrogen electrode. This consists of a platinum electrode with a very spongy surface, saturated with hydrogen gas at a pressure of 1 atm. and immersed in a solution that is normal with respect to hydronium ions. Such a solution contains 1 gram-ionic weight of hydronium ions per liter. A platinum pole saturated with hydrogen in this way is essentially an electrode of hydrogen. This electrode is in equilibrium with the hydronium ions of the solution. The potential difference between such an electrode and a solution is arbitrarily assumed to be zero. To measure the electrode potential of any other electrode, an electrochemical cell is set up with the electrode as one-half of the cell and the hydrogen electrode as the other. For example, if the electrode potential of a zinc electrode is to be determined, a cell similar to that of Fig. 127 is used. In such a cell there are three places at which potential differences exist: *viz.*, between each of the metals and their respective solutions, and between the two solutions. These three determine the potential difference between the two metals, *i.e.*, the potential difference of the cell itself. Of these three, the potential difference between the solutions can be reduced to a minimum if a solution of potassium chloride is used in the siphon U tube that connects the two. The electrode potential of the hydrogen electrode is defined as zero, so that the entire electromotive force of the cell, *i.e.*, the potential difference between the zinc and hydrogen electrodes as measured by a voltmeter, is due to the electrode potential of the zinc. The measured potential difference for such a cell is 0.76 volt which is, therefore, the electrode potential of the zinc electrode in a solution containing zinc ions at normal concentration. For metals more active than hydrogen, *i.e.*, with greater electrolytic-solution tensions, the metal is negative with respect to the solution, and the sign of the electrode potential is, therefore, negative also. For less active metals than hydrogen, the sign of the electrode potential is positive.

The electromotive series of metals is obtained by arranging the metals in an order determined by their electrode potentials with those metals with the most negative electrode potentials first and those with the most positive, last.

TABLE 44.—ELECTRODE POTENTIALS OF METALS IN CONTACT WITH NORMAL SOLUTIONS OF THEIR IONS

Metal	Ion	Potential, volts	Metal	Ion	Potential, volts
K	K^+	−2.92	Sn	Sn^{++}	−0.14
Ca	Ca^{++}	−2.76	Pb	Pb^{++}	−0.13
Na	Na^+	−2.71	H_2	H_3O^+	0.00
Mg	Mg^{++}	−1.55	Cu	Cu^{++}	+0.34
Al	Al^{+++}	−1.34	Hg	Hg^+	+0.80
Zn	Zn^{++}	−0.76	Ag	Ag^+	+0.80
Fe	Fe^{++}	−0.44	Au	Au^+	+1.5(?)

12. The Daniell, or Gravity, Cell.—This cell makes use of the replacement reaction between metallic zinc and copper ions

$$Zn^0 + Cu^{++} \rightarrow Zn^{++} + Cu^0$$

as its source of electrical energy. It consists essentially of zinc and copper electrodes in solutions of their ions, as shown diagrammatically in Fig. 128. If the solutions contain normal concentrations of zinc and copper ions, the potential difference of the cell will be equal to the difference of the two electrode potentials: *i.e.*, $+0.34 - (-0.76) = 1.10$ volts. However, this may be increased by using a very dilute zinc-ion solution to make the zinc pole as negative as possible with respect to its solution and by using a saturated solution of copper sulfate to give a high concentration of copper ions and, therefore, make the copper pole as positive as possible.

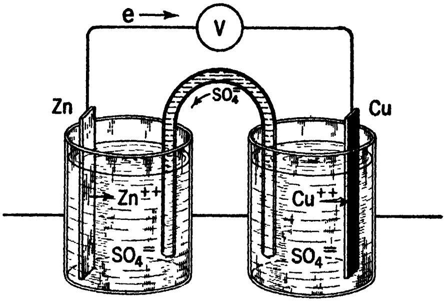


Fig. 128.—The Daniell cell.

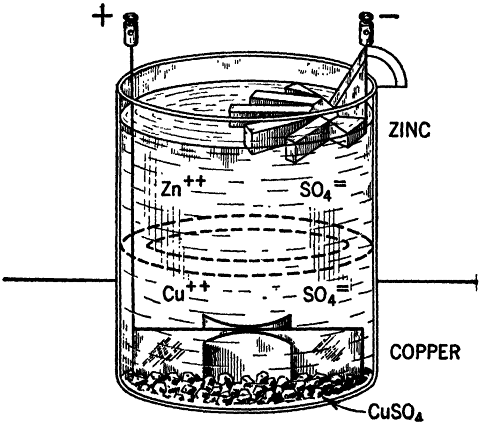


Fig. 129.—The gravity cell.

In the gravity cell, the copper pole is on the bottom (Fig. 129) immersed in a solution of copper sulfate kept saturated by the presence of undissolved crystals of the salt. The zinc electrode is suspended above the copper sulfate solution in a dilute solution of zinc sulfate which is floating on the denser solution of copper sulfate. When the two poles are connected by a wire, electrons flow from the zinc to the copper, *i.e.*, from the more negative to the more positive pole. As electrons leave the zinc pole, the equilibrium between metallic zinc atoms and zinc ions

$$Zn^0 \rightleftarrows Zn^{++} + 2e^-$$

is disturbed and more zinc atoms ionize, leaving their electrons on the pole. As electrons flow into the copper pole, the equilibrium between neutral copper atoms and copper ions

$$Cu^0 \rightleftarrows Cu^{++} + 2e^-$$

is also disturbed. Since electrons are gained by the copper pole, this becomes more negative and copper ions discharge on it by taking up electrons. Two reactions, therefore, are taking place which keep up the flow of electrons. At the negative pole

$$Zn^0 \rightarrow Zn^{++} + 2e^-$$

and at the positive pole

$$2e^- + Cu^{++} \rightarrow Cu^0$$

The total cell reaction is the sum of the two

$$Zn^0 + Cu^{++} \rightarrow Zn^{++} + Cu^0$$

Since the zinc-ion concentration about the zinc pole becomes greater as the cell reaction continues, the zinc pole becomes less negative and the potential difference of the cell falls off.

13. Electrode Potentials and Oxidation-reduction.—The electrode potentials may be used as a quantitative measure of the strength of oxidizing and reducing agents. From the discussion in paragraph 11, *the more positive (or the less negative) the electrode potential of a metal, the less powerful is the free metal as a reducing agent and the more powerful its ion as an oxidizing agent.* Further, it has been possible to determine electrode potentials from which the relative strength of nonmetal oxidizing and reducing agents may be determined. We may, therefore, place the nonmetals in the electromotive series as in Table 45. Any reducing agent will be oxidized by oxidizing agents below it in the series. For example, metallic copper is oxidized to cupric sulfate by hot, concentrated sulfuric acid which is reduced to sulfur dioxide.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

or $$Cu + SO_4^{=} + 4H^+ \rightarrow Cu^{++} + SO_2 + 2H_2O$$

TABLE 45.—THE RELATIVE STRENGTH OF OXIDIZING AND REDUCING AGENTS

	Reducing Agents		Oxidizing Agents
Strong	K		K^+
	Na		Na^+
	Mg	Weak	Mg^{++}
	Al		Al^{+++}
	Zn		Zn^{++}
	Fe		Fe^{++}
	Sn		Sn^{++}
	Pb		Pb^{++}
	H_2		H^+
	H_2S		S
	Cu		Cu^{++}
	I^-		I_2
	Fe^{++}		Fe^{+++}
	Ag		Ag^+
	Br^-		Br_2
	SO_2		H_2SO_4 (conc.)
Weak	Cl^-		Cl_2
	NO		HNO_3
	Cr^{+++}		$Cr_2O_7^{-}$
	Mn^{++}	Strong	MnO_4^-

EXERCISES

1. Define oxidation, reduction, oxidizing agent, reducing agent.

2. Complete and balance by the valence-change method the equations for the oxidation-reduction reactions between dilute nitric acid and each of the following substances: Cu, S, FeO, $Fe(NO_3)_2$, H_2S.

3. Balance each of the above equations by the ion-electron method.

4. Why is zinc a better reducing agent than silver?

5. Why is the silver ion a better oxidizing agent than the zinc ion?

6. What is meant by the normal electrode potential of a metal, and how is it determined?

7. Between which of the following pairs will oxidation-reduction reactions take place: $Na^+ + Br^-$, $H_2S + Fe^{+++}$, $H_2S + Fe^{++}$, $MnO_4^- +$ Fe, $SO_2 + HNO_3$?

8. Complete and balance equations for the reactions that do occur.

9. How could a cell be constructed which could utilize the energy liberated in the reaction

$$Fe + 2Ag^+ \rightarrow 2Ag + Fe^{++}$$

10. If normal solutions of silver and ferrous ions were used, what would be the electromotive force of the cell?

READING REFERENCES

HILDEBRAND: "Principles of Chemistry," Chap. XV, Oxidation and reduction, The Macmillan Company.
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CHAPTER FORTY-ONE

THE ELEMENTS OF GROUP V

The elements of Group V in the order of their increasing atomic weights are nitrogen, phosphorus, arsenic, antimony, and bismuth. Since this group is near the middle of the periodic table, we should expect to find nonmetals at the top but that somewhere, as we go down the group, metallic properties would appear. For this reason, the study of this group provides a good illustration of the variation of properties that we find in a group as the atoms become more complex with increasing atomic weights. The atomic structures of the elements of the group are summarized as follows:

Element	Atomic number	Planetary electrons
N	7	2, 5
P	15	2, 8, 5
As	33	2, 8, 18, 5
Sb	51	2, 8, 18, 18, 5
Bi	83	2, 8, 18, 32, 18, 5

The lowest valence number these elements show in the compounds with hydrogen is -3. In the molecules of these hydrides, *e.g.*, NH_3, three electron pairs are shared with three hydrogen atoms. Each of the elements has the two positive valence numbers of $+3$ and $+5$.

1. Occurrence of Phosphorus.—Since this element is more active than nitrogen, phosphorus does not occur free in nature. Its most abundant occurrence is as calcium phosphate of which the skeletons of all vertebrates are composed. Large deposits of an ore containing the mineral apatite, $3Ca_3(PO_4)_2.CaF_2$, were discovered in 1862 in South Carolina and later in Tennessee, Florida, Virginia, Idaho, Montana, Utah, and Wyoming. We have a known reserve of over 6.5 billion tons in this country, and the average annual output is about 3.1 million tons. These deposits are probably of fossil origin. Phosphorus is also an important constituent of certain organic compounds found in cell nuclei and in muscle and nerve tissue. It is, therefore, an important constituent of the foods of both plants and animals. The phosphorus content of cheese, egg yolk, milk powder, soybeans, and wheat bran is especially high.

TABLE 46.—PHOSPHORUS, SUPPLY AND DEMAND

Source	Known reserves, long tons	Mined, 1937, long tons
Florida	546,000,000	2,996,820
Tennessee	103,000,000	825,099
Western states	5,745,000,000	132,320
Other states	121,000,000	
Total	6,515,000,000	3,954,239

2. Preparation.—Phosphorus was first isolated by the alchemist Hennig Brandt in the seventeenth century by the reduction of its compounds in human urine. Today it is manufactured in relatively large amounts by heating a mixture of phosphate rock, sand, and coke in electric or coke-heated furnaces. The following reactions take place:

$$Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5$$
$$P_2O_5 + 5C \rightarrow 2P + 5CO$$

Phosphorus is condensed from the gaseous products. With the development of the water-power resources of the Tennessee Valley, electric power at low cost, generated near the phosphate deposits, has materially lowered the cost of production. The modern practice is to ship the element itself to the plants that are to convert it into useful compounds. This saves freight costs on inert materials.

3. Properties.—This solid element exists in two forms, *viz.*, red and yellow (or white). *Yellow phosphorus* is formed when the liquid solidifies. It is a soft, waxlike, cream-colored solid, practically insoluble in water but readily soluble in carbon disulfide. If this solution is evaporated out of contact with the air, beautiful transparent crystals form which melt at 44.1°C. The liquid boils at 287°C. This form of phosphorus is very reactive and poisonous. The energy liberated when yellow phosphorus is slowly oxidized by the air appears partly as light, a phenomenon known as phosphorescence. Because of the danger of spontaneous combustion, yellow phosphorus must be kept under water. It should always be handled with forceps, never with the fingers.

When yellow phosphorus is heated at about 250°C. out of contact with air, it is slowly converted into an amorphous powder *red phosphorus*. This change is accompanied by a liberation of energy so that the red form is less active than the yellow. It does not burn until heated to about 240°C. and is not poisonous.

The molecules in phosphorus vapor are tetratomic and should appear as P_4 in equations for reactions of this element. However, this is a refinement in which we shall not indulge.

4. Reactions of Phosphorus.—The element burns to form a dense smoke of the white solid pentoxide.

$$4P + 5O_2 \rightarrow 2P_2O_5$$

The trioxide, P_2O_3, may be prepared by the slow oxidation of the element. The spontaneous combustion of yellow phosphorus may be readily demonstrated by pouring a few cubic centimeters of a solution of the element in carbon disulfide onto a piece of filter paper. In the short time required for the solvent to evaporate, the phosphorus catches fire.

Because of the ease with which the element is oxidized, phosphorus is a strong reducing agent. Mixtures of phosphorus and such oxidizing agents as potassium chlorate and potassium nitrate are dangerously explosive and should under no circumstances be ground together in a mortar with a pestle.

$$5KClO_3 + 6P \rightarrow 5KCl + 3P_2O_5$$
$$5KNO_3 + 2P \rightarrow 5KNO_2 + P_2O_5$$

Nitric acid oxidizes phosphorus to phosphoric acid.

Phosphorus combines directly with the halogens to form trihalides and pentahalides, *e.g.*,

$$2P + 3Cl_2 \rightarrow 2PCl_3$$
$$2P + 5Cl_2 \rightarrow 2PCl_5$$

The trichloride is a colorless liquid and the pentachloride, a solid. These compounds are not salts and are completely hydrolyzed to phosphorous and phosphoric acids, respectively. In their molecules, the valence number of phosphorus is positive.

Phosphorus combines with sulfur to form several different sulfides, *e.g.*, P_2S_5, P_4S_7, and P_4S_3.

5. Matches.—The earliest successful friction matches were tipped with what was essentially a mixture of yellow phosphorus, potassium chlorate, and glue. The use of yellow phosphorus for the purpose was prohibited in this country in 1913; for workers in match factories developed the horrible disease phosphorus necrosis caused by continued exposure to phosphorus vapors. The tip of the modern friction match contains the nontoxic phosphorus sesquisulfide, P_4S_3, as the reducing agent, together with potassium chlorate. Safety matches are tipped with a mixture that contains antimony trisulfide, glass, and potassium chlorate. The striking surface is a mixture of red phosphorus, manganese dioxide, and ground glass.

6. Phosphine, PH_3, is the hydride of phosphorus analogous to ammonia. It may be prepared by the hydrolysis of a metal phosphide

$$Ca_3P_2 + 6HOH \rightarrow 3Ca(OH)_2 + 2PH_3$$

or by the reaction between yellow phosphorus and a solution of potassium hydroxide

$$4P + 3KOH + 3H_2O \rightarrow PH_3 + 3KH_2PO_2$$

The substance formed at the same time is the potassium salt of the monoprotic hypophosphorous acid, H_3PO_2. Prepared in this manner, phosphine ignites spontaneously.

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

Phosphine is a poisonous, malodorous gas. It is less basic than ammonia but will react with hydriodic acid in an analogous manner to form phosphonium iodide.

$$PH_3 + HI \rightarrow PH_4I$$

7. Oxides and Oxygen Acids.—Phosphorus trioxide reacts with cold water to form phosphorous acid.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$

This is a diprotic acid, since only two of its three hydrogen atoms are replaced in neutralization reactions with metal hydroxides.

$$H_3PO_3 + 2NaOH \rightarrow Na_2HPO_3 + 2HOH$$

Several phosphoric acids are known, all of which may be prepared by the reaction of the pentoxide with water.

$$\begin{aligned} P_2O_5 + H_2O &\rightarrow \underset{\text{metaphosphoric acid}}{2HPO_3} \\ P_2O_5 + 2H_2O &\rightarrow \underset{\text{pyrophosphoric acid}}{H_4P_2O_7} \\ P_2O_5 + 3H_2O &\rightarrow \underset{\text{orthophosphoric acid}}{2H_3PO_4} \end{aligned}$$

These acids differ from one another only in the relative amounts of water and of the pentoxide. Recently, a very concentrated phosphoric acid containing 84 per cent phosphorus pentoxide has become available. It is called tetraphosphoric acid and may contain $H_2P_4O_{11}(H_2O.2P_2O_5)$. In all the phosphoric acids, phosphorus has a valence number of +5.

Phosphorus pentoxide is one of the best dehydrating and drying agents because of its strong tendency to react with water. Since this oxide fumes in moist air, phosphorus bombs have been used for smoke screens in warfare.

Orthophosphoric acid has been prepared commercially by treating phosphate rock with dilute sulfuric acid

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$$

followed by separating the insoluble calcium sulfate and concentrating the dilute acid. This process yields an impure product. The best modern practice is to prepare the acid where it is needed from elementary phosphorus, air, and water.

Both phosphorous and phosphoric acids may also be prepared by the hydrolysis of the corresponding chlorides.

$$\begin{aligned} PCl_3 + 3H_2O &\rightarrow H_3PO_3 + 3HCl \\ PCl_5 + 4H_2O &\rightarrow H_3PO_4 + 5HCl \end{aligned}$$

Orthophosphoric acid is a triprotic acid.

$$\begin{aligned} H_3PO_4 + H_2O &\mathrel{\substack{\longrightarrow \\ \leftarrow}} H_3O^+ + H_2PO_4^- & K_1 &= 10^{-2} \\ H_2PO_4^- + H_2O &\mathrel{\substack{\rightarrow \\ \longleftarrow}} H_3O^+ + HPO_4^{=} & K_2 &= 10^{-7} \\ HPO_4^{=} + H_2O &\mathrel{\substack{\rightarrow \\ \longleftarrow}} H_3O^+ + PO_4^{\equiv} & K_3 &= 10^{-12} \end{aligned}$$

8. The Phosphates.—By treating phosphoric acid or phosphorus pentoxide with the appropriate metal hydroxide, phosphates may be prepared. Since orthophosphoric acid is a triprotic acid, two types of acid salts in addition to the normal orthophosphates may be formed:

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + HOH$$
$$NaH_2PO_4 + NaOH \rightleftarrows Na_2HPO_4 + HOH$$
$$Na_2HPO_4 + NaOH \rightleftarrows Na_3PO_4 + HOH$$

The dihydrogen phosphates, or primary phosphates, of which NaH_2PO_4 is typical, are completely ionized as sodium and dihydrogen phosphate ($H_2PO_4^-$) ions. The latter ion is amphiprotic. It can act as a base by combining with a proton to form phosphoric acid.

$$H_2PO_4^- + H^+ \rightleftarrows H_3PO_4$$

Since the primary ionization constant of phosphoric acid is 10^{-2}, the dihydrogen phosphate ion is an exceedingly weak base. Hence dihydrogen phosphates are not hydrolyzed. On the other hand, this ion is itself a weak acid.

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^= \qquad K_2 = 10^{-7}$$

Hence solutions of dihydrogen phosphates react weakly acidic. Their use in baking powders (42-21) depends upon this property.

When dry primary phosphates are heated, water is driven off and the corresponding metaphosphate is formed.

$$NaH_2PO_4 \rightarrow NaPO_3 + H_2O$$

The monohydrogen, or secondary, phosphates, of which Na_2HPO_4, is typical, exist as sodium and monohydrogen phosphate ($HPO_4^=$) ions. This ion is also amphiprotic. It is a relatively strong base since its conjugate acid, the dihydrogen phosphate ion, is a weak acid. Hence secondary phosphates are hydrolyzed

$$HPO_4^= + HOH \rightleftarrows H_2PO_4^- + OH^-$$

and their aqueous solutions are feebly basic. As an acid the ion is very weak.

$$HPO_4^{=} \rightleftarrows H^+ + PO_4^{\equiv} \qquad K_3 = 10^{-12}$$

Hence the phosphate ion is a strong base, and normal phosphates are extensively hydrolyzed.

$$PO_4^{\equiv} + HOH \rightleftarrows HPO_4^{=} + OH^-$$

Therefore, solutions of normal phosphates, like Na_3PO_4, are strongly basic.

When monohydrogen phosphates are heated, the corresponding pyrophosphate is formed.

$$2NaHPO_4 \rightarrow Na_4P_2O_7 + H_2O$$

The test for a phosphate involves first making the solution weakly basic with ammonia. This ensures a high enough concentration of the phosphate ion.

$$HPO_4^{=} + NH_3 \rightleftarrows NH_4^+ + PO_4^{\equiv}$$

Then an ammonium and a magnesium salt are added, and a white precipitate of magnesium ammonium phosphate forms.

$$Mg^{++} + NH_4^+ + PO_4^{\equiv} \rightarrow MgNH_4PO_4\downarrow$$

When this salt is heated, it first decomposes as a typical ammonium salt

$$MgNH_4PO_4 \rightarrow MgHPO_4 + NH_3\uparrow$$

then as a monohydrogen phosphate

$$2MgHPO_4 \rightarrow Mg_2P_2O_7 + H_2O$$

9. Commercial Phosphates.—We have mentioned the importance of phosphates in plant food. Since plants can assimilate mineral foods only if they are in solution, the insoluble calcium phosphate, which occurs in nature, and ground bone are very slow-acting fertilizers. They must first be converted by acids in the soil to the more soluble and hence quicker acting acid phosphates. A quick-acting fertilizer, called *superphosphate*, is manufactured in large tonnages by the action of dilute sulfuric acid on phosphate rock.

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

This primary phosphate is soluble.

Metaphosphates are formed when dihydrogen orthophosphates are heated

$$Ca(H_2PO_4)_2 \rightleftarrows Ca(PO_3)_2 + 2H_2O$$

and revert to the latter when dissolved in water or in a damp soil. Since metaphosphates contain relatively more phosphorus, they represent more concentrated fertilizers and may be transported more economically. They are being manufactured by the action of the pentoxide on phosphate rock.

$$Ca_3(PO_4)_2 + 2P_2O_5 \rightarrow 3Ca(PO_3)_2$$

This reaction is analogous to the formation of metaphosphoric acid from the ortho acid.

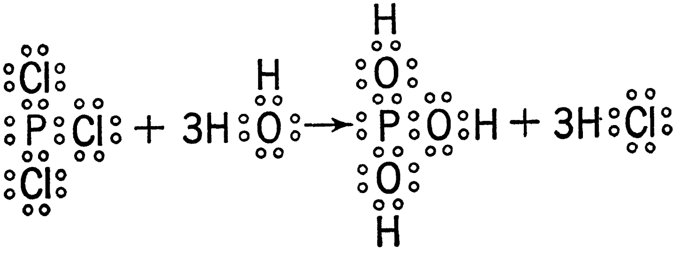
$$H_3PO_4 + P_2O_5 \rightarrow 3HPO_3$$

Sodium dihydrogen phosphate is used in baking powders. The basic reaction of sodium monohydrogen phosphate makes it useful in water softening (48-25).

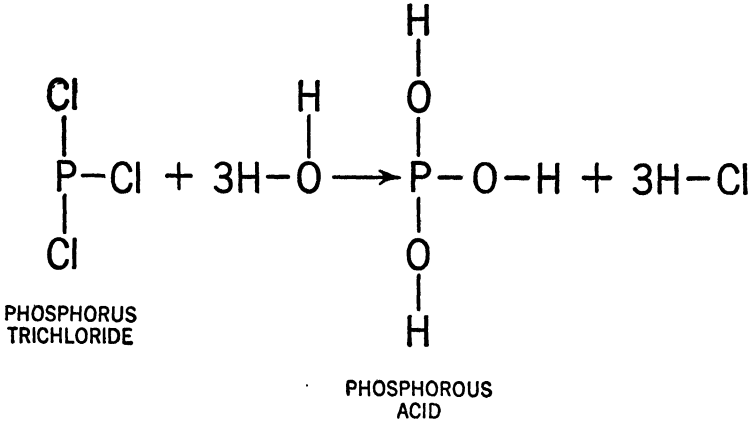
TABLE 47.—PRODUCTION OF PHOSPHATES

Commercial products	1937, long tons	Pure compounds	1935, long tons
Superphosphates	2,391,245	Phosphoric acid	21,200
Other fertilizers	129,655	$Ca(H_2PO_4)_2$	32,600
Stock and poultry feeds	3,324	$CaHPO_4$ and $Ca_3(PO_4)_2$	4,300
Phosphates, phosphoric acid, and ferrophosphorus	429,805	Na_3PO_4	79,200
		Na_2HPO_4	32,200
		$NaPO_3$	4,700
Total	2,954,029	NaH_2PO_4 and $Na_4P_2O_7$	4,100

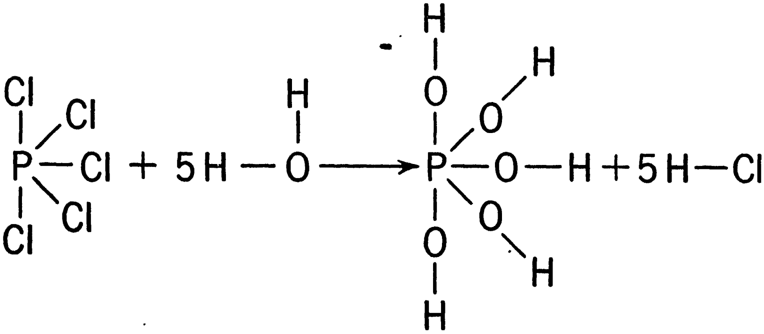
10. The Hydroxides of Nitrogen and Phosphorus.—Let us return to the hydrolysis of phosphorus trichloride (41-7) and study it more carefully. If the electrons, binding the atoms together, are written into the equation, we have



This may be simplified by using a straight line for each covalent bond:

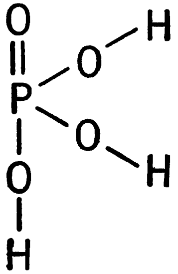


Upon examining this so-called structural formula for phosphorous acid, we make the astonishing discovery that it is a hydroxide of phosphorus. If we examine the hydrolysis of phosphorus pentachloride in the same way, we obtain



The hydrolysis of phosphorus pentachloride.

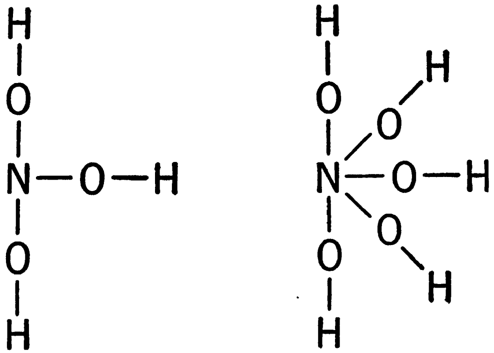
The presence of five hydroxyl groups attached to one phosphorus atom leads to a crowding of atoms and hence to an unstable molecule. Since the water molecule is so stable, we may imagine a hydrogen atom uniting with a neighboring hydroxyl group and leaving its oxygen atom linked by a double bond to the phosphorus atom.



Phosphoric acid.

We now recognize the structural formula for phosphoric acid. This acid is the hydroxide of pentavalent phosphorus.

Consider the hydroxides of trivalent and of pentavalent nitrogen:

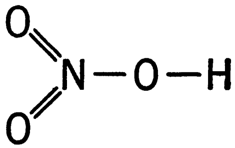


The unstable hydroxides of nitrogen.

Since the nitrogen atom is smaller than that of phosphorus, the crowding of the hydroxyl groups is greater. The trihydroxide loses one water molecule and the pentahydroxide, two; and we have the structural formulas for nitrous and nitric acids, respectively.

$$O=N-O-H$$

NITROUS ACID



NITRIC ACID

11. Definitions of a Nonmetal and a Metal.—If we were to write the structural formulas for other oxygen-containing acids, we should find each to be a hydroxide of a nonmetal. This information has been used to define what is meant by the term nonmetal. *A nonmetal is an element whose hydroxide is an acid, i.e.*, reacts with water to form hydronium ions. Similarly, *a metal is an element whose hydroxide furnishes hydroxyl ions* in water solution.

12. Occurrence and Preparation of Arsenic.—Arsenic occurs in nature in the form of the sulfides orpiment, As_2S_3, realgar, As_2S_2, and arsenical pyrites, FeAsS, and as the arsenides of iron, nickel, cobalt, and silver. In any case it usually occurs as an impurity in metal sulfide ores. When these are roasted it escapes as the trioxide, As_2O_3, which is recovered from flue gases. From this oxide, the other compounds of arsenic are prepared. The element is prepared by heating arsenical pyrites

$$FeAsS \rightarrow FeS + As$$

and by reducing the trioxide by carbon

$$As_2O_3 + 3C \rightarrow 2As + 3CO$$

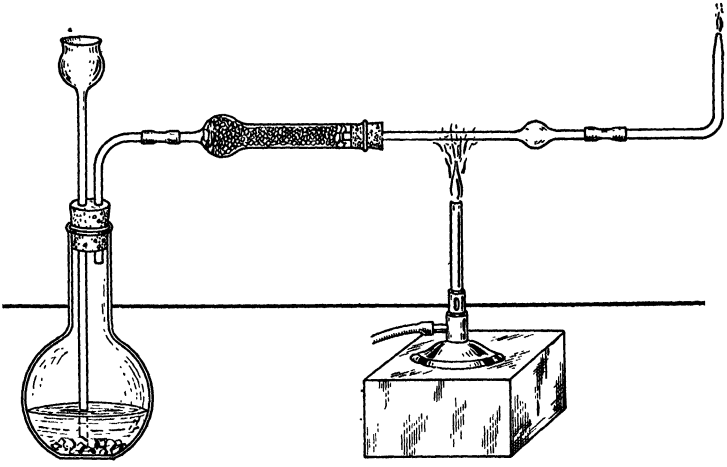


FIG. 130.—The Marsh test for arsenic.

13. Properties and Uses.—Arsenic is a gray crystalline solid. It sublimes to a vapor in which the molecules are As_4. Its combustion in air or oxygen yields the trioxide. It combines directly with the halogens or with sulfur to form halides or sulfides in which its valences are +3 or +5.

Since arsenic compounds are poisonous and have been used to accelerate the demise of unfortunate individuals, a delicate test for arsenic such as the Marsh test is useful. The material to be tested is placed in a flask (Fig. 130) in which hydrogen is generated by the action of hydrochloric acid on zinc. The arsenic compounds are reduced to gaseous arsine, AsH_3, which is dried by passing through calcium chloride and decomposed by the heat of the Bunsen flame into arsenic and hydrogen. Arsenic is deposited as a grey mirror on the cooler portion of the tube beyond the flame.

Arsine is analogous to ammonia and phosphine. Its basic properties are so slight that it will not react with acids. It is exceedingly poisonous.

The free element is used in certain alloys to increase hardness *e.g.*, in lead shot.

14. The Oxides and Hydroxides of Arsenic.—Arsenic trioxide is the raw material from which other arsenic compounds are made. It is very sparingly soluble in water, with which it reacts slightly to form arsenious acid.

$$A_2O_3 + 3H_2O \rightarrow 2H_3AsO_3$$

The pentoxide reacts with water to form arsenic acids analogous to the three phosphoric acids.

$$H_2O + As_2O_5 \rightarrow \underset{\text{metarsenic acid}}{2HAsO_3}$$

$$2H_2O + As_2O_5 \rightarrow \underset{\text{pyroarsenic acid}}{H_4As_2O_7}$$

$$3H_2O + As_2O_3 \rightarrow \underset{\text{orthoarsenic acid}}{2H_3AsO_4}$$

Orthoarsenic acid may be prepared by heating arsenic trioxide with dilute nitric acid.

$$3As_2O_3 + 4HNO_3 + 7H_2O \rightarrow 6H_3AsO_4 + 4NO$$

If we compare the strengths of the acids of the elements in the same group and in the same valence, the acids grow weaker as we go down in the group. Comparing the acids, in which the valence of the elements of this group are pentavalent, nitric is stronger than phosphoric which, in turn, is stronger than arsenic. Similarly, in the +3 valence, the acids in the order of decreasing strength are nitrous, phosphorous, and arsenious.

Basic properties have just begun to make their appearance in trivalent arsenic. Thus arsenic trioxide will not only react as an acidic oxide with sodium hydroxide to form sodium arsenite

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$$

but it will also react to a slight extent as a basic oxide with hydrochloric acid

$$As_2O_3 + 6HCl \overset{\rightarrow}{\longleftarrow} 2AsCl_3 + 3H_2O$$

15. Sulfides of Arsenic.—When hydrogen sulfide is passed into a solution of arsenic trichloride, a yellow precipitate of arsenic trisulfide is formed.

$$2AsCl_3 + 3H_2S \rightarrow As_2S_3\downarrow + 6HCl$$

The yellow pentasulfide precipitates when hydrogen sulfide is passed into a strongly acid solution of arsenic acid.

$$2H_3AsO_4 + 5H_2S \rightarrow As_2S_5\downarrow + 8H_2O$$

These sulfides are soluble in a reagent known as ammonium polysulfide, made by boiling a solution of ammonium sulfide with sulfur. This reagent first oxidizes the trisulfide to the pentasulfide

$$As_2S_3 + 2S \rightarrow As_2S_5$$

and then converts the latter into ammonium thioarsenate.

$$3(NH_4)_2S + As_2S_5 \rightarrow 2(NH_4)_3AsS_4$$

This reaction is analogous in form to the reaction of sodium oxide and arsenic pentoxide

$$3Na_2O + As_2O_5 \rightarrow 2Na_3AsO_4$$

except that sulfur is functioning in the first reaction as oxygen is in the second. The prefix *thio-* indicates a compound in which sulfur has replaced oxygen. Thus H_3AsS_4 is thioarsenic acid. The formation of thioarsenates is important in qualitative analysis.

16. Uses of Arsenic Compounds.—Arsenites and arsenates of sodium, calcium, lead, and copper are important insecticides. Nearly 50,000,000 lb. each of lead and calcium arsenates are used annually. When we realize how important this war against insects is in safeguarding our food supply, we appreciate the importance of arsenic. Organic compounds containing arsenic have found important use in medicine, *e.g.*, salvarsan in the treatment of syphilis.

17. Antimony.—This element has had a very interesting history. Its sulfide was the ancient eyebrow pencil of Oriental women. The free metal was prepared by roasting the sulfide ore with charcoal, and from it vases were made in ancient times. Its most important ore is stibnite, Sb_2S_3 from which the element is obtained either by roasting followed by carbon reduction, or by reducing the ore directly with iron. The free element is hard and brittle with a silver-white metallic luster. It melts at 630.5°C. to a liquid which, like water, expands on freezing. Several allotropic forms are known.

In its reactions, antimony resembles arsenic. It forms the insoluble orange sulfide, Sb_2S_3. The pentasulfide is unstable. The hydride stibine, SbH_3, does not react with acids. The metal is used in several important alloys (47-5), *e.g.*, it contributes the property of hardness to bearing metal, and its expansion on freezing is made use of in type metal.

18. The Hydroxides of Antimony.—We have seen how the acid character of the hydroxides of the elements of Group V has grown weaker as we go down the group. We should have been expecting the appearance of basic properties. These we find to a slight extent in trivalent arsenic. They are more pronounced in the trihydroxide of antimony. This insoluble substance is both a metal hydroxide and an acid and is called an *amphoteric hydroxide* for this reason. It may be precipitated by treating a solution of a salt of trivalent antimony with ammonium hydroxide.

$$SbCl_3 + 3NH_4OH \rightarrow Sb(OH)_3\downarrow + 3NH_4Cl$$

or

$$Sb^{+++} + 3OH^- \rightarrow Sb(OH)_3\downarrow$$

As is the case in the majority of the metal-hydroxide precipitates, antimony hydroxide proves on analysis to be an indefinitely hydrated oxide, $Sb_2O_3.xH_2O$. When the precipitate is treated with an acid, it acts as a base, going into solution as the antimonous ion.

$$Sb(OH)_3 + 3HCl \rightarrow SbCl_3 + 3HOH$$

or

$$Sb(OH)_3 + 3H^+ \rightarrow Sb^{+++} + 3HOH$$

When treated with a metal hydroxide, it acts as antimonous acid. This is a monoprotic acid, and the formula that we use for it in equations is $HSbO_2$. This formula contains one H_2O less than $Sb(OH)_3$, but we are justified in using it since the hydroxide precipitate is $Sb_2O_3.xH_2O$. The equation for its reaction with a metal hydroxide is written

$$HSbO_2 + NaOH \rightarrow NaSbO_2 + HOH$$

or

$$HSbO_2 + OH^- \rightarrow SbO_2^- + HOH$$

The salt formed is sodium antimonite. We shall discuss amphoteric hydroxides in greater detail later (50-2).

Antimonic acid, H_3SbO_4, also shows some basic properties.

19. Hydrolysis of Antimonous Salts.—Antimonous chloride is hydrolyzed but not to the same extent as is phosphorus trichloride (40-10). A basic salt is formed

$$SbCl_3 + 2HOH \rightarrow Sb(OH)_2Cl + 2HCl$$

or

$$Sb^{+++} + 2HOH \rightarrow Sb(OH)_2^+$$

which precipitates minus one molecule of water

$$Sb(OH)_2Cl \rightarrow SbOCl\downarrow + H_2O$$

or

$$Sb(OH)_2^+ \rightarrow SbO^+ + H_2O$$

$$SbO^+ + Cl^- \rightarrow SbOCl\downarrow$$

This SbO^+ is the antimonyl ion and the precipitate, antimonyl chloride. This precipitate is soluble in acids.

$$SbOCl + 2HCl \rightarrow SbCl_3 + H_2O$$

or

$$SbO^+ + 2H^+ \rightarrow Sb^{+++} + H_2O$$

Solutions of salts of trivalent antimony are, therefore, kept acid to prevent hydrolysis.

20. Bismuth is more metallic than antimony. In its lower valence of +3 it is entirely metallic, but in the higher valence it has acidic properties as shown in the salt potassium bismuthate, $KBiO_3$. The trivalent compounds are by far the more important. Its black sulfide, Bi_2S_3, has a very small solubility product. Its salts are hydrolyzed to insoluble basic salts of which bismuth subnitrate, $Bi(OH)_2NO_3$, is typical.

The metal occurs as the sulfide, from which it is prepared by roasting followed by reduction with carbon. It is a tin-white metal melting at the relatively low temperature of 260°C. It is used in low-melting alloys such as Wood's metal, an alloy of bismuth, lead, tin, and cadmium, which melts at 60.5°C. Such alloys are used in automatic-sprinkler systems and in safety plugs in boilers. Its basic salts are used in medicine as antiacids.

EXERCISES

1. What is the economic importance of compounds of phosphorus?

2. How is phosphorus prepared commercially?

3. Write equations for two methods by which phosphoric acid is prepared.

4. Write equations for the ionization of the triprotic phosphoric acid.

5. State whether solutions of each of the following phosphates are acidic or basic: K_3PO_4, K_2HPO_4, and KH_2PO_4. Explain.

6. What ionic reaction takes place when solutions of NaH_2PO_4 and $NaHCO_3$ are mixed?

7. Write balanced equations for reactions by which the following transformations may be accomplished:

$$P \rightarrow H_3PO_4$$
$$Na_2HPO_4 \rightarrow MgNH_4PO_4$$
$$Ca_3(PO_4)_2 \rightarrow Ca(H_2PO_4)_2$$
$$Na_3PO_4 \rightarrow P$$
$$H_3PO_3 \rightarrow H_3PO_4$$

8. Upon what basis is it possible to decide whether an element is a metal or a nonmetal?

9. Show by means of equations that the hydroxide of trivalent antimony is amphoteric.

10. What happens when a solution of bismuth trichloride is poured into a beaker of water? Explain.

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CHAPTER FORTY-TWO

CARBON

Less than 0.2 per cent of the earth's crust is carbon. Yet we can safely say that had carbon been omitted from the roster of elements we should not exist. All organic compounds are compounds of carbon.

1. Occurrence.—Carbon occurs as the pure element in nature in two allotropic forms, diamond and graphite. The Belgian Congo is the world's richest source, although deposits in Brazil and South Africa are important. Owing to the large demands of the war for diamonds in grinding tools and for dies through which wire is drawn, the deposits in Arkansas are being developed. Deposits of graphite, a second allotropic form of carbon, occur in Ceylon, Russia, Germany, Mexico, Madagascar, and Canada. Although anthracite coal is 94 per cent carbon, its carbon atoms are combined with one another and with hydrogen atoms. Hence, strictly speaking, coal contains little free carbon.

Inorganic compounds of carbon include carbon dioxide, in the atmosphere, and carbonates. Limestone, chalk, and marble are calcium carbonate. Magnesite, $MgCO_3$, is abundant, and whole mountain ranges are composed of dolomite, $MgCO_3CaCO_3$. We have mentioned that all organic substances are carbon compounds.

2. Properties.—No one has to describe the beauty of a diamond, but its extreme hardness, which is really its most valuable property, may be overlooked. It is more than twice as hard as its nearest competitor. Hardness is the ability of a substance to resist penetration of its surface by another substance. The relative hardness of two substances can be determined easily by rubbing an edge of one on the surface of the other, and vice versa. The harder substance will scratch the softer. An arbitrary scale of hardness has been established by choosing 10 minerals of varying degrees of hardness to which other substances can be referred. These substances are numbered from 1 to 10 as shown in Fig. 132. However, this scale is misleading. Corundum, number 9 on the scale, is a little over 30 per cent as hard as the diamond. The melting point of the diamond is unknown since it remains a solid at 3500°C.

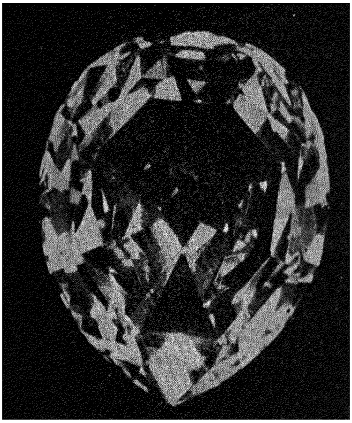

FIG. 131.—Star of Africa diamond. (*Courtesy of American Museum of Natural History, New York.*)

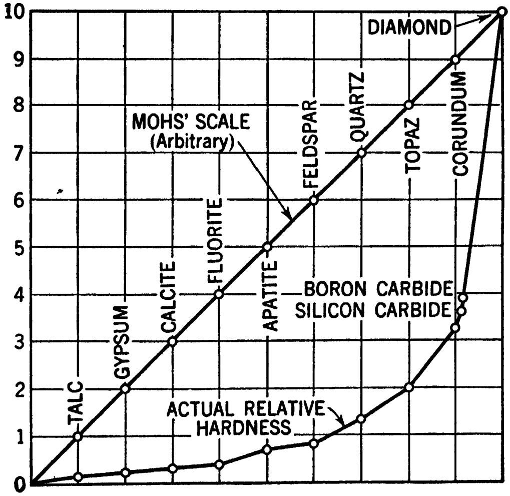

FIG. 132.—Arbitrary and actual scales of hardness.

These two properties, hardness and high melting point, are explained by its crystal structure (Fig. 58, page 162). A diamond is a giant molecule of carbon atoms linked by covalent bonds in such a way that each atom is joined to four equidistant atoms. Such a compact structure held together by strong exchange forces makes for hardness and general stability.

Attempts to prepare diamonds artificially have never even approached commercial success. Moissan in 1893 succeeded in preparing tiny poorly colored diamonds by dissolving carbon in molten iron and then cooling the solution rapidly by pouring it into water. The sudden freezing of a crust of solid iron enclosed a center of molten solution from which carbon crystallized under high pressure.

Graphite, unlike diamond, is a soft substance, which makes an excellent lubricant. Its platelike crystals slide easily over one another. Its crystal structure (Fig. 57, page 161) contains carbon atoms linked together in six-membered rings in giant two-dimensional molecules. The atoms within a plane are closely bound by strong exchange forces, but between parallel planes the distance is greater, and weaker van der Waals forces operate. Hence slippage between planes is easy. Graphite also has an unattainably high melting point. Graphite is prepared commercially by heating coke or coal to a temperature of 3500°C. in an electric furnace, a process discovered by Acheson. The element volatilizes at this high temperature, and the vapors on condensing form graphite. Graphite is used as a lubricant, as crucibles that withstand high temperatures, in carbon electrodes, in paints, and mixed with clay in "lead" pencils. Both diamond and graphite are resistant to the action of chemicals. Although their kindling temperatures are very high, they will burn to form carbon dioxide.

3. Coal.—Thousands upon thousands of years ago in the late Paleozoic era of geologic time, when the climate was humid and rainfall abundant, there flourished in swamps and bogs a luxuriant vegetation, which was destined to become that priceless heritage—coal. These bogs gradually filled with an accumulation of fragmented and rotted plants, mixed with the mud that was washed into them. The result was *peat.* During the formation of peat, microorganisms and fungi brought about a disintegration of the plant tissues. This bacterial action continued until the bog water became too acid and arrested the process of decay. Peat is being formed today wherever similar conditions are found, *e.g.*, in the Dismal Swamp of Virginia and North Carolina and in the Okefenokee Swamp of Georgia. The rate at which it forms depends on the rate of growth and decay of the vegetation. It has been estimated that between 1 to 2 ft. of peat a century were laid in the swamps of the Carboniferous era. In certain parts of the world, peat is used as a fuel mainly by peasants to whom its cheapness recommends it. However, this is offset by its high content of moisture and mineral matter and by the volatile substances given off in its combustion.

The next step in the formation of coal involves a movement of the earth in such a way that the peat beds are buried and subjected to pressure. This results in an increased density; a loss of water, carbon dioxide, methane, and other volatile substances; and the formation of a dehydrated material which acts as a binder. Gradually brown coal, or *lignite*, is formed; followed by soft, or *bituminous*, coal; and finally, by hard, or *anthracite*, coal. Ashley has estimated that some 20 ft. of plant matter will form 3 ft. of peat and, in turn, 1 ft. of coal. If peat is deposited at the rate of 1 ft. a century, 300 years are required to accumulate the material for a seam of coal 1 ft. thick.

4. Composition and Heat Value of Coals.—The chemical reactions that result in the formation of coal from vegetal matter are complex and little understood. Wood is composed chiefly of fibers of a chemical compound cellulose, $(C_6H_{10}O_5)_x$, bound together with another substance, lignin. The conversion of cellulose into coal has been formulated as a first approximation by Parr in the following equations:

$$\underset{\text{cellulose}}{5C_6H_{10}O_5} \rightarrow \underset{\text{lignite}}{C_{20}H_{22}O_4} + \underset{\text{methane}}{3CH_4} + 8H_2O + 6CO_2 + CO$$

$$6C_6H_{10}O_5 \rightarrow \underset{\substack{\text{bituminous}\\ \text{coal}}}{C_{22}H_{20}O} + 5CH_4 + 10H_2O + 8CO_2 + CO$$

The formulas given for lignite and bituminous coal have little significance other than to give some idea of the relative amount of carbon, hydrogen, and oxygen in them. These coals are not simple chemical compounds. They contain, in addition to the elements mentioned, sulfur and nitrogen together with certain non-combustible minerals that appear in the ash when the coals are burned. Table 48 gives the composition of average samples of the various kinds of coal together with their fuel value.

Anthracite coal is used mainly for domestic heating, whereas bituminous coal is either coked or burned for power. The use of lignite as a fuel has not as yet been great. This coal, because of its high moisture content, crumbles to a powder when brought to the surface. It can, however, be briquetted and in this form makes an acceptable fuel. In Germany, some brown coal is coked.

Table 48.—Composition and Fuel Value of the Solid Fuels[1]

Fuel	Carbon	Hydrogen	Oxygen	B.t.u./lb.
Pure cellulose	44.5	6.2	49.3	7,500
Wood	50.0	6.0	44.0	7,400
Peat	60.0	5.9	34.1	9,900
Lignite	67.0	5.2	27.8	11,700
Bituminous coal	88.4	5.6	6.0	14,950
Anthracite coal	94.1	3.4	2.5	15,720

[1] Findlay "Chemistry in the Service of Man," Longmans, Green and Company.

5. Coal Resources.—The known coal resources of the world are given in Table 49. This table makes the world's supply seem so enormous that it gives us a false sense of security—plenty of coal for everybody and even enough for their children and grandchildren. When bituminous coal becomes scarce, there is still the enormous store of lignite to fall back upon. Coal is regarded as a useful commodity which is brought up by the miner from the bowels of the earth to be sold for so much a ton at the pit head and to be used or wasted as its purchaser sees fit. In this country, 300,000,000 tons of coal is used by industry annually and 75,000,000 for heating. The average individual uses 20 tons of coal a

Table 49.—The Coal Resources of the World
(In millions of net tons)

Source	Anthracite	Bituminous	Lignite
North and South America	25,000	2,500,000	3,100,000
Asia	450,000	838,000	1,120,000
Europe	60,000	760,000	40,000
Oceania	72,600	147,000	40,000
Africa	13,000	20,000	12,000
United States	22,000	2,150,000	2,054,000

year. During the past 10 years, as much coal has been burned as in all past history. How long will the supply last? One estimate is that the coal in England will be gone in 350 years and that of the United States in 3,000 years.

Of the coal necessary to produce power in a modern steam plant, a little less than one-third is lost or consumed in mining; 5 per cent is lost or burned in transportation; two-thirds is burned without useful result in the power plant; and only 3.8 per cent is actually converted into useful power. Yet power plants can produce power at so much a horsepower when coal costs so much a ton. No thought is given to the real cost of coal—to the accumulation of the radiant energy of the sun for almost incredible periods of time which it represents. This cost we cannot reckon. We are drawing on a capital that can never be replaced.

6. Charcoal is a very nearly pure form of carbon which is formed when wood is heated out of contact with the air. Under such circumstances, water is driven out of the cellulose molecules of the wood and carbon remains.

$$C_6H_{10}O_5 \rightarrow 6C + 5H_2O$$

The other constituents of the wood are partially decomposed by the heat into such volatile products as combustible gases, acetic acid, wood alcohol, and acetone. These are all valuable by-products. The use of charcoal as a fuel is relatively small. It is easy to ignite, burns without smoke, and leaves little ash. Its use as an adsorbent will be discussed later (44-6).

7. Coke.—Of all the forms of coal, anthracite is the only one whose energy is most efficiently utilized by direct combustion. All other forms should first be converted into gaseous fuel. The direct combustion of a bituminous coal not only is inefficient, but also results in the combustion of volatile substances that are of great usefulness in other fields.

When bituminous coal is heated in a closed retort, it begins to soften at about 350°C. and, as the temperature rises, gives off gases and tarry vapors. The residue, upon cooling, hardens to a gray porous mass called coke. The volatile products contain substances from which fertilizers, high explosives, dyes, medicinals, motorcar fuels, paving and roofing materials, and many other useful commodities are made, together with a fuel gas of great importance. Coke is itself not only a splendid fuel, but also an invaluable agent for reducing iron ores to metallic iron in the blast furnace. One-seventh of all the coal mined in the United States is converted into coke for use by the metallurgical industries, which consume annually some 50,000,000 tons of this fuel.

8. Coke Ovens.—Until quite recently, most of the coke in this country was produced in *beehive coke ovens.* These were filled with bituminous coal, part of which was allowed to burn to coke the rest. The volatile products were allowed to escape through an opening in the top of the oven where they blazed away merrily if wastefully.

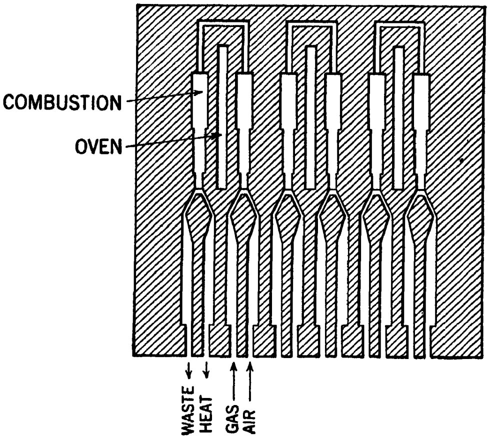

Fig. 133.—Section of a by-product coke oven.

The *by-product coke oven* (Fig. 133) consists of a long, narrow chamber about 30 ft. long, 1 to 2 ft. wide, and 6 to 13 ft. high. It is heated by burning fuel-gas–air mixtures in flues along its sides. The waste heat of the burning gases is used to preheat the entering air and gas. The temperature in the oven is about 1000°C. The by-products are led off as vapors through a flue in the top of the oven. When the coal has been coked, the two ends of the oven are opened and a ram pushes out the coke. The ovens are arranged side by side in batteries of 4 to 100.

The by-products consist of a *fuel gas,* part of which is used to heat the ovens and the rest piped for domestic heating; of *ammonia* gas (NH_3) which is treated with dilute sulfuric acid and converted into ammonium sulfate, a valuable fertilizer;

and of *coal tar*, the raw material from which most of our modern dyes, drugs, and explosives are made.

$$\text{1 ton of bituminous coal} \rightarrow \begin{cases} \text{11,360 cu. ft. of gas} \\ \text{12.4 gal. of coal tar} \\ \text{25 lb. of ammonium sulfate} \\ \text{1,500 lb. of coke} \end{cases}$$

9. Reactions of Carbon.—All forms of carbon burn first to the monoxide and then to the dioxide.

$$2C + O_2 \rightarrow 2CO$$
$$2CO + O_2 \rightarrow 2CO_2$$

Carbon combines directly with sulfur when these elements are heated in an electric furnace.

$$C + 2S \rightarrow CS_2$$

This evil-smelling and very inflammable liquid is an important solvent for rubber vulcanizers and a reagent used in large quantities in the manufacture of viscose rayon (45-6). Some 40,000 tons are used annually. Carbon does not combine directly with the halogens.

Carbon in the form of coke is the most widely used reducing agent for metal oxides in metallurgy (46-2), *e.g.*,

$$SnO_2 + 2C \rightarrow Sn + 2CO$$
$$CuO + C \rightarrow Cu + CO$$

The reaction of carbon with steam forms hydrogen and carbon monoxide.

$$H_2O + C \rightarrow H_2 + CO$$

Oddly enough, carbon is not readily oxidized by oxidizing agents in solution. Concentrated nitric acid converts it ultimately into the dioxide.

10. Fuel Gases.—The advantages of gaseous over solid fuels are obvious: greater ease of distribution, greater efficiency of combustion, better temperature control, and the elimination of the smoke and ash nuisance. The elimination of the smoke nuisance would alone result in a great saving. The Mellon Institute of Pittsburgh has estimated that the annual smoke loss and damage in Pittsburgh alone amounts to $10,000,000, almost as much as its entire fuel bill. In the United States, nearly a billion dollars worth of fuel gases are burned annually. Their use represents the most economical way in which energy can be gained from our fuel resources.

11. Coal Gas.—The evolution of coal gas accompanies the production of coke from soft coal. In city gas plants, the gas is considered to be the main product and coke a by-product. The gas retorts of these plants are of a slightly different type than the by-product coke oven. They consist of long, narrow chambers with a ⌓-shaped cross section. The process and the products, however, are the same as those of the by-product coke oven. The gas must be purified before it can be distributed for domestic heating and lighting. Its composition is given in Table 50.

TABLE 50.—THE COMPOSITION OF THE FUEL GASES
(In per cent)

Gas	CH_4 and other hydrocarbons	H_2	CO	CO_2	N_2	Combustible
Coal.............	42	49	6	0.5	1.5	97
Water............	....	52	41	4.0	3.4	93
Producer..........	3	12	27	2.5	55.0	42
Natural...........	98.8	..	..	...	1.0	99

12. Water gas is produced by blowing steam through hot coal or coke. First an air blast is sent through, in which the fuel burns vigorously and the temperature rises.

$$C + O_2 \rightarrow CO_2 + \text{heat}$$

Then the air is shut off and steam blown through.

$$C + H_2O + \text{heat} \rightarrow CO + H_2$$

As this reaction is endothermic, the temperature falls until it becomes so low that air must again be turned on and the steam turned off. Water gas burns with a blue, nonluminous flame which is useless for lighting purposes unless used with a Welsbach mantle. It is sometimes mixed with the gases that are formed when certain heavy oil petroleum distillates are heated to high temperatures. The products of the cracking of such oil distillates contain hydrocarbons which burn with a highly luminous flame. Water gas enriched with these products is called carbureted water gas. In this form or mixed with coal gas, it is used extensively as illuminating gas for domestic heating and lighting.

13. Producer gas is formed by blowing air or a mixture of air and steam through a deep bed of coals. If air alone is used, the following reactions take place:

$$C + O_2 \rightarrow CO_2 + \text{heat}$$
$$CO_2 + C + \text{heat} \rightarrow 2CO$$

The heat liberated by the first reaction is greater than that absorbed in the second, so that the heated gases must be used as they emerge from the producer or this excess heat will be wasted. For this reason the gas cannot be used economically for domestic purposes. If both air and steam are blown through the coal, a so-called semi-water gas results, since the steam reacts with a part of the coal forming water gas. Since nitrogen must accompany oxygen in the air blast, this inert gas is present to the extent of 50 per cent in "air gas" and 29 per cent in semi-water gas. Despite the fact that the combustion of producer gas yields the smallest number of B.t.u. per cubic foot of any commercial fuel gas, it is, nevertheless, the least expensive gas per unit of heat.

14. Natural Gas.—Certain sections of this country are fortunate in that Nature has prepared and stored for their use a fuel gas of the greatest value. Natural gas consists almost exclusively of hydrocarbons of which methane, CH_4, makes up 80 per cent and ethane, C_2H_6, 18 per cent. It is usually, but not always, found associated with petroleum. Over 50 per cent of our annual gas consumption for heating and lighting is of this gas. In 1923 over 1,000,000,000,000 cu. ft. were used. West Virginia, Oklahoma, Pennsylvania, Ohio, Louisiana, and California are the states that yield the largest quantities of natural gas, in the order named.

15. Carbides.—Calcium carbide is formed when lime and coke are heated in an electric furnace.

$$CaO + 3C \rightarrow CaC_2 + CO$$

This substance is used in the cyanamide process (38-4). Its reaction with water forms acetylene, used in oxyacetylene welding and in the preparation of large numbers of commercially important organic compounds (52-6).

$$CaC_2 + 2HOH \rightarrow Ca(OH)_2 + C_2H_2$$

Carbides of tungsten and tantalum are extremely hard and are used in cutting tools.

Silicon carbide is manufactured by heating sand and coke in an electric furnace.

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

Crystals of this substance are very hard and beautiful. As a matter of fact, when Acheson first prepared them in 1891 he was so dazzled by their purple-black iridescence that he sold them as gems at $560 a pound. Later, because of their hardness, they were sold by the ton at 10 cents a pound and made more money. Now this substance is one of our most important abrasives and is sold under various trade names, *e.g.*, Carborundum and Crystolon. In recent years boron carbide, B_4C, the hardest substance next to the diamond, has appeared on the market as an abrasive. Its manufacture involves heating boron oxide and coke in an electric furnace.

A few metals, *e.g.*, aluminum and iron, form carbides directly. The carbide of iron, Fe_3C, is an important constituent of steel.

16. Carbon Monoxide.—We have already emphasized the poisonous properties of this colorless, odorless gas (8-8). A product of incomplete combustion, its formation by the following reactions should be familiar:

$$2C + O_2 \rightarrow 2CO$$
$$CO_2 + C \rightarrow 2CO$$
$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$

The pure monoxide may be prepared by dehydrating formic acid with concentrated sulfuric acid.

$$HCOOH \rightarrow H_2O + CO$$

Carbon monoxide burns with a blue flame.

$$2CO + O_2 \rightarrow 2CO_2$$

It is a strong reducing agent, *e.g.*,

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

It combines with chlorine in the sunlight or in the presence of a catalyst to form phosgene, one of the war gases and a reagent used in the manufacture of dyes.

$$CO + Cl_2 \rightarrow COCl_2$$

17. Carbon Dioxide.—The combustion of fuels results in the liberation into the atmosphere of hundreds of thousands of tons of carbon dioxide annually. Every ton of carbon burned produces nearly four tons of this gas. It also gets into the air in the exhalation of animals and plants. The atmosphere over cities, quite naturally, contains more of this gas than in the country. The latter contains only about 3.5 parts per 10,000, whereas in crowded ill-ventilated rooms the carbon dioxide content may rise above 1 per cent. The gas is also found dissolved under pressure in natural carbonated springs.

Commercial carbon dioxide is obtained as a by-product of other industries, *e.g.*, from the flue gases of burning coke, or from the gases from limekilns. The carbon dioxide is absorbed from these gases by solution in aqueous potassium carbonate at room temperature. The impurities are not absorbed, and the carbonate is changed to bicarbonate. On boiling the bicarbonate, pure carbon dioxide is liberated by the reversal of the absorption reaction.

$$K_2CO_3 + H_2O + CO_2 \underset{100^\circ}{\overset{30^\circ}{\rightleftarrows}} 2KHCO_3$$

It is sold liquefied under pressure in steel cylinders.

The usual laboratory preparation is by the action of a dilute acid on marble.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

Carbon dioxide is a colorless, odorless gas that is moderately soluble in water. At higher pressures greater amounts dissolve (19-11), a fact made use of in the commercial preparation of carbonated beverages. Its critical temperature is 31.1°C., so that it may be liquefied at room temperature by pressure. Solid carbon dioxide may be prepared by tying a canvas bag around the outlet tube of a cylinder of the liquid which has been tilted at such an angle that its valve end is its lower end. On opening the valve, the liquid is blown out violently into the bag, vaporizing and expanding as it goes. These changes absorb so much heat that some of the carbon dioxide freezes to a white snowlike solid known commercially as *Dry-ice.* At atmospheric pressure, its temperature is about -73°C. Solid carbon dioxide is now manufactured in such quantities that tons of this material are used every day. It has certain advantages over ice as a refrigerant. It does not melt but sublimes to a gas which is very dense, blanketing the refrigerant and the material that is being cooled with a heat-insulating envelope.

Carbon dioxide in the concentrations in which it is usually found is in no sense poisonous. Indeed since it stimulates respiration, a 95 per cent oxygen 5 per cent carbon dioxide mixture is administered along with artificial respiration to induce normal breathing of victims of electrical shock or drowning. If, however, the carbon dioxide content in inhaled air is greater than 10 per cent, drowsiness, repressed respiration, and ultimately death will result.

Carbon dioxide is an excellent fire extinguisher as we have pointed out (8-14).

18. Carbonic Acid.—Carbon dioxide is the anhydride of the unstable carbonic acid.

$$H_2O + CO_2 \rightleftarrows H_2CO_3$$

This weak, diprotic acid ionizes in two steps.

$$H_2CO_3 + H_2O \rightleftarrows H_3O^+ + HCO_3^- \qquad K_1 = 10^{-7}$$

and

$$HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^= \qquad K_2 = 10^{-10}$$

The bicarbonate ion is amphiprotic—a strong base and a very weak acid. The carbonate ion is a very strong base.

If either carbonates or bicarbonates are treated with an acid, the first-formed carbonic acid decomposes into carbon dioxide and water.

$$\begin{aligned} Na_2CO_3 + HCl &\rightarrow NaHCO_3 + NaCl \\ NaHCO_3 + HCl &\rightarrow H_2CO_3 + NaCl \\ H_2CO_3 &\rightarrow H_2O + CO_2 \end{aligned}$$

or

$$\begin{aligned} CO_3^= + H_3O^+ &\rightarrow HCO_3^- + H_2O \\ HCO_3^- + H_3O^+ &\rightarrow H_2CO_3 + H_2O \\ H_2CO_3 &\rightarrow H_2O + CO_2 \end{aligned}$$

The effervescence accompanying such reactions is of course due to the escape of carbon dioxide.

19. Carbonates and Bicarbonates.—Since carbonic acid is so unstable, carbonates and bicarbonates are prepared by the action of carbon dioxide on metal hydroxides. Thus if carbon dioxide is bubbled through a solution of sodium hydroxide, sodium carbonate is formed first, followed by sodium bicarbonate.

$$\begin{aligned} 2NaOH + CO_2 &\rightarrow Na_2CO_3 + H_2O \\ Na_2CO_3 + H_2O + CO_2 &\rightarrow 2NaHCO_3 \end{aligned}$$

When carbon dioxide is bubbled through limewater, calcium carbonate precipitates only to redissolve when the more soluble bicarbonate is formed.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$
$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

These reactions are used as a test for carbon dioxide. The second reaction is of importance in nature. Limestone, $CaCO_3$, is gradually dissolved by natural waters in which carbon dioxide is dissolved. Thus limestone caves are formed. Calcium ions go into solution in the natural waters where they contribute the undesirable property of hardness (48-24).

20. Hydrolysis of Carbonates and Bicarbonates.—Solutions of sodium carbonate, or washing soda, are strongly basic. This is to be expected since the hydrolysis of the strong anion base, the carbonate ion, increases the hydroxyl-ion concentration.

$$CO_3^{=} + HOH \rightleftarrows HCO_3^- + OH^-$$

Sodium bicarbonate, or baking soda, is an acid salt. Yet its aqueous solutions are weakly basic since the bicarbonate ion is an extremely weak acid but a strong base. Its hydrolysis increases the hydroxyl-ion concentration.

$$HCO_3^- + HOH \rightleftarrows H_2CO_3 + OH^-$$

Since these ions, $CO_3^{=}$ and HCO_3^-, are bases, both carbonates and bicarbonates are used extensively to neutralize acids. Sodium bicarbonate is the standard home remedy for acid indigestion. Sodium carbonate is one of the most important basic heavy chemicals (48-4).

21. Baking Powders.—The function of a baking powder is to liberate small bubbles of carbon dioxide to raise the dough. Sodium bicarbonate, or baking soda, is the source of the carbon dioxide, which it releases when mixed with an acid in the presence of water. Any nonpoisonous acid may be used, but it should not be too strong, or else carbon dioxide will be liberated too rapidly. The lactic acid of sour milk has long been used with sometimes uncertain results, since it is difficult to mix the reagents in equivalent amounts. An excess of soda does not improve the quality of biscuits.

Commercial baking powders are dry mixtures of baking soda with either an acid salt or a salt whose hydrolysis results in an acid solution. The tartrate baking powders use cream of tartar, or acid potassium tartrate.

$$KHC_4H_4O_6 + NaHCO_3 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2$$

or

$$\underset{\text{acid}}{HC_4H_4O_6^-} + \underset{\text{base}}{HCO_3^-} \rightarrow C_4H_4O_6^{=} + H_2O + CO_2$$

The phosphate baking powders use the dihydrogen phosphate ion (41-8) as supplied by NaH_2PO_4 or $Ca(H_2PO_4)_2$.

$$H_2PO_4^- + HCO_3^- \rightarrow HPO_4^{=} + H_2O + CO_2$$

Alum baking powders make use of the hydrolysis of the aluminum ion to create the needed acidity. They contain anhydrous alum, $NaAl(SO_4)_2$.

$$Al^{+++} + HOH \rightarrow AlOH^{++} + H^+$$
$$H^+ + HCO_3^- \rightarrow H_2O + CO_2$$

22. Cyanides are salts that contain the cyanide ion CN^-. Of these sodium cyanide is the most important commercially. It is manufactured by heating calcium cyanamide (38-4) with coke and sodium carbonate.

$$CaCN_2 + C + Na_2CO_3 \rightarrow CaCO_3 + 2NaCN$$

All cyanides are deadly poisons. Their solutions are used to extract native silver and gold from the materials with which they are mixed.

Hydrocyanic acid is a liquid under ordinary conditions which boils at 25.7°C., just above room temperature. The vapor has the characteristic odor of almonds so familiar to detective-story addicts. It is prepared in large quantities commercially by the action of sulfuric acid on sodium cyanide.

$$2NaCN + H_2SO_4 \rightarrow Na_2SO_4 + 2HCN$$

This poisonous liquid is shipped in steel drums and carried on specially designed trucks. It is used to fumigate citrus trees to control scale insects.

Hydrocyanic acid is a very weak acid ($K = 10^{-9}$) and the cyanide ion, a strong base. Hence cyanides are hydrolyzed and their solutions are basic.

$$CN^- + HOH \rightleftarrows HCN + OH^-$$

EXERCISES

1. What products are obtained when soft coal is heated in a by-product coke oven, and for what are they used?

2. Show by means of equations methods by which three fuel gases may be prepared from coal.

3. How many tons of carbon dioxide are formed by the combustion of 1 ton of coal?

4. Assuming that oxygen makes up one-fifth of the air by volume, calculate the volume of air under standard conditions required to burn 1 kg. of carbon.

5. Write equations for the reactions that take place when carbon dioxide is bubbled into a solution of calcium hydroxide.

6. Write equations for the hydrolysis of sodium carbonate and of sodium bicarbonate.

7. Why do carbonates react so extensively with as weak an acid as acetic?

8. Explain in terms of solubility product why insoluble carbonates are dissolved by acids.

9. What reaction takes place when a solution of a cyanide is acidified?

10. Why are cyanide solutions basic?

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CHAPTER FORTY-THREE

SILICON AND BORON

These elements are in different groups in the periodic table, silicon in IV and boron in III. Yet their properties and the types of compounds they form are so similar that it is desirable to discuss them in the same chapter.

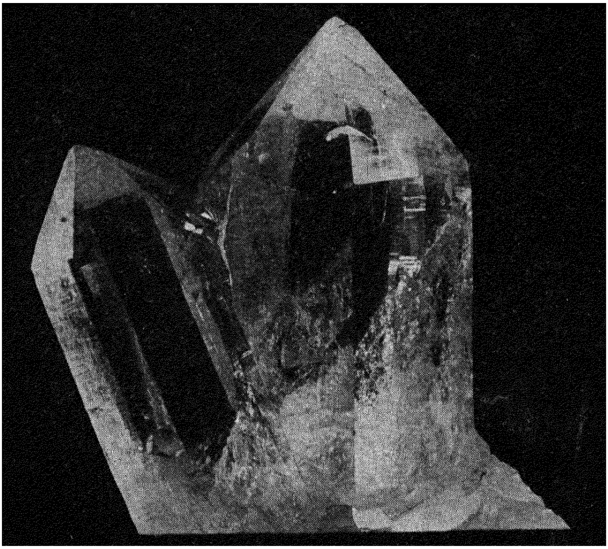

FIG. 134.—Quartz crystals. (*Courtesy of American Museum of Natural History, New York.*)

1. The Elements of Group IV.—Carbon, silicon, germanium, tin, and lead are the elements of Group IV. In many respects, carbon and silicon are similar nonmetals, but in other respects they are markedly different. For example, carbon dioxide is a gas, whereas silicon dioxide is a high-melting solid. Carbonic and silicic acids are weak acids, which we should expect since the nonmetallic properties of the elements decrease from right to left in the table. Although germanium, tin, and lead are progressively more metallic in the order named, their hydroxides are amphoteric. These three elements will be considered in a later chapter.

2. Occurrence of Silicon.—Next to oxygen, silicon is the most abundant element in the earth's crust, over one-quarter of its weight is due to this element. Although the element does not occur free in nature, silicon dioxide, or silica, is the most abundant constituent of sand and sandstone. As the mineral quartz, it occurs in many forms among which are the semiprecious stones amethyst, opal, onyx, and agate. As flint, it gave primitive man a material in which cutting edges could be obtained by chipping. The skeletal structures of certain aquatic microorganisms, the diatoms, are composed of this oxide. In fact their skeletons offer us silica in one of its most finely divided forms, diatomaceous earth, the adsorbent which Nobel used for nitroglycerin to make dynamite.

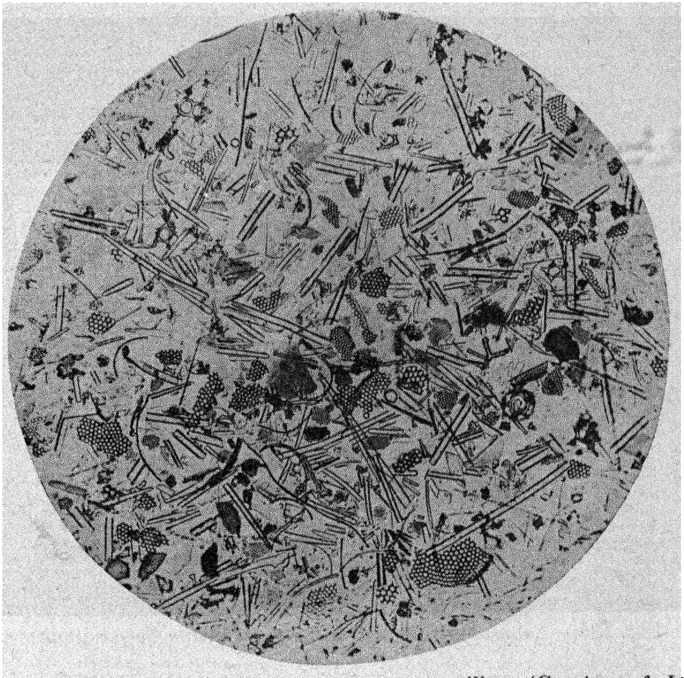

FIG. 135.—The skeletons of diatoms are pure silica. (*Courtesy of Johns-Manville Corporation.*)

Feldspars, the most abundant minerals, are either potassium or sodium aluminum silicates, *e.g.*, $KAlSi_3O_8$, and are found in all granitic rocks. Kaolin may be considered as a compound of the oxides of aluminum, hydrogen, and silicon—$Al_2O_3.2H_2O.2SiO_2$, or $H_2Al_2(SiO_4)_2.H_2O$. Clay is usually a mixture of kaolin, mica, iron oxide, and organic matter. Large deposits of relatively pure kaolin are found in Maryland and North Carolina and at Karlsbad and Meissen in Germany. Mica, asbestos, talc, and soapstone are also silicates.

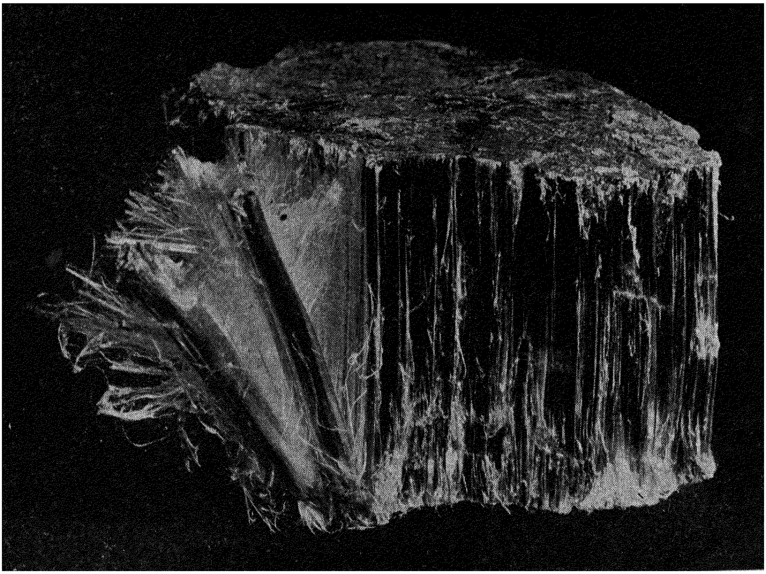

FIG. 136.—Asbestos. (*Courtesy of Johns-Manville Corporation.*)

3. Preparation.—Silicon, which is so useful when combined with other elements, could be prepared by only very expensive methods until recently. At $100 an ounce, its usefulness was decidedly limited. Now it is made on a large scale in 4,000-hp. electric-arc furnaces by heating a mixture of silica rock and coke.

$$SiO_2 + 2C \rightarrow Si + 2CO$$

It now costs 10 cents a pound, which has increased the scope of its usefulness. A steel alloy containing 4 per cent silicon is used in electric transformers. Acid-resistant steels contain about

15 per cent silicon. Aluminum alloys with 8 to 15 per cent silicon and copper-silicon alloys are becoming important. Mixtures of ferric oxide and silica are reduced simultaneously to produce ferrosilicon, which in turn is used to introduce silicon into alloy steels.

4. Properties.—The element has a crystal structure like the diamond and is hard enough to scratch glass. It melts at 1420°C. and boils at 2600°C. The element combines readily with the halogens to form the corresponding tetrahalides, *e.g.*, silicon fluoride. These are either gases or low-boiling liquids which fume strongly in moist air. The element forms silicides with some metals, *e.g.*, $FeSi$, Mg_2Si, and nonmetals, *e.g.*, SiC. It liberates hydrogen from sodium hydroxide solution,

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$$

a process used extensively in the First World War for generating hydrogen for dirigibles and balloons.

Silicon forms a series of hydrides similar to the hydrocarbons but not as extensive.

5. Silica and the Silicic Acids.—Silica, SiO_2, is, of course, insoluble in and does not react chemically with water. However, although the various silicic acids cannot be prepared directly, there is some advantage in considering them as compounds of silica and water. Just as phosphorus pentoxide combines with water in different proportions to form various phosphoric acids, so silica is the anhydride of a still greater number of silicic acids. The two simplest of these are ortho- and metasilicic acids.

$$H_2O + SiO_2 = \underset{\substack{\text{metasilicic}\\ \text{acid}}}{H_2SiO_3}$$

$$2H_2O + SiO_2 = \underset{\substack{\text{orthosilicic}\\ \text{acid}}}{H_4SiO_4}$$

The remainder are polysilicic acids, since they contain more than one silicon atom in their molecules.

$$\left.\begin{array}{l} H_6Si_2O_7(3H_2O\cdot 2SiO_2) \\ H_4Si_2O_6(2H_2O\cdot 2SiO_2) \\ H_2Si_2O_5(H_2O\cdot 2SiO_2) \end{array}\right\} \text{disilicic acids}$$

$$\left.\begin{array}{l} H_{10}Si_3O_{11}(5H_2O\cdot 3SiO_2) \\ H_8Si_3O_{10}(4H_2O\cdot 3SiO_2) \\ H_6Si_3O_9(3H_2O\cdot 3SiO_2) \\ H_4Si_3O_8(2H_2O\cdot 3SiO_2) \\ H_2Si_3O_7(H_2O\cdot 3SiO_2) \end{array}\right\} \text{trisilicic acids}$$

Fortunately for the chemistry student, the acids themselves do not exist as pure compounds; but their salts are important minerals, *e.g.*, orthoclase feldspar, $KAlSi_3O_8$; mica, $KAl_3(Si_3O_{11})\cdot H_2O$.

6. Preparation and Properties of Silicates.—Silicates are prepared by heating metal oxides, hydroxides, or carbonates with silica. Thus the important soluble sodium silicate, or *water glass*, is made commercially by heating soda, Na_2CO_3, with sand.

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

It may also be prepared by substituting sodium hydroxide or sodium oxide for soda.

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$
$$Na_2O + SiO_2 \rightarrow Na_2SiO_3$$

These methods are more expensive, since soda is much cheaper than the other two reagents.

When a solution of water glass is treated with an acid—even one as weak as acetic suffices—silicic acid is formed.

$$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3\downarrow$$

The precipitate that forms, however, has not a composition corresponding to the formula for metasilicic acid, H_2SiO_3, but is an indefinitely hydrated silica, $SiO_2.xH_2O$. If conditions are properly chosen, the precipitate forms as a jelly in which the water of the solution is entrapped. If the precipitate is heated at 300°C. under reduced pressure to remove water, a very porous form of silica, known as silica gel, is obtained. The tremendous surface in the pores of this material makes it a fine adsorbent for gases and vapors.

When water-glass solutions are mixed with those of salts of the heavy metals, metal silicates precipitate, *e.g.*,

$$Na_2SiO_3 + CuSO_4 \rightarrow Na_2SO_4 + CuSiO_3\downarrow$$

Metal silicates may also be prepared in a similar manner to water glass, *e.g.*,

$$CuO + SiO_2 \rightarrow CuSiO_3$$
$$FeCO_3 + SiO_2 \rightarrow FeSiO_3 + CO_2$$

When the earth was yet molten, many reactions of this type were taking place. The kind of silicate formed in any one of these reactions depends upon the proportions of the metal oxides to silica present and to the relative solubility in the molten mass of the silicates that might be formed.

7. **Glass** is essential to our civilization. Without it, the microscope and the telescope would never have been discovered. Astronomy, the science, would never have emerged from astrology. The fight against disease-producing bacteria could never have been waged, for their existence would not have been discovered. Plagues of disease would still be scourging humanity. Indeed, science could never have developed to even a first approximation of its present status without glass. Many more people would be groping their way about in near blindness because their eyesight could not be corrected. In the night no power of illumination better than the candle could be used, and windows would be barred during the cold of winter and during storms.

No one knows how or when glass was first discovered. Pliny gives credit for the discovery of glass to certain Phoenician sailors who used some lumps of natron, a naturally occurring soda, which formed part of the cargo of their ship, as support for their kettles. They were astonished to see a glass form from the soda of the natron, the potash in the wood ashes, and the sand of the beach. Possibly the art of glassmaking was discovered by Egyptian priests. At any rate, glass objects, which have the same composition as modern bottle glass, have been found in Egyptian tombs dating back to 3500 B.C. By 1500 B.C., the glass industry was flourishing in Egypt. In Rome, the industry first became important during the reign of the Caesars. After the fall of the Roman Empire, the art of glassmaking was lost to Europeans, passing to the Orient. It returned during the Middle Ages. During the Renaissance, Venetian glass became famous and reached its highest point in the sixteenth and seventeenth centuries. At the same time, in France and Bohemia, glassmaking began to develop. During the eighteenth century the art of casting plate glass was invented in France, and the glassworks of St. Gobain became famous because of this invention.

During medieval and, indeed, until quite recent times, the manufacture of glass was based on traditional formulas rather than on accurate scientific knowledge. Up until about fifty years ago, although flint glass (*i.e.*, glass containing lead) had been discovered, little systematic investigation was made of the effect of adding other components to the standard mixture of sand and lime with either soda or potash. As in many other fields, Faraday was again the pioneer in trying to extend the scope of glass technology, but his efforts received practically no attention from the glassmakers. The greatest credit for the rise of glass technology to its present position is due to Schott and Abbe in Germany, at Jena, and more recently to Eugene C. Sullivan of the Corning Glass Works of this country.

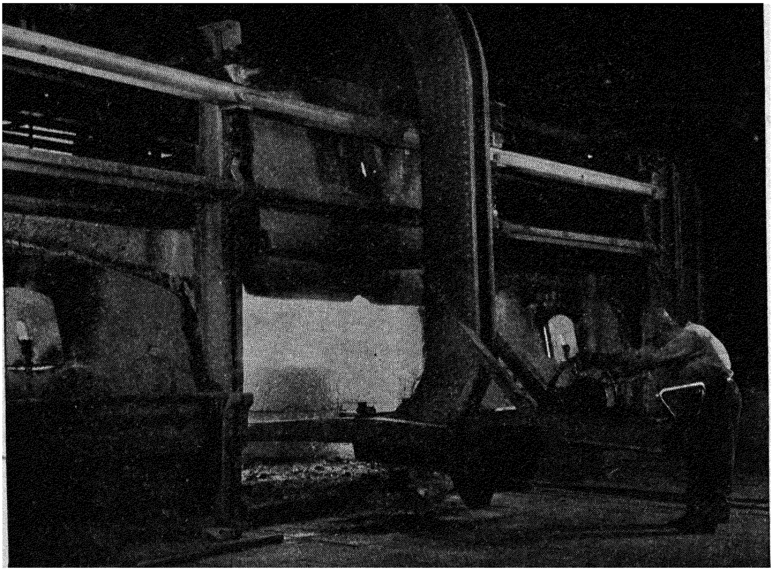

FIG. 137.—Giant electric tongs grasp a clay pot of molten glass to remove it from the furnace. (*Courtesy of Pittsburgh Plate Glass Company.*)

8. The Composition and Manufacture of Glass.—Glass consists essentially of three oxides: lime, CaO; silica, SiO_2; and sodium oxide, Na_2O. These components are obtained from the basic raw materials of glass manufacture: limestone, $CaCO_3$; white sand, SiO_2; and soda ash, Na_2CO_3. An intimate mixture of these components is heated in a crucible of fire-clay brick to above 1260°C. The materials gradually fuse, and carbon dioxide is evolved from the carbonates due to the combined action of heat and the silica. Silicates of sodium and calcium are formed, of which the most important from the viewpoint of the glass manufacturer is the compound $Na_2O.3CaO.6SiO_2$. This compound is characterized by a low melting point, a high viscosity, and an inherent reluctance to crystallize when cooled below its freezing temperature. When molten glass is allowed to cool, crystals do not form. The mass remains a liquid, but its viscosity increases as its temperature falls, until at room temperature it has become as rigid as a crystalline solid.

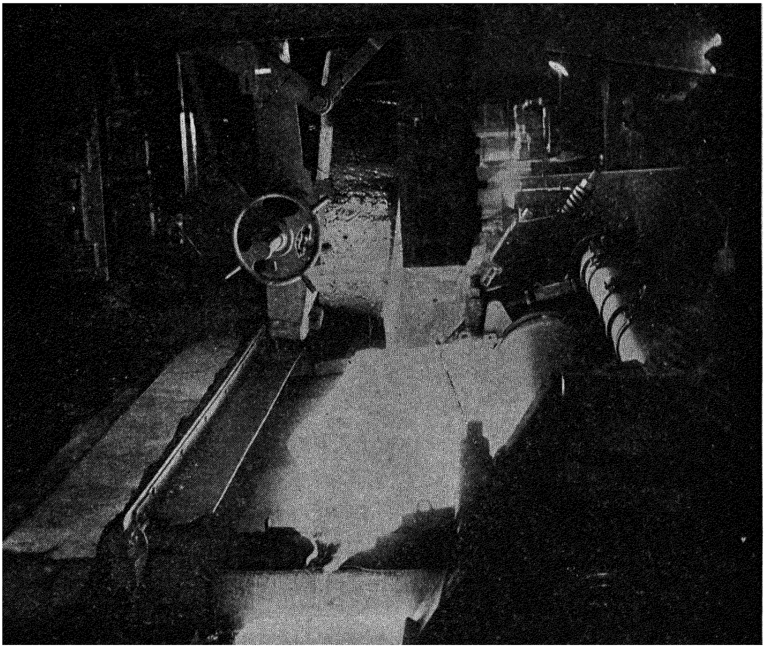

FIG. 138.—Molten glass is being poured between rollers which flatten it to the desired thickness. (*Courtesy of Pittsburgh Plate Glass Company.*)

The simple sand-lime-soda mixture is used in making window or bottle glass. If the sand used is impure, the resulting glass will be colored. A sand that contains oxides of iron, a common impurity, will color the glass green owing to the formation of ferrous silicate, which explains the delightful color of old bottle glass. The addition of a small amount of manganese dioxide will remove the green color by oxidizing the iron.

Window glass has the same composition as bottle glass, except that sodium sulfate is used in place of part of the soda. This improves the strength of the product. The batch is melted in large, rectangular tanks in a continuous process, each tank melting 600 to 1,000 tons daily. The glass is withdrawn from the molten batch as a flat sheet attached to a 5-ft. iron bar.

Plate glass is made by pouring the molten glass on to a steel table and rolling it flat to a thickness of ½ in. with a large steel roller. The plate is then ground flat to a thickness of ¼ in. and finally polished with rouge (ferric oxide).

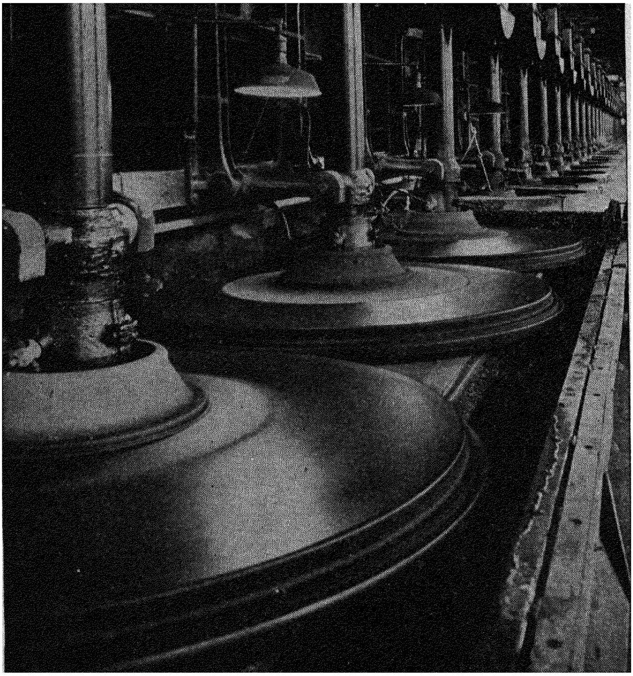

Fig. 139.—Battery of machines for grinding and polishing glass. Sane of increasing fineness is used as an abrasive followed by polishing with rouge under felt-lined wheels. (*Courtesy of Pittsburgh Plate Glass Company.*)

9. Low-expansion Glass.—Everyone knows that glass is fragile. But the recollection of many a student in an elementary chemistry laboratory attempting to boil water in a bottle leads us to suspect that there are some who do not know that ordinary glass will break when suddenly cooled or heated. Yet we now use glass cooking utensils with impunity. Credit for the successful manufacture of the low-expansion glass, used in these utensils, is due to Eugene C. Sullivan and his associates of the Corning Glass Works in this country. This glass expands only about one-third as much as ordinary glass for the same temperature rise. Hence, it is less liable to break if unevenly heated. Otto Schott, the great pioneer in glass technology, of Jena, discovered that adding boric acid to a batch that contains less soda reduces its coefficient of expansion. The Pyrex glass of the Corning Glass Works contains 12 per cent of the oxide of boron (B_2O_3) together with 81 per cent of silica.

TABLE 51.—COMPOSITION OF GLASS

Component	Window	Bottle	Optical	Pyrex	Vycor
SiO_2	71–74	71–74	46	80.6–80.9	96.0
Na_2O	12–15	12–17	0.5	3.8– 4.4	
CaO	8–14	6–8	.....	0.2	
MgO	0–4	0–4	.....	0.2	
Al_2O_3	0.7–2	0.5–3	0.15	1.8–2.0	
Fe_2O_3	0.1–0.2	0.04–0.07	0.02	0.1	
PbO	....	....	44.5		
B_2O_3	....	....	.....	11.9–12.6	3.6

10. Fused Silica.—Quartz, the crystalline form of silica which is found in nature, can be melted in an electric furnace. When cooled, this pure silica melt shows the same reluctance to crystallize that characterizes the silicate glass melts. It forms a glass that, until recently, was very difficult to obtain in a transparent form. Owing to the efforts of Berry and his coworkers of the General Electric Company, fused silica, more transparent than glass, is now available. It is made by controlling the pressure in the electric furnace so as to remove air bubbles. Fused-silica glass has such a low coefficient of expansion (5.5×10^{-7}, or one-tenth that of glass) that when heated red hot it can be plunged into water without breaking. Further, it is transparent to ultraviolet light, a very valuable property. Fused silica, although as yet expensive, is being rapidly put to new uses.

Within the last few years, a glass containing 96 per cent silica has been placed on the market under the trade name of Vycor. The chemical composition of the original batch is not noticeably different from a normal borosilicate glass. However, after a preliminary heat-treatment, the metal oxides in the glass are extracted with acid. After this, the slightly porous glass is heated to a moderate temperature, whereupon a clear, transparent glass is obtained with a coefficient of expansion nearly that of fused quartz. Further, there are no metal oxides left in such glass vessels to dissolve in the solutions contained in them.

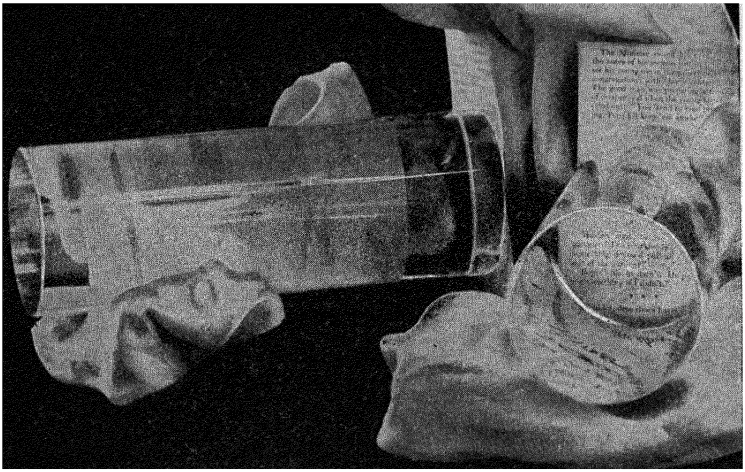

Fig. 140.—Cylinder of clear quartz glass ground and polished. (*Courtesy of General Electric Company.*)

11. Colored Glass.—Colored glasses are made in several different ways. Red glass was first made by pouring a solution of a gold salt over the sand to be used in the batch. Upon cooling, a yellow glass is obtained which, when heated in a smoky flame and again allowed to cool, turns to a beautiful ruby-red. The color is due to colloidal particles of gold (44-10). More recently colloidal selenium, an element that resembles sulfur and is a waste product of copper refining, has replaced the more costly gold. When selenium is used, zinc oxide replaces lime in the batch and cadmium sulfide and charcoal are added. Orange glass can also be made with selenium by using a lime-soda instead of a zinc-oxide batch. Pink or purple glass contains silicates of nickel or manganese. Amber or yellow glass contains colloidal sulfur and carbon. These glasses are especially opaque to the shorter wave-lengths of visible light, which are so active chemically in decomposing light-sensitive substances. Hence, bottles of amber or brown glass are used as containers for these substances. Green glass contains silicates of iron. Deep-blue glass contains cobalt oxide. White opaque glass is made by adding a fluoride and feldspar.

12. Silicon Tetrafluoride.—Hydrofluoric acid reacts with silica to form the colorless gas silicon tetrafluoride.

$$SiO_2 + 4HF \rightarrow SiF_4\uparrow + 2H_2O$$

This acid will also attack silicates, *e.g.*,

$$CaSiO_3 + 6HF \rightarrow CaF_2 + SiF_4 + 3H_2O$$

and it is upon this type of reaction that the ability of hydrofluoric acid to etch glass depends.

13. Occurrence of Boron.—Boron does not occur free in nature but as boric acid, H_3BO_3, and as salts of polyboric acids. Boric acid is deposited when the waters from certain hot springs in Italy cool. In the Death Valley of Southern California and in the neighboring Mojave Desert lie large deposits of the important minerals borax, $Na_2B_4O_7{\cdot}10H_2O$; rasorite, $Na_2B_4O_7{\cdot}4H_2O$; colemanite, $Ca_2B_6O_{11}{\cdot}5H_2O$; and ulexite, $NaCaB_5O_9{\cdot}8H_2O$. Borax deposits are also found at Teele's Marsh and Rhodes Marsh in Nevada and at Searle's Marsh in California.

14. Important Compounds of Boron.—The two most important compounds of boron are borax and boric acid. Boron in Group III is trivalent, and since its hydroxide is an acid, boron is a nonmetal. Although the oxide B_2O_3, as in the case of silica, is insoluble in water, the relationship between it and the various boric acids may be summarized as follows:

$$\begin{aligned}
H_2O + B_2O_3 &= \underset{\textbf{metaboric acid}}{2HBO_2} \\
3H_2O + B_2O_3 &= \underset{\textbf{orthoboric acid}}{2H_3BO_3} \\
H_2O + 2B_2O_3 &= \underset{\textbf{tetraboric acid}}{H_2B_4O_7} \\
3H_2O + 5B_2O_3 &= \underset{\textbf{pentaboric acid}}{2H_3B_5O_9} \\
2H_2O + 3B_2O_3 &= \underset{\textbf{hexaboric acid}}{H_4B_6O_{11}}
\end{aligned}$$

You will recognize these acids in the form of their naturally occurring salts, mentioned in the preceding paragraph.

Borax is prepared from its crude ore or from rasorite by recrystallization from water, and from a calcium ore like colemanite by treatment with the proper amount of soda.

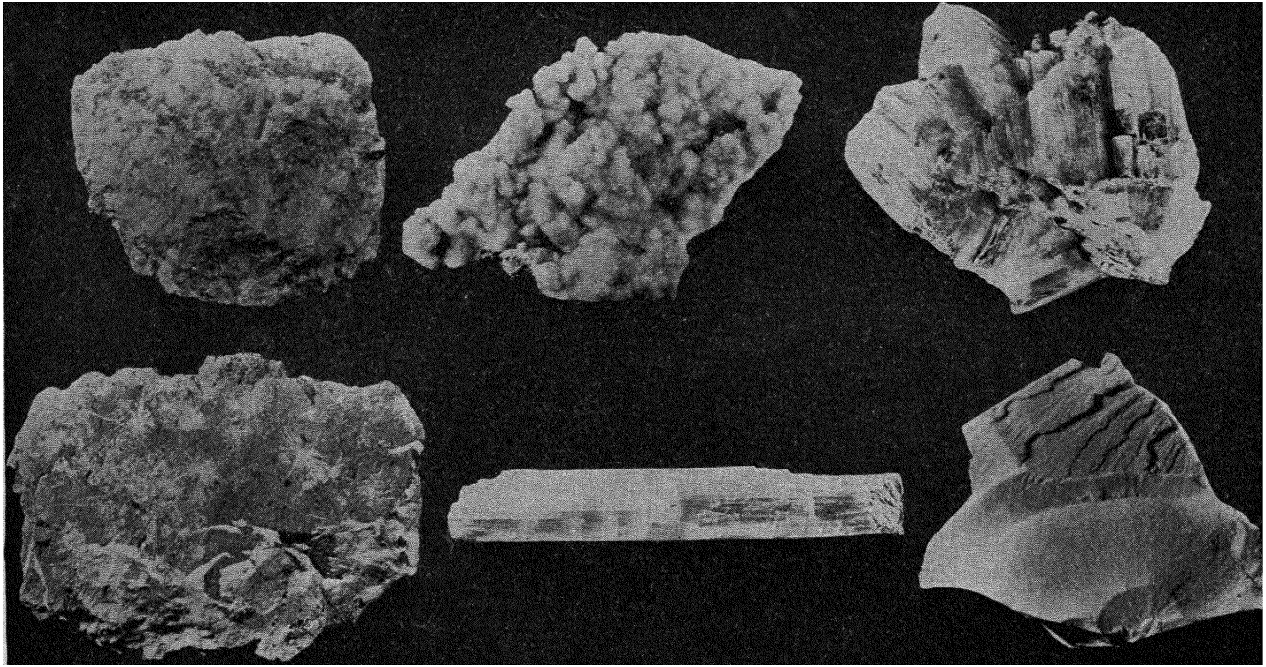

FIG. 141.—Boron minerals, ulexite, colemanite, rasorite, kramerite, kernite, and priceite. (*Courtesy of Pacific Coast Borax Company.*)

Since the boric acids are very weak acids, the various borate ions are strong bases. Hence all borates will react with acids to form orthoboric acid.

$$Na_2B_4O_7 + 2HCl \rightarrow 2NaCl + H_2B_4O_7$$
$$5H_2O + H_2B_4O_7 \rightarrow 4H_3BO_3$$

This acid is used as a mild antiseptic and is frequently sold under the older name boracic acid. When heated, the acid loses water, forming first metaboric, then tetraboric acid, and finally the oxide.

$$H_3BO_3 \rightarrow HBO_2 + H_2O$$
$$4HBO_2 \rightarrow H_2B_4O_7 + H_2O$$
$$H_2B_4O_7 \rightarrow 2B_2O_3 + H_2O$$

We have discussed the use of the oxide in borosilicate glasses. When boric acid is treated with sodium hydroxide, borax is formed.

$$4H_3BO_3 + 2NaOH \rightarrow Na_2B_4O_7 + 7H_2O$$

Solutions of borax in water are mildly basic, owing to the hydrolysis of the borate ion. For this reason, borax is used extensively as a water softener. When borax is heated, its water of crystallization is lost and the anhydrous salt fuses to a transparent borax glass. When fused with metal oxides, the corresponding metal metaborates are formed. Since many of these are colored, this type of reaction has been made the basis of bead tests for certain metals. Powdered borax is fused on a loop of platinum wire into a transparent bead. If this bead is heated with cobalt oxide, for example, a blue glass containing cobalt metaborate is formed.

$$Na_2B_4O_7 + CoO \rightarrow 2NaBO_2 + Co(BO_2)_2$$

The property of forming glasses possessed by boron oxide and by borax is extensively used for enameling ironware.

Sodium perborate is formed by the combined action of sodium hydroxide and hydrogen peroxide on borax.

$$Na_2B_4O_7 + 2NaOH + 4H_2O_2 \rightarrow 4NaBO_3 + 5H_2O$$

It is a valuable antiseptic and bleaching agent.

EXERCISES

1. Discuss the relationship of silica to the various silicic acids and silicates.

2. Why are the vast majority of the reactions into which silicon compounds enter dry-fusion reactions?

3. How is water glass prepared commercially?

4. Reasoning by analogy, what compounds would you predict might be formed when silica is fused with each of the following: Na_3PO_4, $CaSO_4$?

5. Write equations for the reactions that take place when sand, lime and soda are fused together.

6. Write equations showing the preparation of two silicates used to color glass.

7. What reactions are responsible for the etching of glass by hydrofluoric acid?

8. Write the equation for the formation of boric acid from borax.

9. What is formed when boric acid is heated?

10. Explain the formation of a blue glass bead when borax is heated with cobalt oxide.

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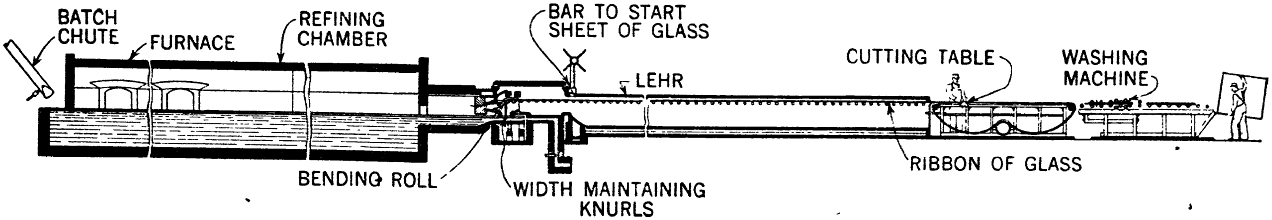
Diagram of the Continuous Process for Making Sheet Glass



Up to 1000 tons of the ingredients from which glass is made are melted daily in the furnace. The glass is pulled out on an iron bar as a flat ribbon: passes between knurls and rollers which govern its width and thickness, respectively; and then moves slowly through the heated lehr. or annealing oven. Here the glass is cooled so gradually and uniformly that internal strains are avoided. Finally, it is cut into large sections. (*Courtesy of Libbey-Owens-Ford Glass Company.*)

CHAPTER FORTY-FOUR

THE COLLOIDAL STATE

About the middle of the last century Thomas Graham, a professor of chemistry at University College, London, was investigating the diffusion of dissolved substances through the pores of parchment paper and animal membranes. He found that a certain class of substances like salt and sugar could diffuse through such membranes, whereas such substances as gelatin, glue, and similar materials did not have this ability. The substances of the former class were usually crystalline, whereas those of the latter tended to be amorphous. He proposed the name crystalloids for substances of the first class and colloids (gluelike, from the Greek) for those of the second.

Graham's distinction was based on what he considered to be a fundamental property of substances. Salt, for example, was always a crystalloid and never a colloid. The term colloidal has taken on a new significance since Graham's time. It now refers to a state of aggregation of the particles of which a substance is made up rather than to any intrinsic property of the substance itself.

1. The Colloidal State of Aggregation.—If we were to crush and grind up the relatively coarse crystals of which solids are ordinarily composed, the particles would become smaller and smaller, until we should require a lens or even a powerful microscope to see them. Theoretically, we might continue this process of subdivision until each individual particle consisted of a single molecule. Further than this we cannot go without decomposing the substance chemically. The limit to the power of resolution of a microscope is about 0.0005 mm., or to use the smaller unit the micron, so often employed to express microscopic diameters, 0.5μ. The micron is equal to 10^{-3} (1/1,000) mm. and the millimicron, 10^{-6} (0.000001) mm. The symbol μ is used for the micron and $\mu\mu$ for the millimicron. Particles of this diameter are some 1,000 times larger than the largest molecule and some 500,000 times larger than the hydrogen atom. A considerable range of particle sizes lies beyond the microscope, between the limits of microscopic visibility and the molecular state. Such particles, consisting of molecular aggregates, are colloidal. They lie in what Findlay has called "the twilight zone of matter."

Particles of colloidal size play an important rôle in many different fields of human activity. Among some of the important industrial problems in which colloids are involved may be listed water purification and sewage disposal; lubrication; flotation of ores; adsorbents; tanning; dyeing; brick, pottery, glass, and porcelain manufacture; rubber; milk and dairy products; baking and breadmaking; varnishes, paints, and pigments; fire extinguishers; photography; precipitation of mist and smoke; etc. Some of these applications of colloid chemistry we shall have occasion to study later in this chapter. The fact that living organisms are built up of tissues whose structure is made up of particles of colloidal dimensions is an indication that colloids play an important role as the medium in which life's processes take place.

TABLE 52.—TYPES OF COLLOIDAL SUSPENSION

Disperse phase	Dispersing medium	Example
Gaseous bubbles	In a gas	Impossible
	In a liquid	A foam
	In a solid	Air in certain porous minerals
Liquid drops	In a gas	A mist or a fog
	In a liquid	An emulsion
	In a solid	Water in butterfat
Solid grains	In a gas	A smoke
	In a liquid	Colloidal gold in water
	In a solid	Sodium in blue salt crystals

2. Types of Colloidal Suspension.—Bancroft has pointed out that colloid chemistry is the study of bubbles, drops, grains, filaments, and films. Bubbles of a gas, drops of a liquid, and grains of a solid are states of aggregation, all of whose dimensions may be colloidal. On the other hand, two of the three dimensions of a filament and only one dimension of a film may be of colloidal size. The study of the behavior of all these is within the province of colloid chemistry. In a true solution, we have learned that the particles of the solute are of molecular size or smaller. In a colloidal suspension, particles of colloidal dimensions are dispersed in a solid, liquid, or gaseous medium. There are, therefore, nine combinations, as in the case of true solutions, but one of these is impossible as a type of colloidal solution, since all gases form true solutions with one another. Of the types given in Table 52, the mists, fogs, smokes, emulsions, and colloidal grains in a liquid will be of greatest interest to us.

3. Recognition of a Colloidal Suspension.—A colloidal suspension can be distinguished from a true solution by means of a phenomenon known as the *Tyndall effect.* You have all noticed how the path of a beam of light in an otherwise dark room is outlined by the reflection of the light upon the colloidal dust particles that are in the air. In a uniformly lighted room, these particles are invisible. If the air of the room were absolutely dust free, we could not see the path of the light, for the molecules in the air are too small to give visible reflections. Dust-free air is a true solution, since no particles in it are larger than single molecules. When a powerful beam of light is passed through any true solution, its path cannot be followed. On the other hand, under the same condition, the path of a beam of light will be outlined in a colloidal suspension, each colloidal particle reflecting the light.

Under a high-power microscope, colloidal suspensions appear just as homogeneous as true solutions, for the suspended particles in the colloid are too small to be seen. However, by using the Tyndall effect in conjunction with a microscope of high power, Siedentopf and Zsigmondy introduced in 1903 the use of an ultramicroscope by the aid of which the presence of particles whose diameters are as small as 10^{-6} cm. can be detected. These are only one hundred times larger than the hydrogen molecule. In the ultramicroscope (Fig. 142) an intense beam of light at right angles to the line of vision of the microscope is focused to a point in the colloidal suspension by means of a lens. The microscope is then focused on this point of light. Using ultraviolet instead of visible light, the reflection of light on still smaller particles can be photographed, since the shorter the wave-length of the light, the stronger is the reflection.

4. The Brownian Movement.—Under the ultramicroscope, colloidal particles are seen as tiny points of light that seem to be in perpetual motion. This motion was discovered in 1827 by a Scotch botanist, Dr. Robert Brown, the keeper of the botanical department of the British Museum. You will be interested in his own report of this discovery.

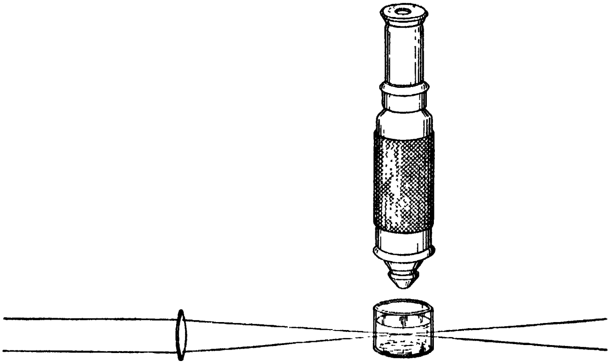


FIG. 142.—An ultramicroscope.

> Extremely minute particles of solid matter, whether obtained from organic or inorganic substances, when suspended in pure water, or in some other aqueous fluids, exhibit motions for which I am unable to account and which, from their irregularity and seeming independence, resemble in a remarkable degree the less rapid motions of some of the simplest animalcules of infusions. That the smallest moving particles observed appear to be spherical, or nearly so, and to be between 1/20,000 and 1/30,000 in. in diameter; and that other particles of considerably greater and various size, and either of similar or very different figure, also present analogous motions in like circumstances.

The cause of the Brownian movement was long in doubt. But with the development of the kinetic theory of the nature of heat came the realization that here was another example of the same sort of perpetual motion as that of the molecules themselves. The classical experiments of Jean Perrin, director of the laboratory of physical chemistry of the University of Paris, proved quantitatively the correctness of this hypothesis. By a process of fractional centrifugalization, he was able to obtain colloidal suspensions of gamboge and gum mastic in water in which the suspended particles were of the same size. This size he measured directly under the microscope, and knowing the density of these particles, he was able to calculate their mass. By direct observation, he could also determine their velocity and, hence, calculate their kinetic energy. The results of his calculations were astounding. For particles varying in mass from 60,000 to 1, he found that their mean kinetic energy at the same temperature was the same and identical with that of the molecules of a gas. His largest particles were some 10^{11} heavier than the hydrogen molecule. Yet each had the same kinetic energy. His results have been summarized in the law of equipartition of energy: At the same temperature, every freely moving particle in space has the same kinetic energy. This inherent kinetic energy of colloidal particles is one of the factors that helps to keep them in suspension in a medium.

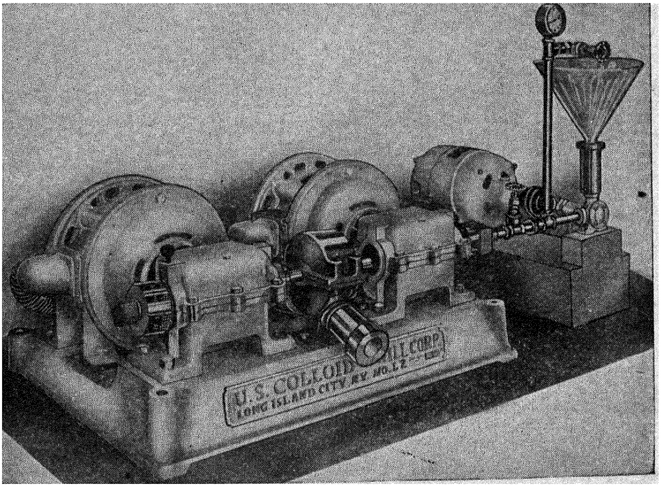


FIG. 143.—Colloid mill. (*Courtesy of United States Colloid Mill Corporation.*)

5. Preparation of Colloidal Suspensions.—The methods by which colloidal suspensions may be prepared may be divided for convenience into two types. The first involves breaking down coarser particles to colloidal size, a process called *peptization,* and the second, the building up of colloidal particles from molecules or ions, is called *coagulation.*

The most obvious method of peptizing a solid is grinding. Grinding mills (Fig. 143) have been invented in which solid particles can be reduced to colloidal size. These have been of great practical importance in the preparation of paint pigments, colloidal fuel which flows through pipes like a liquid, fillers for paper and rubber, and in many other industries. By the use of a colloid mill, particles as small as 0.01μ can be obtained.

An analogous method to grinding, which can be applied to the preparation of emulsions, is shaking. This results in breaking up one of the liquids into smaller and smaller droplets which are suspended in the other liquid. Since two smaller droplets are less stable than a larger one, these droplets show a relatively great tendency to coalesce when the shaking is stopped. This can be prevented by the addition of an emulsifying agent, which forms a membrane about the droplets of the dispersed phase. The preparation of a stable mayonnaise dressing is an example of the use of an emulsifying agent. A salad oil, which is a liquid fat like cottonseed oil, is dispersed in vinegar, a dilute solution of acetic acid in water, by either shaking or, more easily, beating with an egg beater. An egg is added as the emulsifying agent. This coats the oil droplets and prevents their coalescence.

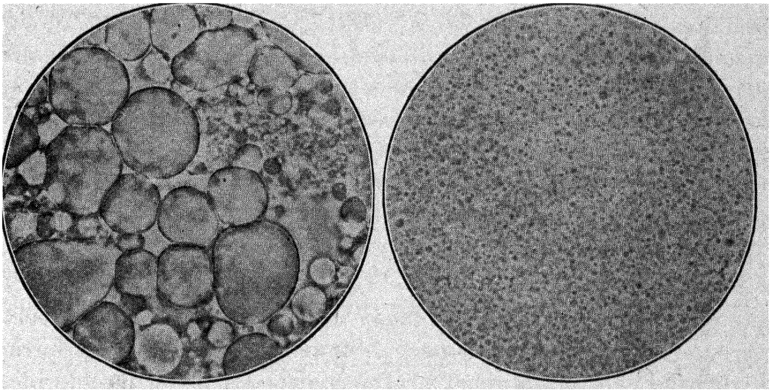


FIG. 144.—Mayonnaise dressing made by a regular mixer and that made by a colloid mill. (*Courtesy of United States Colloid Mill Corporation.*)

The substances that Graham originally called colloids, like glue and gelatin, are peptized by merely placing them in a suitable peptizing medium; *i.e.*, they go into colloidal suspension instead of into true solution.

The coagulation methods, which involve the formation of colloidal particles from molecules or ions, depend, in general, on the rapid formation of substances that are insoluble in the medium in which the reaction is carried out. We have pointed out (16-10) that in order to grow large crystals from a solution it must be kept only slightly supersaturated so as to give an opportunity for the molecules or ions coming out of solution to fit themselves into the structure of crystals that have already been formed instead of forming new crystals. Conversely, the crystals that come out of an enormously supersaturated solution are small, because of too rapid crystallization. When a chemical reaction between electrolytes results in the formation of an insoluble compound, precipitation, *i.e.*, almost instantaneous crystallization, takes place. Under such circumstances, the crystals are very finely divided. Precipitates of certain substances are of colloidal dimensions. For example, when hydrogen sulfide reacts with the hydroxide of trivalent arsenic, a colloidal suspension of arsenious sulfide results.

$$3H_2S + 2As(OH)_3 \rightarrow As_2S_3\downarrow + 6HOH$$

the particles of which are so finely divided that they pass freely through the pores of filter paper. Similarly, suspensions of ferric hydroxide can be obtained by the hydrolysis of ferric chloride.

$$FeCl_3 + 3HOH \rightarrow Fe(OH)_3\downarrow + 3HCl$$

Colloidal suspensions of an inactive metal can be conveniently prepared by treating a solution containing the ion of the metal with reducing agents. These give electrons to the metal ions and reduce them to neutral atoms of the metal. Dilute solutions of gold chloride are readily reduced to form suspensions by tannin, a mild reducing agent.

6. Adsorption.—Some of the most important properties of colloidal particles depend upon the enormous surface that such particles possess in proportion to their mass. As a given amount of material is continuously subdivided, its total surface area rapidly increases. This is brought out in Table 53.

The molecules in the surface are in a unique position. Unlike those in the interior, they are not surrounded on all sides by other molecules. The forces of intermolecular attraction are unsatisfied on the surface side of these molecules. Hence there is a tendency for them to hold molecules of other substances onto their surface. This is called "adsorption." Langmuir has proposed a theory that substances adsorbed on surfaces in this way are in a layer not more than one molecule in thickness. Very porous substances, like charcoal, silica gel, or fuller's earth, are good adsorbents because of their relatively large surface. Charcoal is used to adsorb coloring matter from sugar solutions. Its ability to condense vapors on its surface saved many lives during the First World War. It is a fortunate circumstance that adsorption is a selective process. The charcoal of gas masks adsorbs the molecules of toxic vapors strongly but lets nearly all the oxygen and nitrogen molecules by. In general, the more readily a gas can be condensed, the more strongly it will be adsorbed. This we should expect because the forces of intermolecular attraction are strongest in such gases. Fuller's earth is used extensively for decolorizing special petroleum preparations, for example, in the preparation of white vaseline and Nujol. Cottonseed oil seems to be more acceptable for use as a salad oil after it has been bleached by this adsorbent. The activity of catalysts depends to a large extent on the area of their surfaces, which indicates that adsorption plays an important role in catalytic phenomena.

TABLE 53.—PROGRESSIVE SUBDIVISION OF A CUBE

Length of edge	Number of cubes	Total surface
1 cm.	1	6 cm.^{2}
1 mm.	1,000	60 cm.^{2}
0.1 mm.	1×10^6	600 cm.^{2}
0.01 mm.	1×10^9	6,000 cm.^{2}
1 μ	1×10^{12}	6 m.^{2} (64.6 ft.^{2})
0.1 μ	1×10^{15}	60 m.^{2}
0.01 μ	1×10^{18}	600 m.^{2}
1 $\mu\mu$	1×10^{21}	6,000 m.^{2} (1.5 acres)
0.1 $\mu\mu$	1×10^{21}	60,000 m.^{2} (15 acres)

One of the most important applications of adsorption phenomena is in the field of metallurgy in ore flotation (46-2). A low-grade sulfide ore, for example, is finely ground and beaten up by means of a stream of air in a mixture of water with a little pine oil. The oil is adsorbed by the sulfide ore and the water by the rocky gangue. The oiled mineral is carried to the surface by air bubbles coated with oil. The gangue sinks to the bottom. Over 60,000,000 tons of ore are concentrated by this process annually in the United States.

The process of dyeing textile fibers is one of adsorption of the dye by the fiber. Both the dye particles and the fiber are of colloidal dimensions, and their large surface area makes adsorption relatively easy. Cotton fibers do not adsorb dyestuffs as readily as silk and wool, so that mordants are frequently used to aid in the fixation of the dye. Colloidal aluminum hydroxide is deposited in and on the cotton fibers by dipping the textile in a solution of an aluminum salt which is then hydrolyzed to the hydroxide by steam. The colloidal mordant then adsorbs the dye.

7. Charges on Colloidal Particles.—A difference in potential exists between the colloidal particles of the disperse phase and the dispersing medium; *i.e.*, some kinds of colloidal particles are more negative and others more positive than the medium in which they are suspended. This is probably caused by the preferential adsorption on the surface of the colloid of ions, which are present in all solutions to a greater or lesser extent. The presence of such charges can be readily demonstrated by placing electrodes in a colloidal suspension and applying an external electromotive force. Under such circumstances, the colloid particles behave like ions. If they are positively charged, they migrate to the cathode, and vice versa. This migration is called *cataphoresis*. In general, colloidal oxide or hydroxide particles tend to adsorb positive ions and hence to become positively charged. On the other hand, colloidal metals or sulfides tend to be negatively charged.

The fact that the particles of a given colloid are charged alike causes them to repel each other and so to prevent their coagulating into larger particles, which would settle more rapidly. Together with the Brownian movement, these two factors are mainly responsible for colloid particles remaining in suspension. For this reason, any means of destroying the electrical charges on colloid particles will tend to cause coagulation into larger particles, resulting in the precipitation of the colloid. Ions of opposite charge, especially if their valence is high, are able to precipitate colloids. Thus, a positively charged ferric hydroxide colloid is rapidly precipitated by adding a soluble phosphate solution containing the $PO_4^{\equiv}$ ion, and a negatively charged arsenious sulfide colloid is coagulated by a solution containing the Al^{+++} ion. As one might expect, two oppositely charged colloids will precipitate each other, *e.g.*, colloidal ferric hydroxide and arsenious sulfide. To stabilize a colloid, all ions must be removed from the dispersing medium. This is accomplished by *dialysis*, a process invented by Graham. The colloidal suspension is placed in a parchment container which, in turn, hangs in pure water. Water is allowed to pour slowly into the colloid. The offending ions diffuse through the parchment pores, but the colloidal particles do not because of their size.

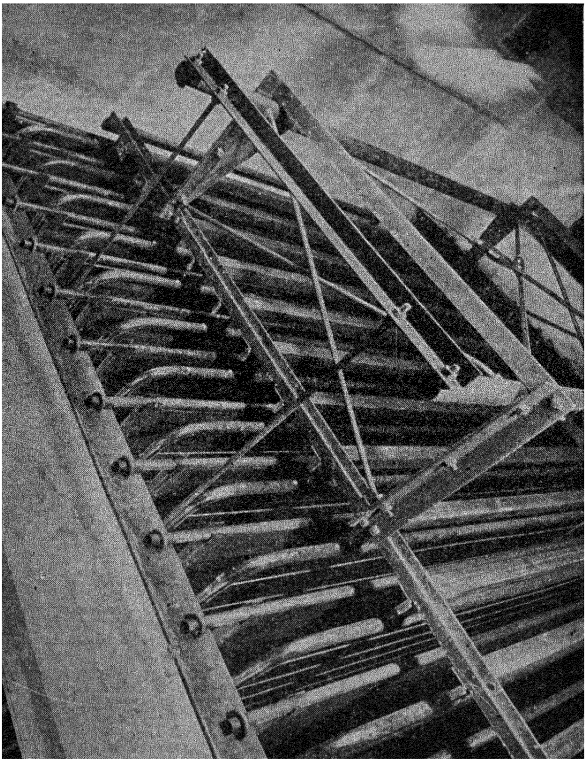


FIG. 145.—Cottrell precipitator. (*Courtesy of Western Precipitation Company.*)

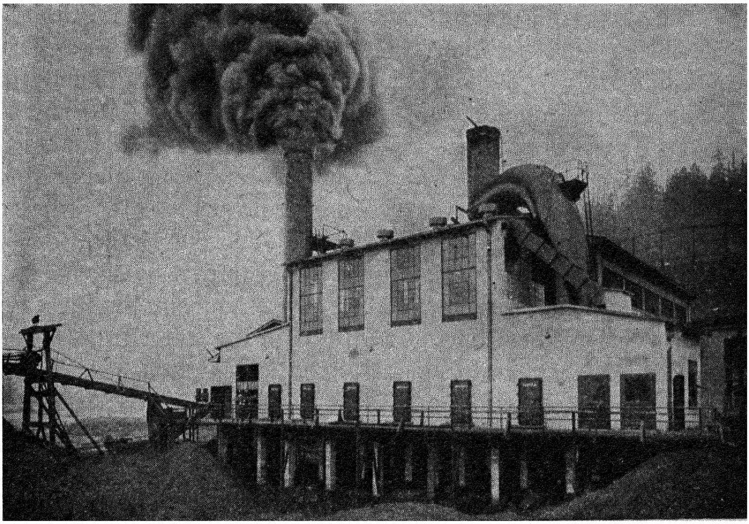
The formation of deltas at the mouths of rivers that flow into the sea is due to the precipitation of colloidal clay and sand particles from the fresh river water by the ions of the salts in the sea water.

8. Cottrell Precipitation.—Colloidal dusts or mists suspended in air are likewise electrically charged. Such suspended particles escaping from the flues of chemical plants not only represent in many cases the loss of a valuable product, but also, in some instances, are destructive to the vegetation and dangerous to the health of the inhabitants in their vicinity. Smelters of sulfide minerals, such as those of copper and lead, and sulfuric acid plants had long been subject to fume litigation and, in some instances, had been forced to stop operation by injunction proceedings on the part of the United States Forestry Service because of the widespread deforestation caused by their fumes until a process of electrical precipitation of fumes and smokes was developed by Cottrell, an American chemist. The flue gases are passed between two electrodes, one of which is of large area and the other usually a wire upon which are many asbestos fibers or mica crystals. The plate electrode is of opposite charge to the charge on the suspended particles. These migrate to the plate, are discharged, and at once coalesce into larger droplets or coagulate into larger grains. Precipitation is practically complete. By this process a nuisance has been done away with, and the recovery of valuable products from the flue gases has more than paid for the cost of operating the precipitation.

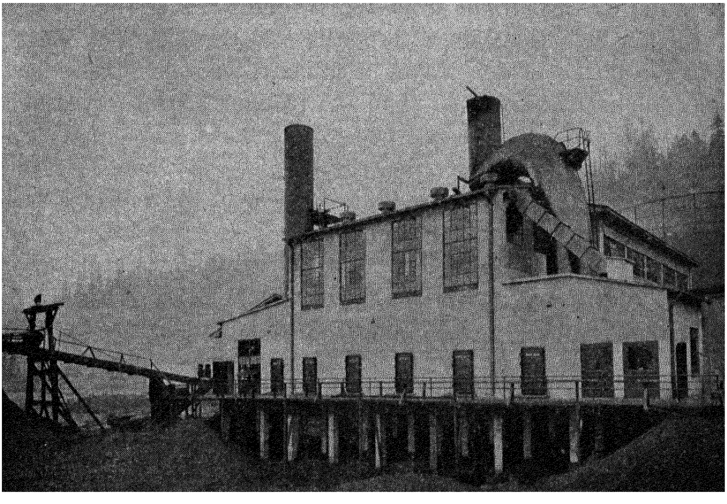
9. Protecting Colloidal Particles.—We have mentioned the use of an emulsifying agent in stabilizing emulsions. An emulsifying agent goes to the interface between the droplets of the liquid of the dispersed phase and the liquid medium in which these are suspended. Thus it prevents coalescence of the colloidal droplets and makes the emulsion more stable. The adsorption of such protecting films by colloidal particles is one of their most valuable properties, for it enormously increases their stability.

The emulsions of oil droplets in water and of water droplets in oil are of practical importance as greases. The use of soaps as emulsifying agents for these emulsions is interesting, for the type of soap determines which of the two phases, the water or the oil, shall be the dispersed phase. A sodium soap (55-7) will disperse oil in water, whereas a calcium or an aluminum soap will do the opposite.

Colloidal suspensions of solids are often made more stable by the addition of a third substance—in this case a deflocculating agent which acts similarly to an emulsifying agent. Colloidal suspensions of clay in water are used extensively in the so-called ceramics industries, *i.e.*, in the manufacture of pottery of all kinds and bricks. Acheson, the American chemist who discovered



The precipitator with electrical current off.



The precipitator in operation.

FIG. 146.—Cottrell precipitator at the plant of the Portland Gas & Coke Company, Portland, Oregon. This precipitator collects lampblack, tar, mist, and fume from rotary carbon briquette driers. (*Courtesy of Western Precipitation Company.*)

how to make carborundum, the abrasive, and artificial graphite in the electric furnace, found that when tannin is present in clay suspensions they become more plastic and that bricks made from this material are much stronger. Perhaps this discovery explains why the Israelites suffered when the Egyptian Pharaoh denied them the use of straw with which to make brick. Some plasticizing agent, similar to tannin, is present in the straw.

Acheson was able to make use of the deflocculating action of tannin in another way. When artificial graphite, which he was making from coal, is shaken with a dilute aqueous tannin solution, it is dispersed as colloidal particles in the water from which it shows little tendency to settle. Such colloidal suspensions of Deflocculated Acheson Graphite in water he called Aquadag ("dag" from the first letters of the words Deflocculated Acheson Graphite); these are important lubricants.

10. Optical Properties of Colloidal Suspensions.—You have all, no doubt, noticed the beautiful colors of thin films of oil or of soapy water in soap bubbles. These colors are due to the reflection of white light from the two surfaces of the film. The angle at which the light strikes the two surfaces may be such that the crests of the waves of certain wave-lengths reflected from one surface correspond to the troughs of the waves of the same wave-lengths reflected from the other surface of the film. This would mean complete interference, so that the colors corresponding to these waves would not appear in the reflected beam. As a result, this beam would no longer be white light, but would be composed of the complementary color. Many emulsions are beautifully colored for this reason. The blue color of certain bird feathers or of blue eyes is due to no pigment, but to the effect that we are discussing. We find in the feathers and in blue eyes a structure of many colloidal air bubbles suspended in a solid medium. These scatter blue light but transmit red, which is absorbed by the dark ground.

Colloidal suspensions of metals are often highly colored. Colloidal gold suspensions vary in color from red to violet, depending on the size of the particles. This is due to selective reflection, a phenomenon that is too complicated to consider here.

11. Gels.—Colloidal suspensions may be divided into two classes depending upon whether the forces of attraction between the colloidal particles of the disperse phase and the medium are small or great. Colloidal suspensions in which these forces are small are called *lyophobe* colloids, and those in which they are great, *lyophile* colloids. The suspensions of lyophobe colloids, such as colloidal metals, sulfides, or hydroxides, are characterized by a viscosity which does not differ greatly from that of the medium and by a great sensitiveness to coagulation by electrolytes (44-7). On the other hand, suspensions of lyophile colloids are, in general, much more viscous than the pure medium in which they are suspended and show a great tendency to "set" to a jelly or gel on cooling. Such substances as gelatine and agar-agar are of this type. The gel is probably due to the linking together of the colloidal particles to a network of fibrils or chains that entrap the liquid medium in which they are suspended (Fig. 147).

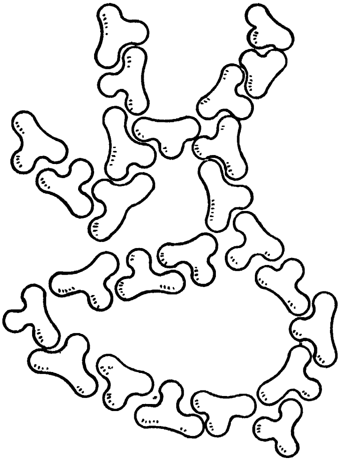


FIG. 147.—Gel structure.

EXERCISES

1. What is a colloidal suspension, and how may one be recognized?
2. What factors keep colloidal particles in suspension?
3. What is the distinction between peptization and coagulation methods of preparing colloids?
4. What is adsorption? Why does it take place?
5. What is cataphoresis?
6. How may colloids be precipitated?

7. What is the function of an emulsifying agent?
8. What type of structure favors gel formation?

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CHAPTER FORTY-FIVE

ELECTROLYSIS AND ELECTROMETALLURGY

The chemistry of the metals will be in large measure a review of what we have been studying. It is obviously impossible to study nonmetals without considering their reactions with metals and the properties of the compounds formed. Only when we consider the problems of metallurgy, the characteristic physical properties of metals and their alloys, and the specific reactions of metal ions will new material be introduced. For these reasons, it seems best not to consider the chemistry of each metal separately as we have done with the nonmetals.

1. Reduction of Metals.—Metallurgy is defined as the science of the extraction of metals from their ores. Since a metal in any of its compounds has a positive valence, the preparation of a free metal involves reduction. Here the discussion of the electromotive series, which we studied earlier (40-13), will be again useful. You will remember that the higher the position of a metal in this series, the more readily is the free metal oxidized and the more difficult is the reduction of its ion. From this generalization, it should be obvious that those metals near the bottom of the series only will occur free in nature; and that the order in which the metals were discovered in history must be approximately the reverse of their order in the electromotive series. It has been pointed out (17-2a) that when a direct current of electricity is passed through an electrolyte reduction occurs at the cathode, since this is the pole into which electrons are flowing. At this pole, reduction of the ions of the active metals can be accomplished under suitable conditions. This is the method by which such metals are prepared; but before we discuss electrometallurgy, a study of electrolysis will be helpful.

Electrolysis may be defined as the chemical reactions resulting from the passage of a direct electric current through an electrolyte. In electrolysis we are interested in the mechanism by which the ions of the electrolyte are discharged at the electrodes. At the cathode some positive ion is discharged and at the anode, a negative ion. The electrodes are connected to a source of direct current which acts as an electron pump drawing a stream of electrons into its positive pole and forcing them out of its negative pole. The source of direct current may be a series of electrochemical cells, such as a storage battery, or the leads from a direct-current generator. The cathode of the electrolysis cell is connected to the negative pole of the current source and the anode of the cell to the positive pole as shown in Fig. 148. Electrons are, therefore, being pumped into the cathode and out of the anode of the electrolysis cell. Under such circumstances, the cathode becomes negatively and the anode positively charged. Under the influence of these charged electrodes, the positive ions in the solution will migrate to the cathode and the negative ions to the anode. At each electrode a discharge of ions takes place, but since what happens at the anode is more or less independent of what occurs at the cathode, we may consider each process separately.

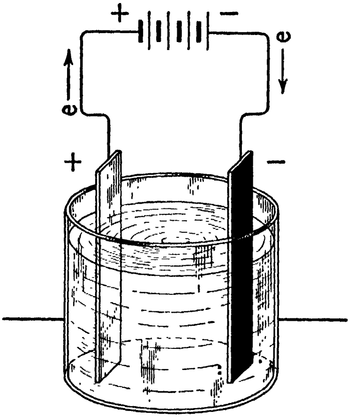

Fig. 148.—An electrolysis cell.

2. Discharge of Cations.—It must always be kept in mind in considering the mechanism of electrolysis that in addition to the ions of the electrolyte there are always present in all aqueous solutions the ions of water, H_3O^+ and OH^-. These ions migrate in the electrical field just as do the ions of the electrolyte, the hydronium ions moving to the cathode and the hydroxyl ions, to the anode. At the cathode, two ions in general present themselves to be discharged—the positive ion of the electrolyte and the hydronium ion from water. Which of the two is discharged depends upon their relative positions in the electromotive series of metals. The ion of a metal below hydrogen is easier to discharge (more accurately, can be discharged at a lower voltage) than the hydronium ion. Hence if the positive ion of the electrolyte is one of copper, mercury, silver, or gold, it will be discharged in preference to the hydronium ion. On the other hand, the ion of a more active metal is more difficult to discharge than the hydronium ion so that the latter will be discharged. The actual mechanism of discharge of a positive ion involves the acquisition from the cathode of a number of electrons, equal to the positive charge on the ion, and hence the formation of a neutral atom of the free metal. In general,

$$X^{+n} + ne^- \rightarrow X^0$$

or to give specific examples,

$$\begin{gathered} Ag^+ + 1e^- \rightarrow Ag^0 \\ Cu^{++} + 2e^- \rightarrow Cu^0 \\ Au^{+++} + 3e^- \rightarrow Au^0 \end{gathered}$$

The neutral metal atoms are insoluble in water and usually form a metallic plating on the cathode. If the hydronium ion is discharged, the first step is the same.

$$H_3O^+ + 1e^- \rightarrow H^0 + H_2O$$

However, since neutral atoms of hydrogen show a great tendency to combine in pairs to form the stable diatomic molecule of hydrogen gas, this will next occur

$$2H^0 \rightarrow H_2$$

and the gas will come out of solution in small bubbles on the surface of the cathode. When hydronium ions are discharged in this way, the equilibrium between undissociated water molecules and the hydronium and hydroxyl ions is disturbed in such a way that more water molecules will dissociate as hydronium ions are discharged.

$$2H_2O \rightarrow H_3O^+ + OH^-$$

This results in an increase in the hydroxyl-ion concentration, and the solution about the cathode becomes more basic.

In other than acid solutions, the concentration of the hydronium ion is so low that it is highly probable that the appearance of hydrogen at the cathode is the result of the direct reduction of water molecules by electrons.

$$2HOH + 2e^- \rightarrow H_2 + 2OH^-$$

3. Discharge of Anions.—To the anode migrate the negative ion of the electrolyte and the hydroxyl ion of water. At this pole a change must occur which liberates electrons to the pole and, therefore, must be an oxidation. In general, the simple nonmetal anions are more readily oxidized than the hydroxyl ion. The relative ease of oxidation decreases in the order $S^{=}$, I^-, Br^-, Cl^-, OH^-. Hence these ions are more readily discharged than the hydroxyl ion.

$$S^{=} \rightarrow S + 2e^-$$
$$2I^- \rightarrow I_2 + 2e^-$$
$$2Br^- \rightarrow Br_2 + 2e^-$$
$$2Cl^- \rightarrow Cl_2 + 2e^-$$

When the negative ion of the electrolyte contains oxygen, as in the cases of the sulfate and nitrate ions, oxygen gas is evolved by the reaction

$$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$$

or, more simply,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

and the solution becomes acidic in the neighborhood of the anode.

4. Typical Electrolyses.—Let us apply these general rules to the electrolysis of solutions of several typical electrolytes. In a solution of cupric chloride, there are four ions Cu^{++}, Cl^-, H_3O^+, and OH^- in addition to water molecules. Upon electrolysis, cupric ions will be discharged at the cathode

$$Cu^{++} + 2e^- \rightarrow Cu$$

and chloride ions at the anode

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

In this example both of the ions of the salt are discharged.

If a solution of sodium sulfate is subjected to electrolysis, the products are hydrogen at the cathode

$$2HOH + 2e^- \rightarrow H_2 + 2OH^-$$

and oxygen at the anode

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Neither ion of the salt is discharged.

5. Electrolytic Conduction.—From the foregoing discussion, it is evident that the current of electricity does not pass through the solution as it does through a metallic conductor. The effect, however, is the same, for electrons are removed from the cathode by the discharge of the positive ions and other electrons are deposited on the anode by the negative ions. In metallic conduction, a continuous stream of electrons moves through the metal. We should also note that oxidation or a loss of electrons takes place when negative ions are discharged at the anode, and that reduction takes place when positive ions gain electrons at the cathode.

6. Electroforming of Metals.—Since the electric current shows a reducing action at the cathode, it may be used to reduce the ions of active metals to neutrality, provided the voltage is high enough (40-13). This, however, cannot be done in aqueous solution, for the hydronium ion of water would then be discharged instead of the ion of the active metal. Fortunately, electrolysis can be carried out in the absence of water by passing the current through a melted electrolyte. Fusion as well as solution gives mobility to the ions, which are fixed in the solid crystal, and permits them to move in an electrostatic field.

The discovery of the voltaic or electrochemical cell, by Volta, an Italian physicist, about the year 1800 made possible for the first time the production and the study of electric currents. Sir Humphry Davy, at that time the secretary of the Royal Society of London, soon began experiments at the Royal Institution with what was then probably the largest voltaic battery in the world. By 1807, he reported the preparation of sodium and potassium by the electrolytic decomposition of fused sodium and potassium hydroxides. His own words used in reporting this epoch-making discovery will interest you.

> Under these circumstances, a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower or negative surface there was no liberation of elastic fluid; but small globules, having a high metallic luster, and being precisely similar, in visible characters to quicksilver, appeared; some of which burnt with explosion, and bright flame, as soon as they were formed, others remained, and were merely tarnished, and finally covered with a white film which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash.

In the next year he was able to report the isolation of the elements of barium, calcium, and magnesium for the first time, again by the same means.

Today, the metals sodium and magnesium are being made on a commercial scale by methods that are essentially the same as those used by Davy over one hundred years ago.

7. Metallurgy of Sodium.—The alkali metals lithium, sodium, potassium, rubidium, and cesium are placed in Group I of the periodic table. These metals may be prepared by the electrolysis of their fused chlorides or hydroxides. Sodium is the only metal of the group prepared in large quantities commercially.

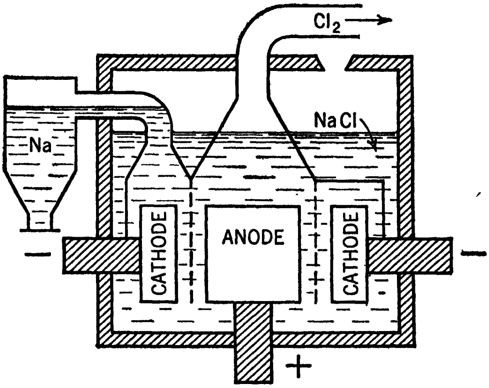

FIG. 149.—Downs cell.

In the Downs cell (Fig. 149), the melted chloride (m.p. 800.4°C.) is subjected to electrolysis. Chlorine gas forms at the carbon anode.

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

The metal in the liquid state is formed at the cathode

$$Na^+ + e^- \rightarrow Na$$

rises through the molten salt, and runs over into a trap from which it can be withdrawn.

The Castner process employs the more expensive but more easily melted sodium hydroxide (m.p. 318.4°C.). At this temperature, the hydroxyl ion is dissociated to a certain extent into hydrogen and oxide ions. The latter is discharged at the anode

$$2O^{=} \rightarrow O_2 + 2e^-$$

and both sodium and hydrogen ions at the cathode

$$2H^+ + 2e^- \rightarrow H_2$$
$$Na^+ + e^- \rightarrow Na$$

The world production of sodium is about 25,000 tons annually. The alkaline earth metals calcium, strontium, and barium of Group II are prepared similarly.

8. Sources of Magnesium.—The need of light, strong alloys for airplanes and in the pistons of high-speed engines has increased tremendously the demand for magnesium since the outbreak of the Second World War. This is shown in Fig. 150. The total production for the last war of 284,000 lb. was used almost entirely for the manufacture of flares, which made use of the brilliant white light of burning magnesium. Now it is planned to increase the capacity of this country to produce magnesium to 400,000,000 lb., which has been characterized as "far beyond even unreasonable requirements." In any case, it would seem fair to predict that the use of magnesium after the war will be so widespread that it will take its place with the common metals.

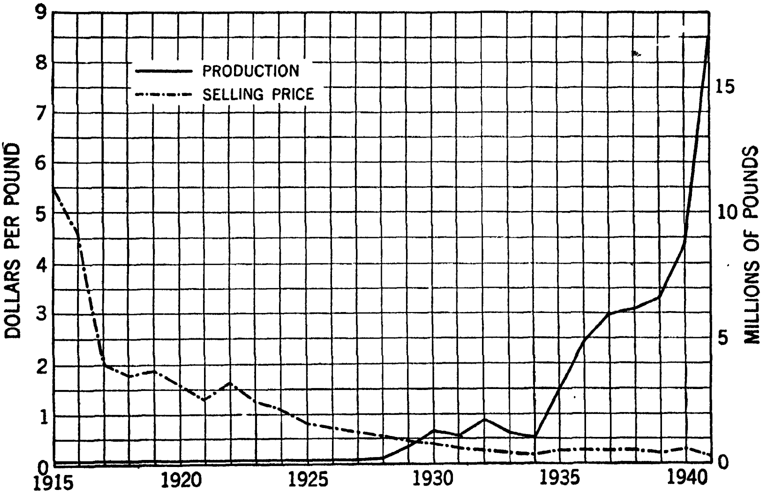

FIG. 150.—Production of magnesium.

The magnesium ion accounts for but 3.73 per cent of the weight of the salts dissolved in sea water. The average salt content of all the oceans is about 3.5 per cent. Nevertheless, there are 9 billion tons of magnesium in every cubic mile of sea water. Occasionally, a body of salt water is cut off from the ocean by an upheaval of the ocean bottom and a salt lake results. As time goes on, the salts in it become more concentrated by evaporation until eventually they begin to crystallize out of solution; and salt beds form. In these, magnesium appears as carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, and to a lesser extent as the sulfate, $MgSO_4 \cdot H_2O$. The natural brines at Midland, Mich., contain as much as 10 per cent of magnesium salts. We have mentioned that whole mountain ranges are composed mainly of dolomite $CaCO_3 \cdot MgCO_3$, and the occurrence of magnesite, $MgCO_3$.

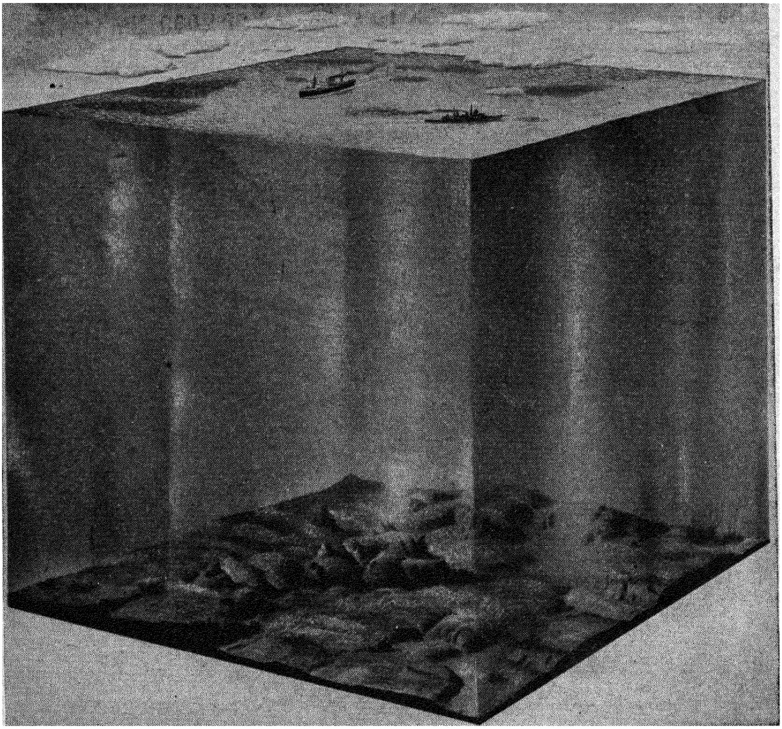

Fig. 151.—There are nine billion tons of magnesium in one cubic mile o sea water. (*Courtesy of the Dow Chemical Company.*)

9. Magnesium Chloride from Sea Water.—At a mammoth plant at Freeport, Tex., magnesium is precipitated as magnesium hydroxide from sea water. Oyster shells ($CaCO_3$) from Galveston Bay are heated in kilns to form lime, CaO,

$$CaCO_3 \rightarrow CaO + CO_2$$

which is then slaked with water

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The slaked lime is added to sea water until the pH has risen to 11, whereupon the hydroxide precipitates.

$$Mg^{++} + 2OH^- \rightarrow Mg(OH)_2$$

This is treated with hydrochloric acid, a by-product of the final electrolysis (see below), and magnesium chloride is formed.

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2HOH$$

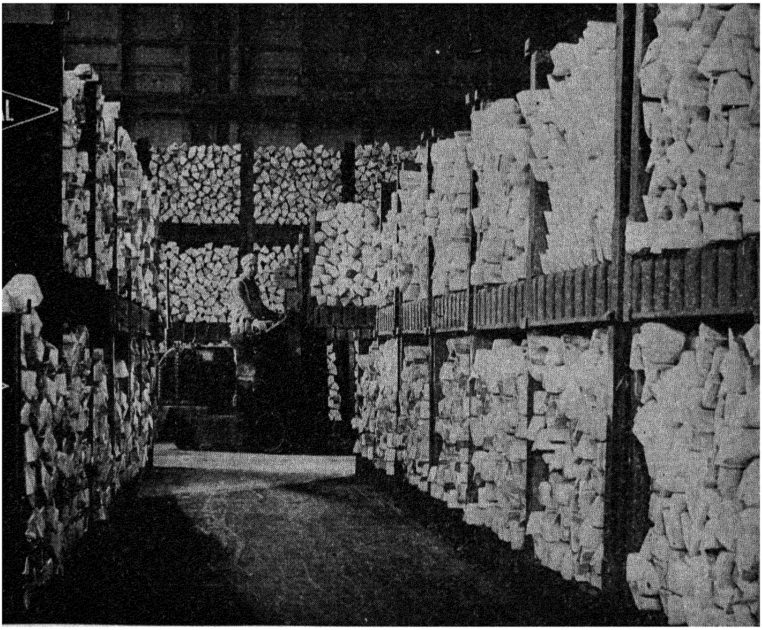

FIG. 152.—Magnesium ingots in storage. (*Courtesy of the Dow Chemical Company.*)

10. Electroforming of Magnesium.—The metal is obtained by the electrolysis of the fused chloride obtained from sea water or from the Michigan brines. A steel tank serves as the cathode from which the molten metal rises to float on the surface of the chloride. Chlorine is formed at the graphite anode.

Hydrochloric acid for the solution of the hydroxide precipitate is obtained by the following reaction between the chlorine, obtained from the electrolysis, air, and natural gas which is abundant in this region:

$$4Cl_2 + 2CH_4 + O_2 \rightarrow 2CO + 8HCl$$

11. Magnesium from Magnesite and Dolomite.—In California, magnesium is obtained from magnesite by carbon reduction, the Hansgirg process.

$$MgCO_3 \rightarrow MgO + CO_2$$
$$MgO + C \rightarrow Mg + CO$$

The Pidgeon process reduces magnesium oxide, obtained from dolomite, by silicon in the form of ferrosilicon.

$$MgCO_3 \rightarrow MgO + CO_2$$
$$CaCO_3 \rightarrow CaO + CO_2$$
$$2MgO + Si \rightarrow 2Mg + SiO_2$$

Finally the calcium oxide reacts with the silica to form an infusible dicalcium silicate. These reactions are carried out at 1150°C. and under diminished pressure. The metal distills from the reaction mixture and is condensed in a condenser attached to the retort.

12. Aluminum.—This element was first isolated in 1827 by reducing aluminum chloride by metallic potassium.

$$AlCl_3 + 3K \rightarrow 3KCl + Al$$

In 1854, Henri Sainte-Claire Deville, with the financial backing of Emperor Louis Napoleon, was able to manufacture aluminum on a factory scale, using sodium, which he prepared electrolytically, to reduce aluminum chloride. At first (in 1855) aluminum sold at $90 a pound, but by 1886 its price was reduced to $12 and over 5,000 lb. were produced annually. In those days, aluminum was used to make jewelry. Paul Héroult, who later developed the process by which aluminum is manufactured today, tells the following amusing story:

> At that time I had a friend who since then became my partner, but for the time being we both were "dead broke." We had pawned everything in sight and also other things which were not in sight. Finally my partner had a bright idea. He brought from home a stick of aluminum about six inches long, which was valued very highly by his family as a personal souvenir of Sainte-Claire Deville. As we handed it to the pawnbroker, the latter said: "What is that—bar silver?"

We said: "Better than that, that is aluminum." "Aluminum," he said, "What is that?"

He weighed it in his hand and said: "Why! Is that hollow?"

We said: "No, that is aluminum and it is worth 120 francs per kilo."

After some thought he said: "Well, I will give you 2 francs for it."

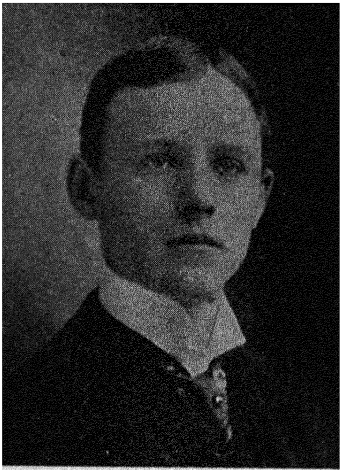

Fig. 153.—Charles Martin Hall. (*Courtesy of Aluminum Company of America.*)

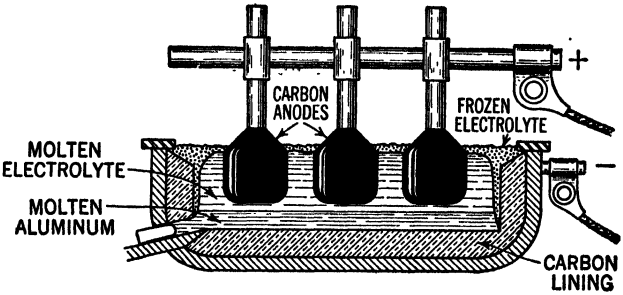

Fig. 154.—Preparation of aluminum by electrolysis.

In 1886, two young men, working independently, one in France (Héroult) and the other in this country (Hall), discovered the same process for making aluminum electrolytically. Charles Martin Hall, the American, was then twenty-two years of age and had been graduated from Oberlin the year before. Héroult was of the same age. Their process consisted in dissolving a purified form of the mineral bauxite, Al_2O_3, in melted cryolite,

Na_3AlF_6, and in passing a current of electricity through this melt at a sufficiently high voltage to reduce the aluminum at the cathode (Fig. 154):

$$Al^{+++} + 3e^- \rightarrow Al$$
$$2O^{--} \rightarrow O_2 + 4e^-$$

In 1888, a small plant was in successful operation at New Kensington near Pittsburgh, Pa. This plant produced aluminum for $2 a pound at the start. Soon larger plants were erected at Niagara Falls N. Y., and the price of aluminum dropped until now its market price is around 20 cents a pound. With this price reduction, there came many new uses of aluminum from the prosaic pots and pans of the kitchen to the ribs of a mighty Zeppelin. Hall tells the story of his success in his address of acknowledgment of the Perkin Medal in the *Journal of Industrial and Engineering Chemistry*, Vol. 3, page 143, March, 1911. You will find it most interesting.

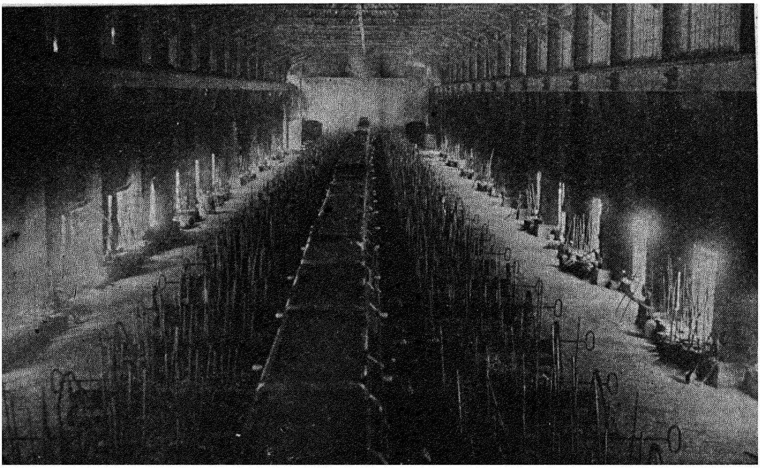

FIG. 155.—Cell room for the electrolytic production of aluminum. (*Courtesy of Aluminum Company of America.*)

EXERCISES

1. How does the electromotive series of metals help in predicting what products are obtained at the cathode during electrolysis?
2. Why is it impossible to obtain aluminum by subjecting an aqueous solution of a salt of this metal to electrolysis?
3. What evidence is there that water may be a diprotic acid?

4. Explain why the solution around the cathode becomes basic when potassium sulfate solutions are electrolyzed?

5. Why in the above case does solution around the anode become acidic?

6. Predict the products at each electrode when solutions of the following salts are subjected to electrolysis: $AgNO_3$, $ZnCl_2$, NaI, and Na_2CO_3.

7. How is magnesium extracted from the sea? What nonmetal is now prepared from this same source?

8. How is aluminum prepared?

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CHAPTER FORTY-SIX

METALLURGY

Our anthropoid ancestors learned to use stones as tools long before they descended from the treetops. Darwin tells of an ape that used a stone to crack nuts and carefully hid it under the straw of his bed for future reference. Early man discovered that flint could be chipped and that the chipped edge was sharp. For some one hundred thousand years thereafter, he contented himself with tools and weapons of stone until he discovered the use of metals. Certain of these occur free in nature in small quantities. Among these silver and gold first attracted his attention. As early as 5000 B.C., the Egyptians were making jewelry and dishes of these precious metals with exquisite craftsmanship. Copper also occurs free in nature but in rather small quantity. Iron, the most useful metal of all, is seldom found free, and then only in meteorites and in relatively small masses in Greenland. The great bulk of the metals of the world lie beneath the surface combined with other elements. It was not until after the art of smelting these ores was discovered by man that metals began to play any important role in his life.

The fact that copper and tin could be obtained from their oxide ores by smelting with charcoal was discovered very early, as was the fact that the addition of small amounts of tin to copper produced a hard alloy, bronze, from which edged tools of a far superior quality could be made. This discovery marked the beginning of the Bronze Age in Greece some five thousand years ago. Oddly enough, the metallurgy of iron seems to have been worked out some eight hundred years later in Greek and Roman history, although iron ores are far easier to smelt. In India, the art of smelting iron ores was developed at an early date. About A.D. 500 a pillar of pure iron, weighing 55 tons and rising to a height of 24 ft., was erected at Kytub near Delhi.

1. Metallurgy.—An *ore* may be defined as a mineral that contains a metal in sufficient quantity to make its extraction profitable. An iron ore must contain at least 50 per cent iron to be classed as a good ore. On the other hand, ores containing as little as 2 per cent or even less of copper or nickel are worth mining. *Metallurgy* is the art of extracting metals from their ores. The more active a metal, the less likely will be its occurrence in the free, or *native*, state. The metals at the bottom of the electromotive series are, however, found native. Gold, silver, platinum, and copper are all found native and so is mercury, although this heavy liquid is found only occasionally where it has been trapped in pockets in the rock. Oxide ores are rather common. Some of these are very important. Hematite, Fe_2O_3, is the most important iron ore. Other oxide ores include bauxite, $Al_2O_3.3H_2O$; magnetite, Fe_3O_4; limonite, $Fe_2O_3.3H_2O$; and cassiterite, SnO_2. Sulfide ores are very abundant and many of them are important: sphalerite, ZnS; galena, PbS; chalcocite, Cu_2S; cinnabar, HgS; and argentite, Ag_2S. Of the carbonates found in nature, siderite, $FeCO_3$; smithsonite, $ZnCO_3$; cerussite $PbCO_3$; magnesite, $MgCO_3$; and certain carbonates of copper are the only ones of any importance as ores. Calcium carbonate, $CaCO_3$, or calcite, however, is important as a building stone in the form of limestone or marble, as a flux in metallurgy, and as the material from which lime, CaO, is obtained.

The compounds of the more active metals, potassium, sodium, and magnesium, found in nature, are usually soluble chlorides or sulfates. These are found in the sea and to a lesser extent in salt deposits, formed by the drying up of salt lakes.

Since most metallic ores are compounds, the problem of metallurgy consists in devising methods by which the elements, combined with the metals in their ores, can be removed from them. The removal of the rocky materials, or gangue, with which the ore is mixed is still another problem. A metallurgist is sometimes working with a material 98 per cent of which he does not want to get the 2 per cent that he does. Usually a *flux* is added to aid in the removal of the gangue. When the gangue is acidic, a basic flux is added, and vice versa. The gangue is usually composed of sand or sandstone (mainly SiO_2) and of silicate rocks. As such it is acidic. The silicate rocks melt readily at furnace temperatures but the silica, SiO_2, does not. The flux used to remove the silica is limestone. This decomposes into lime and carbon dioxide when heated.

$$CaCO_3 \rightarrow CaO + CO_2$$

The basic lime then reacts with the acidic silica to form the readily fusible calcium silicate.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

The melted silicates form a *slag* that is insoluble in and floats on top of the molten metal. The two liquid layers can then be tapped off at different levels.

2. Typical Metallurgical Operations.—Most ores contain small percentages only of the metal for which they are mined. These ores must, therefore, first be concentrated. The ore is usually crushed, ground, and then shaken with water which washes off the lighter rocky impurities. Sometimes a little oil, which will adhere to the ore particles but not to the gangue, is added to a suspension of finely ground ore in water and air is blown through. The oil rises to the surface as a froth (44-6), carrying the ore particles with it. The gangue falls to the bottom in the water layer. This process of *oil-froth flotation* has been extremely valuable in the concentration of low-grade copper ores.

If the ore is a native metal, little need be done after concentration. The ore is sometimes melted with a suitable flux as in the case of copper. Gold and silver are either dissolved out from the gangue with a cyanide solution or amalgamated[1] with mercury by washing the crushed ore over amalgamated copper plates. The amalgam of the precious metals is scraped from the plates and the mercury distilled off in a suitable retort. If these metals have been extracted by a cyanide solution, they are precipitated from the latter by the addition of metallic zinc which replaces the less active noble metals.

If the ore is an oxide, the oxygen is usually removed from combination with the metal by heating it with coke. Oxide ores of iron and tin, for example, are treated in this way.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$
$$SnO_2 + 2C \rightarrow Sn + 2CO$$

Sulfide ores are first roasted, *i.e.*, burned in a blast of air. The sulfur in them burns to the gas sulfur dioxide, and the metal is usually converted to the oxide except in the case of the inactive metals below copper in the electromotive series whose oxides

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[1] The alloys of mercury are called amalgams.

are unstable at the temperature of roasting.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$HgS + O_2 \rightarrow Hg + SO_2$$

The sulfur dioxide is not wasted but is usually converted into sulfuric acid. The oxide of the metal is then reduced with coke or by some other means.

Carbonate ores are first decomposed by heat into the oxide of the metal and carbon dioxide.

$$FeCO_3 \rightarrow FeO + CO_2$$
$$ZnCO_3 \rightarrow ZnO + CO_2$$

The oxide is then reduced to the free metal.

3. The Metallurgy of Tin.—The most important ore of tin is the oxide (SnO_2), cassiterite, or tinstone. The largest deposits are in the Malay States, the East Indies, and Thailand (Siam). Smaller deposits are found in China, Nigeria, and Bolivia. The tin of the ancient and medieval world was brought to centers of civilization by Phoenicians from the Islands of the Cassiterides as the British Isles were then known. These old tin mines were near Cornwall, England. The production of tin metal in 1939 was nearly 160,000 tons, of which 51 per cent was smelted in British Malaya, 25 per cent in the United Kingdom, 10 per cent in the Netherlands, 8 per cent in the East Indies, and 6 per cent in China. Although nearly 40 per cent of this tin was used in the United States, this country itself produces only a negligible amount. In May, 1941, construction was started on a tin smelter in Texas which is to use Bolivian ore to produce 18,000 tons annually.

After concentration and a preliminary roasting to convert metal-sulfide impurities to oxides, the ore is readily reduced with carbon.

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

The low melting point of tin (232°C.) makes it possible to melt the metal away from other metal impurities.

4. Iron Ores.—Iron is probably the most abundant of all the elements. The earth's core for a distance of some 2,000 miles from the center is probably nearly pure iron. This we assume from the high density of the earth as a whole as compared with that of its crust, from the fact that the earth is magnetic, and from the known composition of meteorites. In the earth's crust, however, it is the fourth element in abundance and occurs to the extent of 5 per cent. Since man has never bored into the earth for a greater distance than a mile and a half, it is unlikely that the tremendous store of iron that lies some 1,500 miles beneath the earth's surface will ever be tapped.

Few of us have ever seen pure iron. A silver-white metal, it tarnishes quickly upon exposure to moist air, first becoming black and then red. Because of the ease with which iron corrodes and the nonprotective character of its oxide, very little iron is found native in the earth's crust. As might be expected, its oxide ores are the most important. Of these hematite, or ferric oxide, Fe_2O_3, is the chief American ore. The largest deposits in the world are of hematite in the Lake Superior region of this country near Marquette, Mich., and Duluth, Minn. These supply over 85 per cent of the iron ore used in the United States. Another important iron-ore bed extends from New York to Alabama in the Appalachian Mountains.

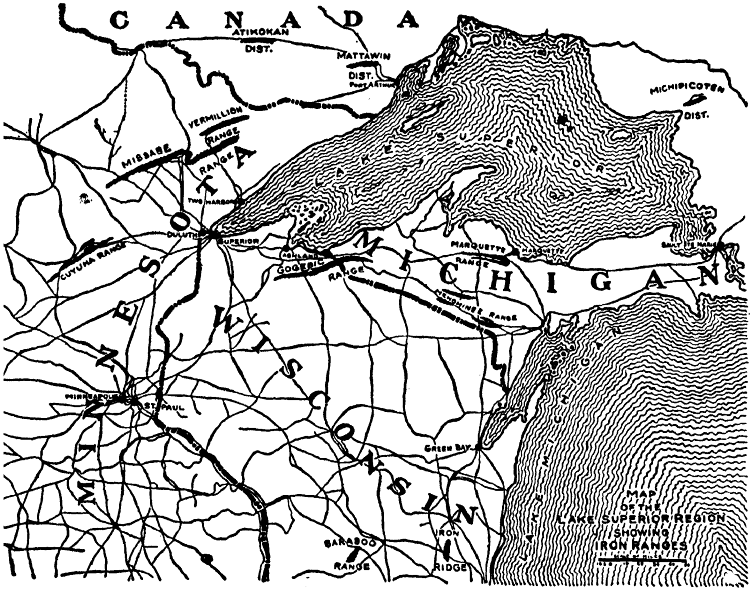

FIG. 156.—Location of ore ranges in Minnesota, Wisconsin, and Michigan.

Other oxide ores of iron are magnetite, Fe_3O_4, the black, magnetic oxide of iron, and limonite, $Fe_2O_3.3H_2O$, or bog iron ore. The latter was extensively mined during colonial times in this country. A carbonate ore siderite, $FeCO_3$, is of very small importance in this country but is mined extensively in England. Iron pyrite, a sulfide of iron (FeS_2), is not used as an iron ore but is mined as a source of sulfur (36-1).

5. The Blast Furnace.—The first step in the metallurgy of iron consists in heating together iron ore, coke, and limestone in a blast furnace. This is a huge chimneylike structure, some 90 ft. high with a maximum diameter of 25 ft. Its principal parts are shown in Fig. 158. The charge is carried to the top of the furnace by a pair of skips which run up an inclined railway. It consists of ore, coke, and limestone in the proportions of 2 tons of ore to 1 ton of coke and ¼ ton of limestone. In the top of the furnace are two trap doors shaped like inverted cones. The charge falls upon the upper cone which is then lowered to allow the materials of the charge to fall upon the lower cone. The upper cone is then raised, sealing the top of the furnace, and the lower cone lowered which allows the charge to fall into the furnace. The stack and bosh are filled with solid materials held up in the furnace by the inclined walls of the bosh. Molten iron and slag drip from the solid materials into the crucible below. Preheated air is blown through a set of pipes called tuyères which enter the furnace below the bosh. The exhaust gases leave the furnace at

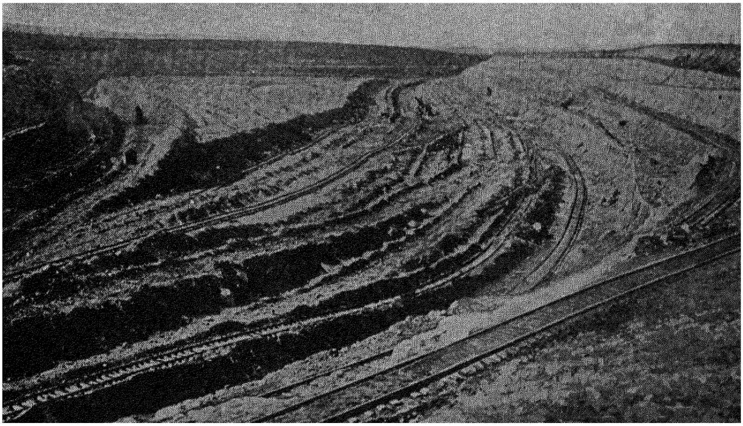

Fig. 157.—An open-pit iron mine. (*Courtesy of United States Steel Corporation.*)

the top through a large pipe called the downcomer. The furnace is encased in steel plates and lined with firebrick.

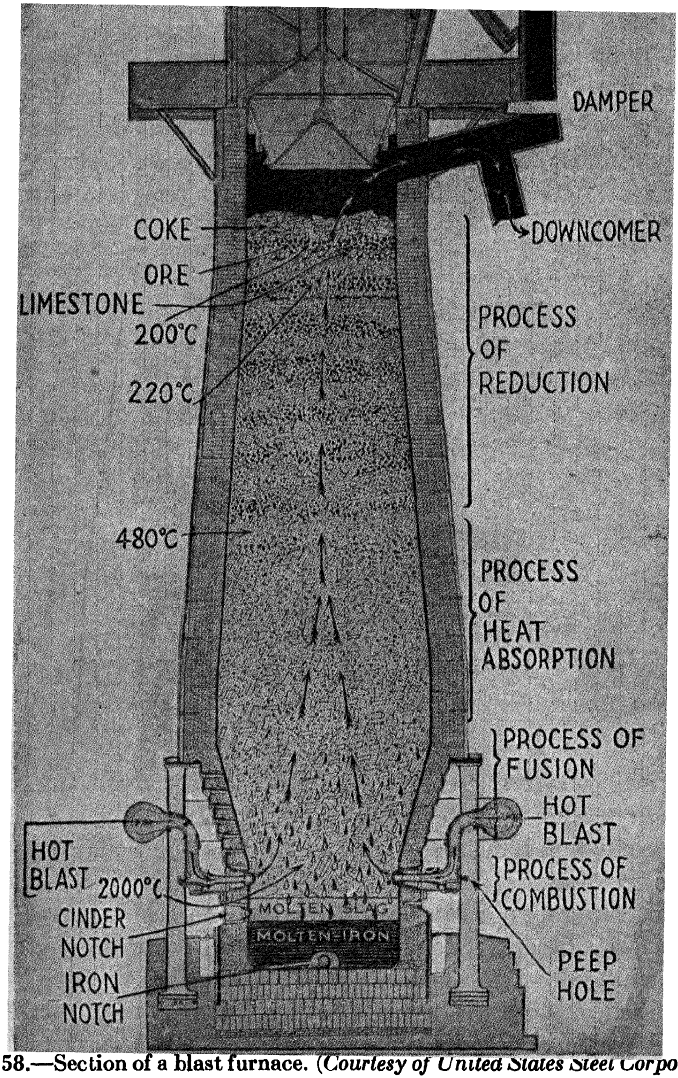

Fig. 158.—Section of a blast furnace. (*Courtesy of United States Steel Corporation.*)

The blast furnace has two functions: to reduce the ore to metallic iron, and to remove the gangue as slag. Coke is added to the ore to accomplish the former and limestone, the latter function. Let us see how this is done. At the tuyères, the coke burns fiercely in an excess of air to carbon dioxide and generates a temperature of some 2000°C.

$$C + O_2 \rightarrow CO_2$$

Almost immediately, the carbon dioxide is reduced to the monoxide as it filters through the supernatant layers of hot coke.

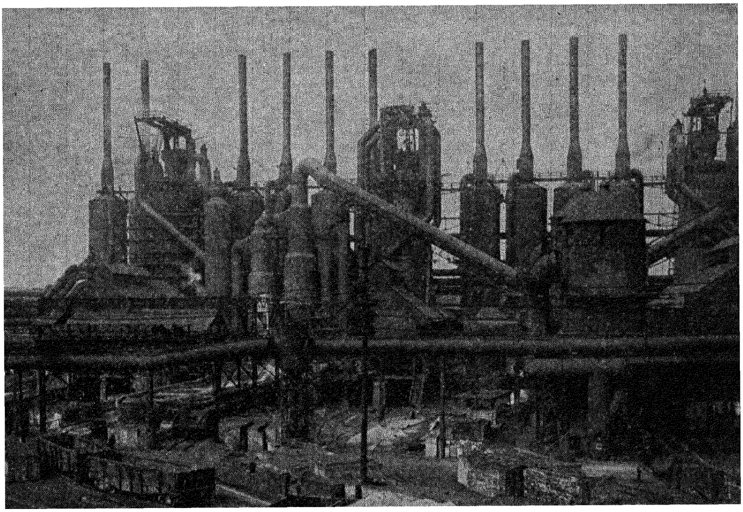

FIG. 159.—Blast furnaces and stoves. (*Courtesy of United States Steel Corporation.*)

$$C + CO_2 \rightarrow 2CO$$

The ore is, therefore, bathed in this gas which reduces it to metallic iron.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

This reduction probably takes place in steps.

$$\begin{gathered} 3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \\ Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \end{gathered}$$

The metal in the liquid state drips down into the crucible from which it can be tapped from time to time through the iron taphole.

The ore contains a gangue of readily fusible silicates and the less fusible silica, SiO_2. The flux of limestone is added to react with silica and convert it into the lower melting calcium silicate. Near the middle of the stack, the limestone decomposes into lime and carbon dioxide.

$$CaCO_3 \rightarrow CaO + CO_2$$

Further down, the lime combines with the silica, forming calcium silicate.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

This, together with the already melted silicates of the gangue, drips into the crucible and floats as a slag on top of the molten iron. It is tapped off through the cinder notch.

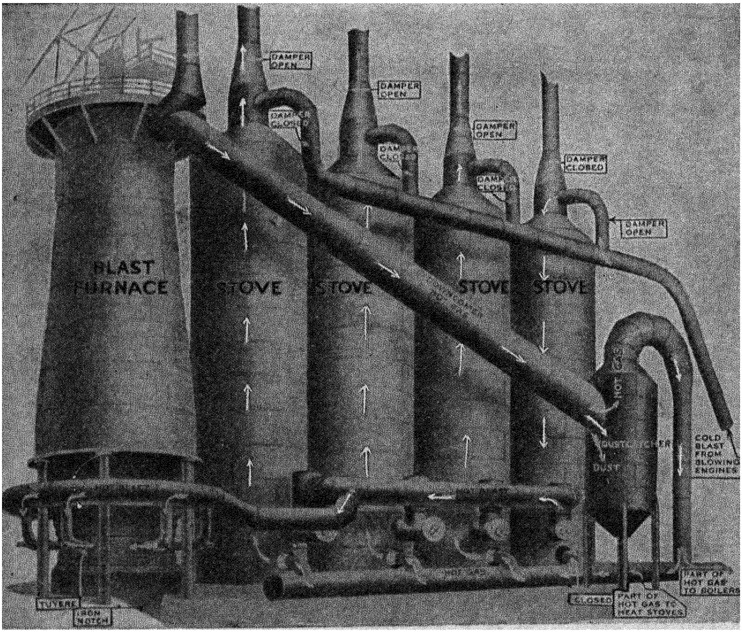

FIG. 160.—How the air blast is heated. (*Courtesy of United States Steel Corporation.*)

The slag does not carry with it all the impurities in the original ore. Some are reduced and find their way into the metal product, *e.g.*, manganese, phosphorus, silicon, and sulfur.

$$MnO_2 + 2C \rightarrow Mn + 2CO$$
$$SiO_2 + 2C \rightarrow Si + 2CO$$
$$Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5$$
$$P_2O_5 + 5C \rightarrow 2P + 5CO$$

6. The Products of the Blast Furnace.—There are three products of the blast furnace: flue gas, slag, and pig iron.

The flue gas, because of its high temperature and its content of carbon monoxide, contains considerable heat value. Part of this gas is burned in the hot blast stoves that preheat the air blast. Each furnace has four of these, each of which is as large as the furnace itself and is filled with a checkerwork of firebrick. A mixture of blast-furnace gas and air burns in two of the stoves to heat up its checkerwork, while fresh air for the blast furnace is heated by the other stoves. Every half-hour the flow of gas and air is reversed, so that newly heated stoves can now heat the air blast and the cooled stoves can be heated again by the burning fuel gas. Not all of the fuel value of the gas is extracted by the stoves. The remainder is burned for power for the entire steel plant.

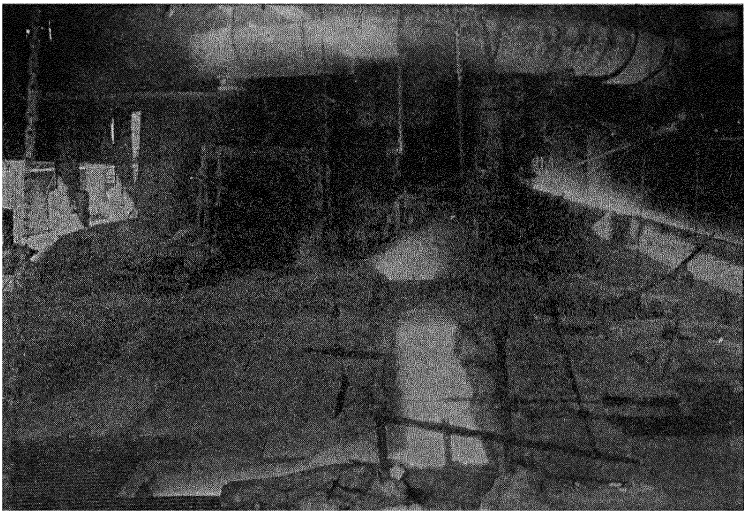

FIG. 161.—Tapping a blast furnace. (*Courtesy of United States Steel Corporation.*)

The slag consists mainly of silicates of calcium, magnesium, aluminum, and iron. It is used to some extent in cement manufacture and, combined with tar, in road paving.

The metal product is called pig iron, or cast iron. It contains 2 to 4.5 per cent carbon, 0.7 to 3 per cent silicon, 0.1 to 0.3 per cent sulfur, 0 to 0.1 per cent phosphorus, and 0.5 to 1 per cent manganese. Over three-quarters of the pig iron produced by the blast furnaces of this country is converted into steel. The remainder is cast into ingots called pigs weighing about 150 lb. each. It is hard and brittle, and its ductility and tensile strength are low. In compressive strength, however, it is high. It has a lower melting point than pure iron because of its impurities and can readily be cast in intricate molds. It cannot be forged.

The operation of the blast furnace is continuous until repairs of the lining become necessary. Some furnaces have been kept in operation for several years. The average furnace will produce daily 1,000 tons of pig iron, 400 to 500 tons of slag, and 1,400 tons of flue gas. This country produces about 50,000,000 tons of pig iron annually.

7. Wrought Iron.—The eighteenth century had no use for steel, but it did need a form of iron that could be forged. Before the introduction of large numbers of blast furnaces, old forge iron was made in small quantities at a time by heating together bog iron ore and charcoal. The slag was hammered out while the iron was reheated in "finery" forges from time to time. This produced an iron that was purer than pig iron and for this reason was a malleable form. With the introduction of the blast furnace, however, iron was made in larger quantities but in a form that could not be forged because its high carbon content had rendered it brittle. This iron had to be purified in hearths and with hammers before it could be wrought.

Then, in 1784, Henry Cort, an Englishman, invented the puddling furnace for converting pig iron into wrought iron. This consists of a low hearth, a grate behind a low partition, upon which a fire is built, and an arched roof to reflect the flame down upon the hearth. The charge consists of 500 lb. of molten pig iron, low in sulfur and phosphorus, and some iron oxide, either as ore or rusty scrap iron. The latter acts as an oxidizing agent, oxidizing the carbon of the pig iron into carbon monoxide which burns further to the dioxide when it bubbles to the surface of the iron.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$
$$2CO + O_2 \rightarrow 2CO_2$$

The silicon and manganese are also oxidized in a similar manner, but the oxidization products in this case are solids and form a slag. As the purity of the iron becomes greater, its melting point rises until it partially solidifies to a pasty mass. This is rolled into several balls, each weighing about 150 lb. These are removed from the furnace, dripping with slag, and squeezed between the jaws of a "squeezer" to force out as much of the slag as possible. There is usually about 1 per cent of slag in wrought iron. It is tough and tenacious and does not rust so readily as steel or pig iron. Most of the wrought iron is used directly for making chains, anchors, bolts, etc., but some is converted into crucible, or tool, steel.

The invention of the puddling furnace led to a much wider use of iron. Anchor ropes were replaced by anchor chains of malleable iron. Wooden pipes no longer carried water and gas to the cities. The wooden rails, along which coal cars were pushed, were gradually replaced by rails of malleable iron. Small amounts of steel were made by the costly cementation process, by heating together wrought iron and charcoal in a closed retort at red heat for days. In this way the carbon slowly penetrated the iron; and a very excellent quality of steel was the result. Such steels are made today and are converted into cutlery, edged tools, gun barrels, and the drive shafts of steamships, but they are much too costly for large-scale use. The industries and the railroads about 1850 were crying for a cheap steel.

8. Steel.—The high carbon content of pig iron is responsible for the hardness and brittleness of this form of iron. Traces of phosphorus make iron very brittle when cold, whereas a small amount of sulfur will do the same thing to the hot metal. The complete removal of these impurities results in a soft, tough product of high malleability but of low tensile strength and incapable of holding a cutting edge. Steel is a form of iron that contains between 0.5 and 1.5 per cent carbon; enough to increase the hardness and tensile strength of pure iron but not enough to make the iron so brittle that it cannot be machined.

9. The Bessemer Process.—In 1855, Sir Henry Bessemer introduced the steelmaking converter that bears his name and revolutionized the iron and steel industry. The Bessemer converter (Fig. 162) is a pear-shaped steel vessel, 12 to 20 ft. high and 10 to 16 ft. in diameter. It is lined to a thickness of 20 to 30 in. with a siliceous refractory material held together with fire clay. This lining is acidic in character since it is made up largely of a nonmetallic oxide (SiO_2). The converter is mounted on trunnions on which it can be tilted to pour out its charge. One of these is hollow to admit a blast of air into the converter through 15 tuyères in its bottom. Each tuyère is some 30 in. long and 6 in. in diameter and has eight $\frac{9}{16}$-in. holes running from top to bottom through which the air enters the charge.

Molten pig iron is tapped from the blast furnace every 4 hr. and run into a train of huge ladles which carries it to the mixer, a large reservoir from which the molten metal is withdrawn from time to time to charge a Bessemer converter. The charge, consisting of about 20 tons of molten pig iron, is poured from a ladle into the top of the converter in its horizontal position. The air is then turned on and the converter tipped back to vertical. The impurities, carbon, silicon, and manganese, burn violently in the air blast, actually raising the temperature of the charge. The silicon and manganese burn away first, followed finally by carbon. The flame is at first an orange-yellow tinged with blue. Then when carbon alone remains, the flame becomes brighter and is accompanied by a shower of sparks. Finally, the flame dies down and, since the melting point of iron rises as the impurities are removed and as there is no other source of heat than the combustion of these impurities, the charge must then be poured or it would freeze in the converter. The blow lasts 10 to 15 min. Since the charge is now nearly pure iron, the proper amount of carbon,

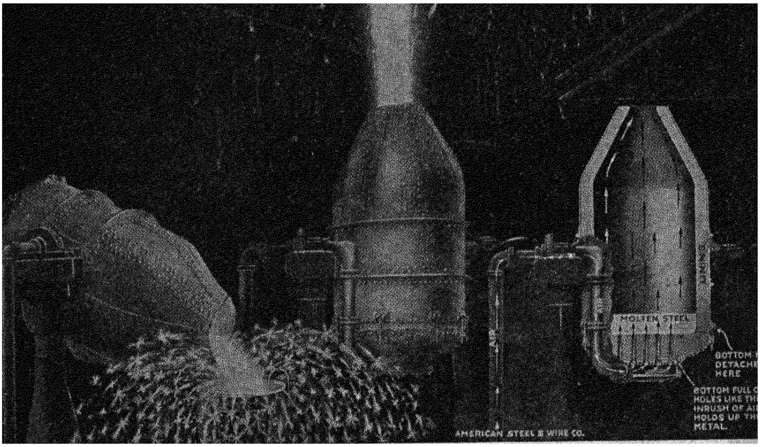

FIG. 162.—The Bessemer converter. (*Courtesy of United States Steel Corporation.*)

manganese, and silicon is added in the form of spiegeleisen, a high-carbon iron alloy, to produce a steel of the desired properties. The manganese removes any combined oxygen from the iron, and the silicon combines with any trapped air bubbles.

The contents of the converter are poured into a ladle which is then carried to a position over a train of ingot molds. A plug in the bottom of the ladle is opened, and the molten steel pours into the molds below. The steel ingots, each weighing from 1,000 to as much as 8,000 lb., are taken to a soaking pit where they are kept at a uniform high temperature to relieve the stresses that develop when the metal solidifies in the mold.

The Bessemer converter produces a steel that is suitable for rails and construction purposes. It is slightly less expensive than the open-hearth process but is an inferior grade of steel. There are several reasons for this. In the first place, the blow is so short that control of its duration by chemical analysis of the metal is impossible. The composition of the finished product cannot, therefore, be regulated with the accuracy possible in the open-hearth process. Also phosphorus cannot be removed from pig iron by this process. This element is oxidized during the blow, but it does not enter the slag. It is reduced to free phosphorus again by the carbon added after the blow is complete. For this reason pig iron, whose phosphorus content is very low, must be used in the Bessemer. This means the smelting of a low-phosphorus ore in the blast furnace which is more expensive.

The invention of the Bessemer process for making steel was responsible for the tremendous expansion of the iron industry. Cheap steel was now available. The railroads responded, and mile after mile of new road beds were constructed. Literally thousands of new uses for steel were developed. Until about 1876, in this country all steel was manufactured in acid-lined converters. Vast quantities of iron ore with too high a content of phosphorus for this process lay undeveloped. Then came the introduction of the basic open-hearth process, and these ores immediately became available.

10. The Open-hearth Process.—In 1856, a few years after the invention of the Bessemer converter, the Siemens brothers developed a gas-fired, open-hearth furnace in England for the production of steel from pig iron. In 1864, the Martin brothers erected at the Sireuil Iron Works in France a Siemens furnace which introduced the regenerative principle of gas firing in this type of furnace. Such a furnace is shown diagrammatically in Fig. 163. These furnaces are built of steel and brick and are arranged several in a row. Each contains a shallow, oval-shaped

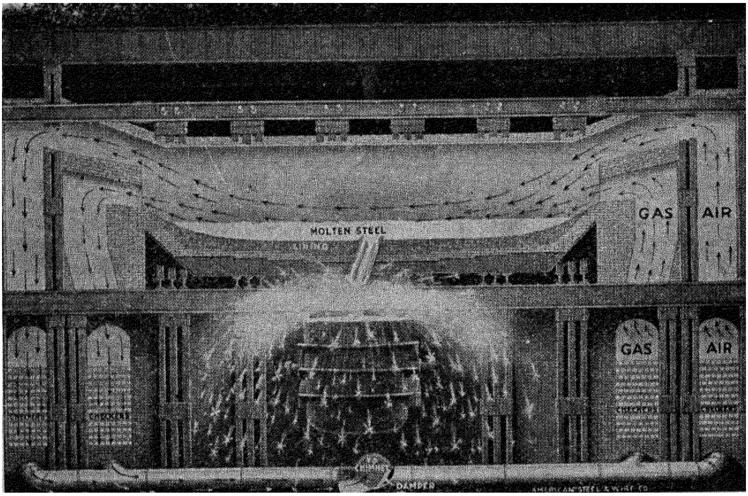

FIG. 163.—Diagram of an open-hearth furnace. (*Courtesy of United States Steel Corporation.*)

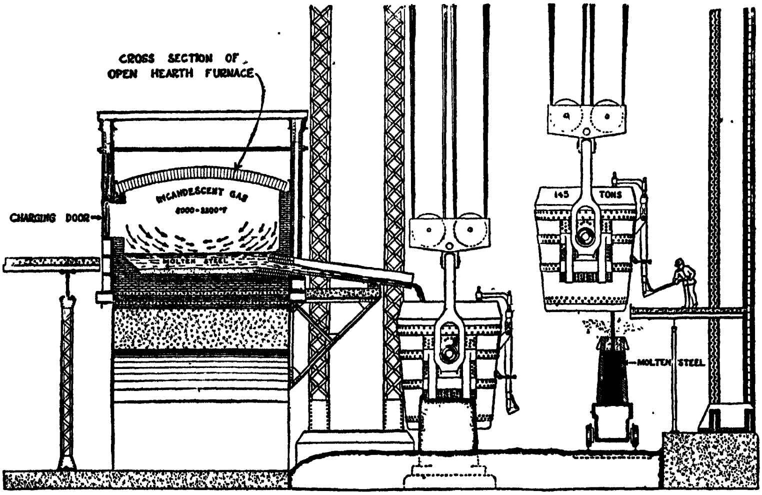

FIG. 164.—Cross-section of an open-hearth furnace. (*Courtesy of United States Steel Corporation.*)

basin, or open hearth, some 35 ft. long, 13 ft. wide, and 2 ft. deep capable of holding a charge of 75 tons. The hearth has a basic lining of magnesite, $MgCO_3$, or dolomite, $MgCO_3.CaCO_3$. These carbonates are decomposed into their respective oxides by the heat of the furnace

$$MgCO_3 \rightarrow MgO + CO_2$$
$$CaCO_3 \rightarrow CaO + CO_2$$

both of which, as oxides of metals, are basic oxides. A fuel gas, either natural or producer gas, and air are passed through separate flues over heated checker-brick and thence through ports into the furnace. Here combustion takes place and a flame as from a gigantic blast lamp plays over the charge in the hearth. The hot gases pass out through ports on the other side of the furnace where they heat the other sets of checker-brick. After about half an hour, the current of gases is reversed. Gas and air now pass over the freshly heated checkers and, in leaving the furnace, heat those which have been cooled on the opposite side.

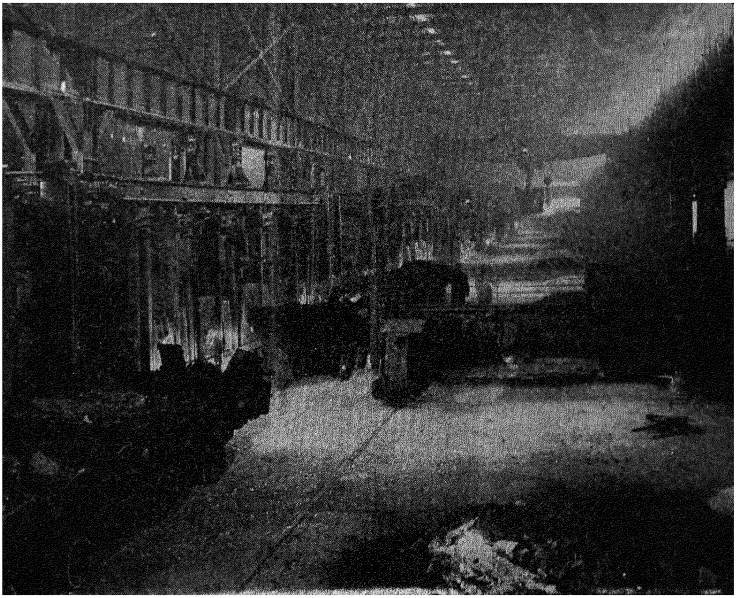

FIG. 165.—Charging platform of a battery of open-hearth furnaces. (*Courtesy of United States Steel Corporation.*)

In this way, the temperature constantly rises and an important fuel economy is accomplished.

The charge consists of pig iron, rusty scrap steel, iron ore, and limestone. First limestone, then scrap iron, and finally pig iron are dumped on the hearth through a door in the rear of the furnace by charging machines. Molten pig iron is poured from a ladle into the furnace through a door at its front. The heat of the burning gases melts the pig iron and decomposes the limestone flux.

$$CaCO_3 \rightarrow CaO + CO_2$$

Then the ore is added and an excess of air blown into the flame. The oxygen of this air together with that of the oxide ore oxidizes the impurities.

$$\begin{gathered}3C + Fe_2O_3 \rightarrow 3CO + 2Fe\\ 6P + 5Fe_2O_3 \rightarrow 3P_2O_5 + 10Fe\\ 3S + 2Fe_2O_3 \rightarrow 3SO_2 + 4Fe\\ 3Mn + Fe_2O_3 \rightarrow 3MnO + 2Fe\\ 3Si + 2Fe_2O_3 \rightarrow 3SiO_2 + 4Fe\end{gathered}$$

The oxides of carbon and sulfur, formed in this way, go off as gases. The remaining oxides react with each other and with the lime, CaO, of the flux to form slag.

$$\begin{gathered}3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2\\ CaO + SiO_2 \rightarrow CaSiO_3\\ MnO + SiO_2 \rightarrow MnSiO_3\end{gathered}$$

In this way all the impurities, including the phosphorus which the Bessemer converter cannot remove, are taken out of the molten metal. The course of these reactions is followed at first by dipping out a sample of the batch, allowing it to solidify, and noting its appearance when fractured. Toward the end of the run, the test blocks are sent to the chemical control laboratory for a rapid analysis. From the results of the analyses, the proper amount of spiegeleisen to add to the charge can be calculated. Aluminum is also added in small quantity to remove the oxygen from any ferric oxide that may have been formed. The furnace is then tapped (Fig. 166). A "heat" lasts 8 to 12 hr. The molten steel is cast in ingots and placed in soaking pits as in the case of Bessemer steel.

The basic open-hearth process offers certain advantages over the Bessemer:

1. The temperature can be controlled more accurately due to the use of an external source of heat and of iron ore as the oxidizing agent.
2. Pig iron from lower grade ores can be used.
3. The composition of the metal can be more accurately followed and controlled.

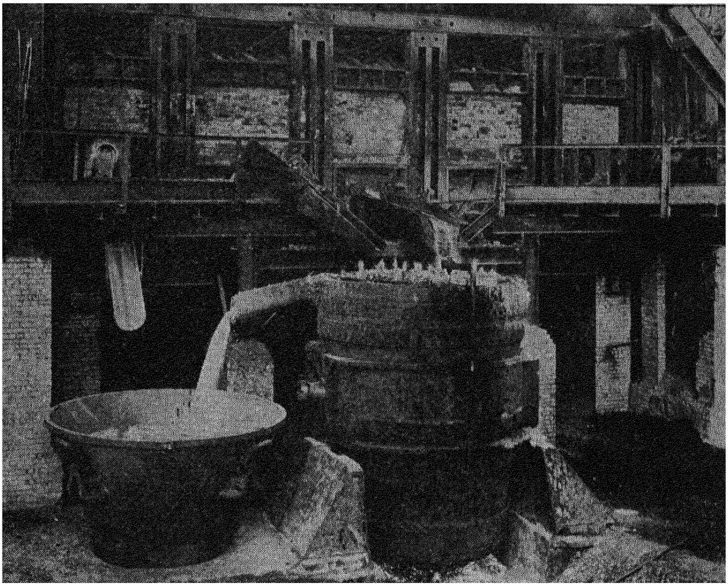

FIG. 166.—Tapping an open-hearth furnace. (*Courtesy of United States Steel Corporation.*)

4. Scrap iron and iron ore can be converted into steel requiring less pig iron and hence fewer blast furnaces for the production of the same amount of steel.

Since 1880, in this country the demand for open-hearth steel has steadily increased until today over three-fourths of the steel is produced in open-hearth furnaces.

11. The Electric Furnace.—A very high grade of steel is now being made in electric furnaces (Fig. 167). These are usually used to further refine Bessemer or open-hearth steel. They produce a denser steel that is free from blowholes due to occluded gases.

12. Aluminothermy.—Goldschmidt introduced the use of aluminum in place of carbon to remove the oxygen from oxide ores. Expensive, aluminothermy is used for preparing small quantities of very pure, carbon-free metals like manganese, tungsten, titanium, molybdenum, and vanadium which are subsequently alloyed with iron or copper.

13. Reduction of Sulfide Ores.—Of the common metals zinc, lead, nickel, copper, silver, and mercury occur as important sulfide ores. These ores are invariably roasted and then reduced to the free metal.

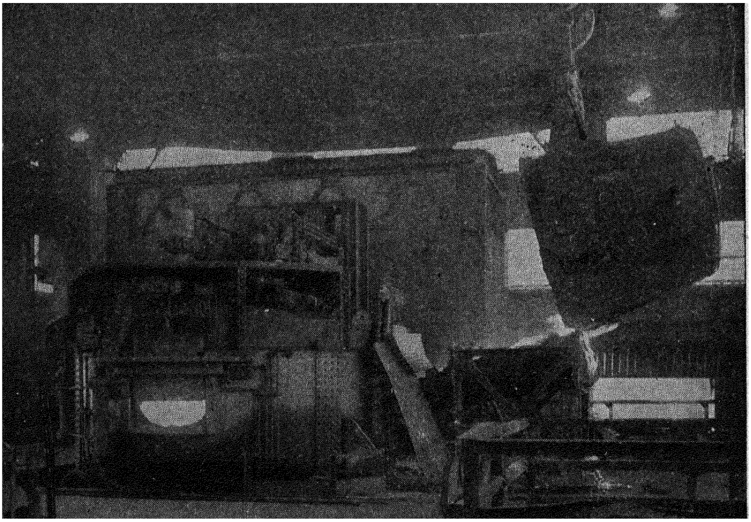

FIG. 167.—An electric steel furnace. (*Courtesy of United States Steel Corporation.*)

14. Metallurgy of Zinc.—The principal ores of zinc are the sulfide, sphalerite, ZnS, and the carbonate, smithsonite, $ZnCO_3$. Oklahoma, Kansas, Missouri, and New Jersey produce the greatest amounts. The sulfide ore is first concentrated by oil flotation and then roasted to the oxide.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

The oxide, mixed with fine coal, is heated white-hot in cylindrical clay retorts arranged in rows of four to six retorts in height and about one hundred long on both sides of a furnace heated by burning producer gas. Each retort contains about sixty pounds of roasted ore. Upon reduction the zinc distills into condensers

$$ZnO + C \rightarrow Zn + CO$$

from which the liquid metal is drawn to be cast in molds of cast iron. The ingots are sold as spelter.

A more recent process involves roasting the sulfide at lower temperatures to the soluble sulfate

$$ZnS + 2O_2 \rightarrow ZnSO_4$$

which is leached from the ore with dilute sulfuric acid. Upon electrolysis of this solution, zinc is deposited on the cathode. Of the total annual zinc production of 500,000 tons in the United States, this process produces over 100,000 tons.

15. Metallurgy of Mercury.—Mercury occurs chiefly as the red ore cinnabar, HgS, in Italy, Spain, Austria, Mexico, the United States (California and Oregon), and Japan. Since its oxide is unstable at the temperature at which the sulfide is roasted, the free metal distills away.

$$HgS + O_2 \rightarrow Hg + SO_2$$

16. Metallurgy of Lead.—This metal was well known to the ancient Egyptians and Romans. Its most important ore is galena, PbS; of lesser importance are cerussite, $PbCO_3$; anglesite, $PbSO_4$; and crocoite, $PbCrO_4$. The principal lead-producing state is Missouri, followed by Idaho, Utah, and Colorado. Mexico and the United States produce about half the world's annual production of 1,700,000 tons. The remainder is smelted in Spain, Australia, Germany, and Canada.

The ore is concentrated by oil flotation and then partially roasted to the oxide and the sulfate.

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \rightarrow PbSO_4$$

A blast furnace is then charged with roasted ore mixed with fresh ore, limestone, and coke. Here several different reactions result in the reduction of lead.

$$PbO + C \rightarrow Pb + CO$$
$$PbS + 2PbO \rightarrow 3Pb + SO_2$$
$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2$$

The iron oxide, present originally in the gangue, is reduced to the metal by coke and then does its share by reducing lead.

$$PbS + Fe \rightarrow Pb + FeS$$

The limestone removes silica as in the iron blast furnace.

Ores from the Rocky Mountain district contain silver and, in some cases, gold. Their extraction from molten lead by the Parkes process is profitable. A small amount of zinc, in which the noble metals are more soluble than in lead, is added to the molten lead. Insoluble in lead, the zinc extracts the noble metals. The upper zinc layer is skimmed off, and zinc is distilled away from the less volatile noble metals.

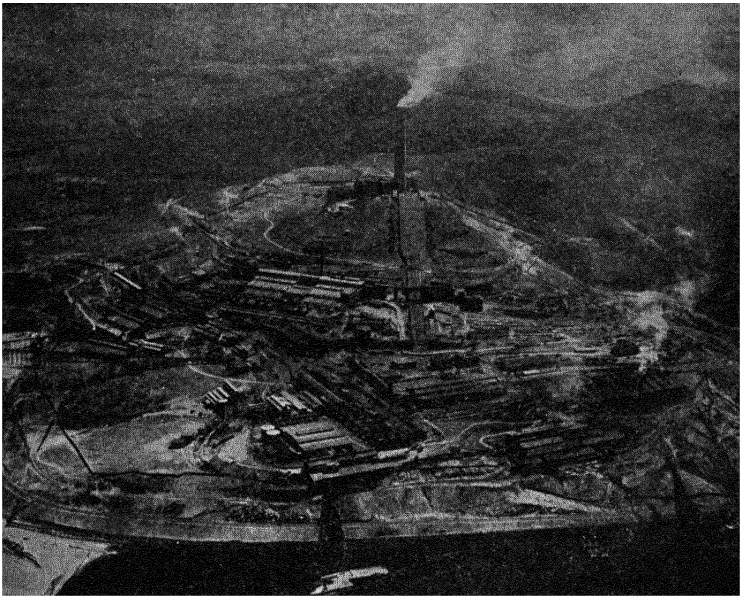

FIG. 168.—Aerial view of a copper smelting plant. (*Courtesy of Anaconda Copper Mining Company.*)

Lead may be refined electrolytically by the Betts process, which had best be discussed later (46-19).

17. Metallurgy of Copper.—Copper occurs mainly in sulfide and oxide ores. The most important copper ore in this country is chalcocite, or copper glance, Cu_2S. Large quantities of this mineral have been found in the Butte region of Montana and in the Bonanza mine in Alaska. Other sulfide ores are bornite, $3Cu_2S.Fe_2S_3$; chalcopyrite, $Cu_2S.Fe_2S_3$; enargite, $3Cu_2S.As_2S_5$; and covellite CuS. Cuprite, Cu_2O, is the most important oxide ore and is usually found in strata lying above sulfide ores. Among the other copper ores are malachite, $CuCO_3.Cu(OH)_2$; azurite,

$2CuCO_3.Cu(OH)_2$; and chrysocolla, $CuSiO_3.2H_2O$. Small amounts of copper occur native in the Lake Superior region.

The sulfide ores are first crushed and then reduced to a powder in ball mills. They are then concentrated by flotation, which saves 95 per cent of the copper in the ore and gets rid of two-thirds of the ore. The concentrated ore is next partially roasted to remove part of the sulfur and to convert any iron sulfide into the oxide, in which form it goes into the slag. From the roasting furnace the "calcine," as the roasted ore is now called, is charged into a reverberatory furnace together with some silica, SiO_2, to slag the iron oxide and lime to make the slag more fusible. The furnace is heated by either an oil or a powdered-coal flame. Further concentration of the copper takes place in this furnace. Its products are slag, which consists mainly of silicates of iron and calcium, and the metal product "matte" which is composed of 42 to 45 per cent copper and 23 to 25 per cent sulfur. The molten matte then goes to a converter, which is shown in cross section in Fig. 169. This converter is made of a shell of steel plate and lined with magnesia, MgO, brick. It is mounted on large steel trunnions which permit its being tilted to pour out its charge. The interior dimensions of a typical copper converter are 15 ft. high and 16 ft. in diameter. Such a converter will take a 65-ton charge of matte. A blast of air is blown through the charge through holes near the bottom of the converter for some 35 min. in which the copper sulfide is further roasted. From time to time, more matte and some raw ore, to aid in slag formation, are added. The chemical reactions that take place in the converter are complex. The iron, which is present in the matte, is

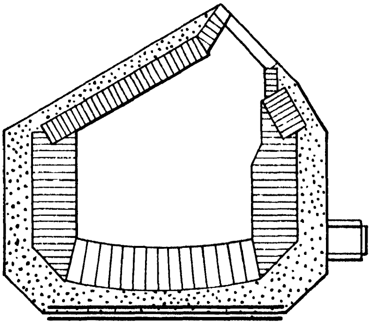

FIG. 169.—Cross section of a copper converter.

removed as silicate in the slag.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \rightarrow FeSiO_3$$

The copper sulfide is converted into metallic copper. Probably all these reactions take place.

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

The molten copper is then taken to a smaller furnace in which air is again blown through the metal to remove the last traces of iron. The air blast in so doing converts a small amount of copper into its oxide. This oxygen is removed by a process known as "poling." Green poles are forced beneath the surface of the molten copper. The wood is charred and the charcoal, thus formed, removes oxygen from the copper oxide. The copper is then cast in ingots to be refined further by means of the electric current. Such ingots are about 99.3 per cent copper, but the presence of even traces of arsenic lowers the electrical conductivity of the metal to such an extent that this impurity must be removed by electrolytic refining (46-19).

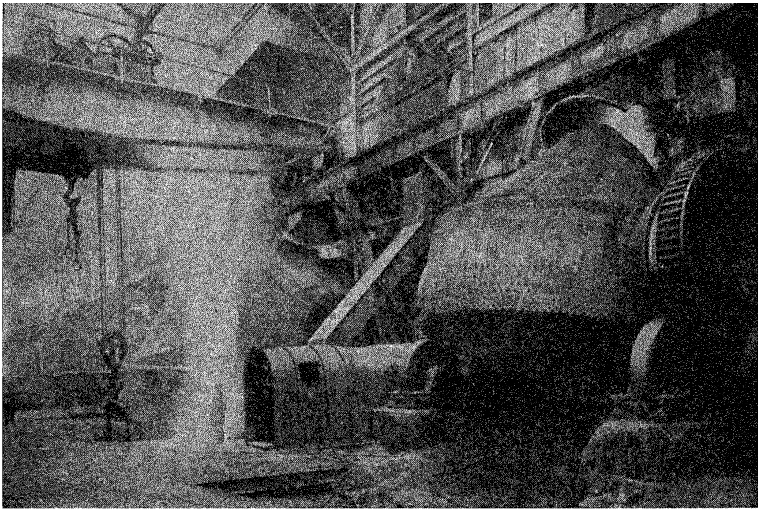

FIG. 170.—Copper converters. (*Courtesy of Anaconda Copper Mining Company.*)

The world produces over a million tons of copper annually, of which half is produced in this country. Because of its high ductility and electrical conductivity, the principal use of copper is in electrical transmission. Because of its comparative chemical inertness, boilers, pipes, gutters, leaders, etc., are made of it. Some of its alloys are very important, among which are brass, an alloy of copper and zinc, and bronze, an alloy of copper and tin.

18. Metallurgy of Nickel and Cobalt.—The best nickel ore pentlandite is a sulfide of the four divalent metals, nickel, copper, cobalt, and iron, which is found at Sudbury, Ontario. From this ore nearly 90 per cent of the world's supply is produced. The treatment is complicated but similar to the smelting of the sulfide of copper. Monel metal, an alloy of copper and nickel with some iron, is made directly from the smelting of the ore. This silver-white alloy is corrosion resistant and is used for kitchen countertops and sinks.

The separation of nickel from copper by the Mond process is ingenious and involves the formation of the volatile nickel carbonyl, $Ni(CO)_4$, when mixed oxides of the two metals are reduced by water gas.

$$NiO + 5CO \rightarrow CO_2 + Ni(CO)_4$$

Heated to a higher temperature, this compound decomposes into the metal and carbon monoxide. Nickel and copper may also be separated by electrolysis, since the copper ion is more readily discharged than the nickel ion. (Why?)

Nickel and cobalt may also be separated by the Mond process. Cobalt metal is obtained by reducing the oxide with aluminum.

19. Electrorefining of Metals.—Certain metals, notably copper, are needed in large quantities in very pure form. The electric current in many cases offers the best means of accomplishing the desired purification. Exceedingly pure copper is needed in large quantity as an electrical conductor, and traces of impurities lower its conductivity greatly. The cell, used to refine copper electrolytically, consists of one electrode of pure copper, the cathode, and an ingot of impure copper as the anode, immersed in a solution of copper sulfate (Fig. 171). A direct current at low voltage (0.4 volt) is used. Hitherto we have considered the electrodes to be composed of some inert material like carbon or platinum. When such electrodes are used, ions are discharged at each electrode. However, when more active metals than platinum are used as anodes, neutral atoms of these may become ions by leaving electrons on the electrode. The impure anode of copper contains as impurities more active metals, such as zinc, and less active ones, such as silver and gold. When the current is turned on, sulfate ions of the electrolyte and the hydroxyl ions of water migrate to this electrode. If the electrode were inert, the hydroxyl ions would be discharged, but now neutral metal atoms of the anode ionize instead. The more active the metal, the more readily does it ionize (40-8), so that of the four metals, zinc, copper, silver, and gold, zinc will ionize at the lowest voltage.

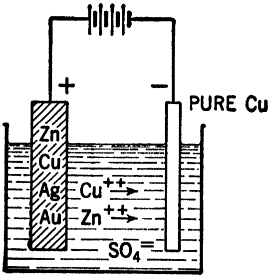

FIG. 171.—Electrorefining of copper.

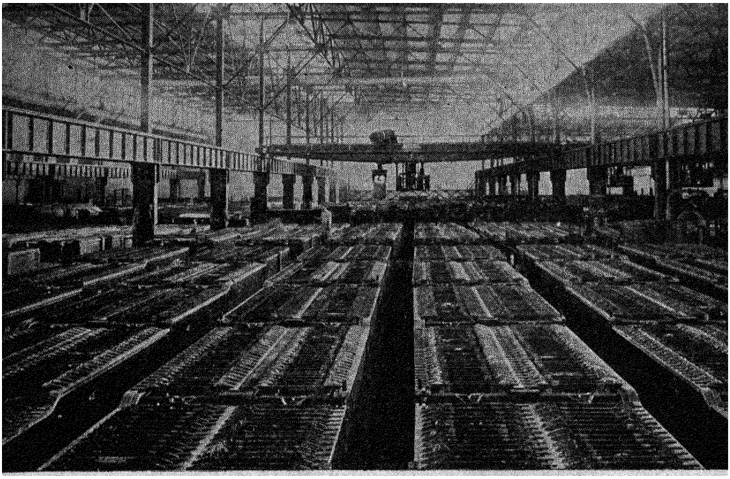

FIG. 172.—Cell room, copper electrolytic refinery. (*Courtesy of Anaconda Copper Mining Company.*)

$$Zn^0 \rightarrow Zn^{++} + 2e^-$$

All the zinc, therefore, goes into solution as zinc ions. But these atoms are so few in comparison with the atoms of copper that the latter ionize also.

$$Cu^0 \rightarrow Cu^{++} + 2e^-$$

Silver and gold, however, require a higher voltage to ionize, so that these remain as neutral atoms and fall to the bottom of the cell as a sludge, which is naturally a valuable by-product of the process.

Three positive ions zinc, hydronium, and copper migrate to the cathode. Of these, the copper ion discharges at the lowest voltage. Hence it alone plates out on the cathode of pure copper.

$$Cu^{++} + 2e^- \rightarrow Cu^0$$

In addition to the noble metals recovered from the anode sludge, the modern electrolytic copper refinery produces most of the arsenic trioxide used in the manufacture of insecticides and the nickel sulfate used to electroplate nickel. Selenium is another by-product used in the manufacture of ruby glass. This is another example of the chemist bringing down a flock of birds with one stone.

The electrolytic refining of zinc makes possible the separation of cadmium, a metal that occurs in zinc ores. Twelve million pounds of cadmium are recovered annually in this way.

The Betts process for the electrolytic refining of lead uses as an electrolyte a solution of lead fluosilicate, $PbSiF_6$, with crude lead anodes and thin sheets of pure lead as cathodes. The removal of the impurities causes a marked decrease in the hardness of lead.

EXERCISES

1. Define the following terms: metallurgy, ore, mineral, rock, gangue, flux, slag.
2. Summarize by means of equations the chemical reactions involved in extracting metals from carbonate, sulfide, and oxide ores.
3. What are the functions of the iron blast furnace? With what is it charged? Write equations for the principal reactions that occur in it. What are its products?
4. How do pig iron, wrought iron, and steel differ in physical properties and in composition?
5. Compare the Bessemer and the open-hearth processes as to cost and as to quality of product.
6. What reactions result in the removal of phosphorus in the open-hearth process?
7. Why cannot limestone be used as a flux in a Bessemer converter?
8. How would it be possible to purify by electrolysis a copper ingot containing small amounts of iron and silver?

9. If a deposit made up of a mixture of the sulfides of mercury, zinc, and iron were discovered, could you suggest a method by which the metals could be separated from the mixture and from each other?

10. How is aluminum used in the metallurgy of other metals?

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CHAPTER FORTY-SEVEN

THE METALS AND THEIR ALLOYS

The physical properties that the uncombined metals possess have proved far more useful than those of the nonmetals. For this reason, metals are far more familiar to the layman. Further, metals may be melted together to form many useful alloys.

1. Packing of Atoms in Crystals.—The structure units in the crystals of a metal obviously must be its atoms. These may be imagined as spheres of the same diameter. It will be instructive to consider how efficiently such spheres could be packed in a container (Fig. 173). Each sphere in the second layer, marked with dotted lines, is placed in a triangular hollow formed between three balls of the first layer. A choice is offered when the third layer is packed. The balls of this layer may be placed in the hollows marked *B* in which case they lie directly above balls in the first layer. This type of packing is found in crystals of the hexagonal close-packed type. The second choice places the balls of the third layer in the hollows marked *A*; here they do not lie

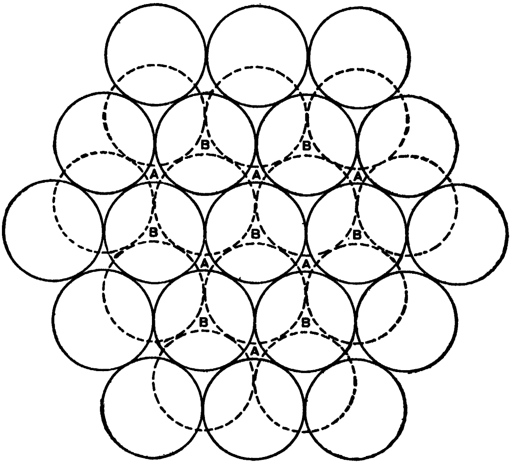

FIG. 173.—Close-packed atoms in metal crystals.

directly above those in the first layer. Not until the fourth layer do we find the balls lying in positions corresponding to those of the first layer. The second type of packing is called face-centered cubic. A third type of packing, the body-centered cubic, is only slightly less efficient than the two types we have been studying.

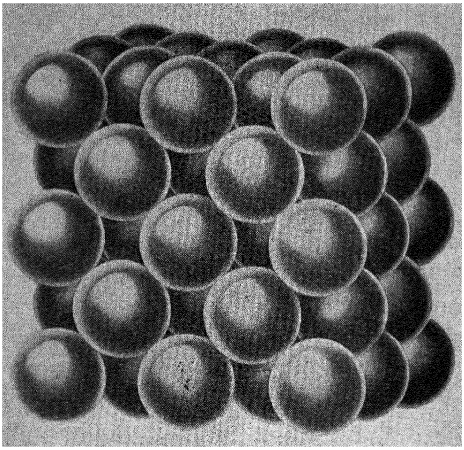

FIG. 174.—Face-centered-cubic type of packing of atoms. Copper, nickel, and silver crystals are of this type.

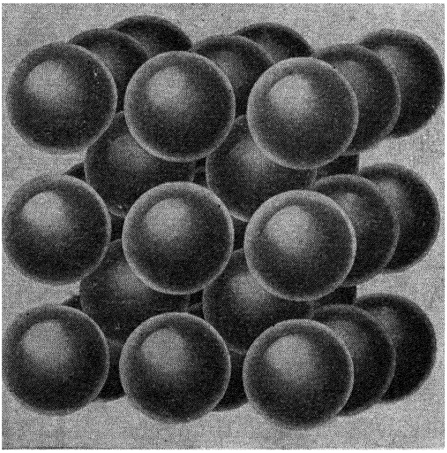

FIG. 175.—Atoms packed in a body-centered-cubic pattern. Crystals of chromium and iron are of this type.

Nearly all metals crystallize in one of these three forms. This is an indication that, in most cases, considerations of packing are predominant in determining metal crystal structure.

2. The Metallic Bond.—When covalent bonds link atoms together in giant molecules as in the diamond structure, the angles between bonds are more or less fixed in space; the crystal structure is rigid and hard to deform. If relatively small molecules are the units, high sublimation rates and low melting points are characteristic, since weak van der Waals forces hold the crystal together. Metals are, in general, good conductors of electricity. They are ductile, which permits them to be drawn into a wire, and they are malleable, *i.e.*, they can be hammered into shape. These properties are almost unique. They indicate that a different type of bonding exists in metal crystals.

We have learned that the valency electrons in metal atoms are easily lost. In metal crystals, there is good evidence that these electrons lead a more or less free existence between tightly packed metal ions. Their freedom accounts for the high electrical conductivity. As the temperature is decreased, the kinetic energy of vibration of the metal ions decreases and the electrons find easier passage. At the temperature of liquid helium, all metals become superconductors. The close packing of the ions provides a maximum number of "planes of flow" along which slippage may occur as if on ball bearings. This accounts nicely for the malleability and ductility of metals. It also suggests the reason why metal crystals do not break along cleavage planes as readily as do other types of crystals. When a material "gives" under a stress, breakage is less likely.

3. Properties and Uses of the Metals.—To save space, these are summarized in Table 54.

4. Alloys.—When two or more metals are melted together and the melt is allowed to solidify, the resulting product is called an alloy. Alloys have been known since ancient times. In fact, bronze, the alloy of copper and tin, was so important to the ancient world that its name has been given to a whole era of human development.

The study of the structure of alloys has resulted in the knowledge of how to make them with the desired properties for a given use. This study is a branch of metallurgy called physical metallurgy. An alloy of two metals may be either one or a combination

TABLE 54.—PROPERTIES AND USES OF THE METALS

Metal	Melting Point, °C.	Density	Ductility	Relative malleability	Electrical conductivity	World annual production, tons	Cost per pound	Important uses
Sodium......	97.5	0.97	1	1	7	25,000	16¢	Synthesis of organic compounds; manufacture tetraethyl lead
Magnesium..	651	1.74	..	..	6	8,500	25¢	In alloys of low density for parts of airplanes and engines; flashlight powders and pyrotechnics; synthesis of organic compounds; deoxidizer in metallurgy
Aluminum...	660	2.70	4	5	4	634,500	21¢	Light alloys for aircraft; electrical conduction, cooking utensils; paints; thermite welding; flash bulbs in photography; deoxidizer
Zinc.........	419.4	7.14	8	8	8	1.612,000	6¢	Galvanized iron; brass; dry cells; reducing agent
Iron.........	1535	7.86	5	9	10	129,000,000	1.3¢	See paragraphs 46-6 and 46-8
Nickel.......	1452	8.90	6	..	9	124,500	35¢	Catalyst for hydrogenation of organic compounds; plating; alloys
Chromium...	1615	7.1	..	5	..	400,000	85¢	Plating; stainless steel; alloys
Tin..........	231.9	7.31	9	6	11	159,000	48¢	Plating; foil; alloys
Lead........	327.5	11.34	..	7	12	1,856,500	5¢	Pipes; chamber process (H_2SO_4); storage batteries; alloys
Copper......	1083	8.92	7	4	2	2,365,700	12¢	Electrical conduction; pipes; boilers, gutters; alloys
Silver........	960.5	10.5	3	3	1	180	$5.10	Tableware; coins; jewelry; mirrors; electrical conduction
Gold........	1063	19.3	2	2	3	200,	$510	Coins; jewelry, ruby glass

of three types. (1) If the metals do not dissolve in each other's crystals, the alloy may consist of a mixture of pure crystals of each component. (2) If the components are soluble in the solid state, the alloy may consist of crystals that are solid solutions containing both components. (3) The two metals may react chemically to form a compound. Many valuable alloys of each of these types are known.

For example, the lead-antimony alloys are of the mixture type. Antimony alone is too brittle and lead too soft for certain purposes. Type metal, an alloy of lead and antimony with some tin added, has some of the hardness of antimony but lacks its brittleness and, in addition, has a lower melting point. Solder, an alloy of lead and tin, must of course be low melting. An alloy of the composition of 37 per cent lead and 63 per cent tin has the lowest melting point of any alloy of these metals. This alloy is used as "tin" solder. A slightly higher percentage of lead, 67 per cent, is used in "plumber's" solder. This melts at a higher temperature but is of the pasty consistency necessary for a "wiped joint."

Many copper-nickel alloys of the solid-solution type are of importance; among these may be mentioned copper coins, the caps of rifle bullets (20 per cent nickel), and a wire of high electrical resistance which varies little with the temperature and finds use, therefore, in electrical temperature-measuring devices. Certain Canadian ores contain sulfides of copper and nickel which on smelting produce an alloy of these metals containing 67 per cent nickel and 28 per cent copper with the remaining 5 per cent iron and manganese. This is called Monel metal, has high tensile strength and ductility, and is remarkably resistant to corrosion.

Solid-solution alloys of many other metals are of technical importance. Many of the gold alloys are of this class. Gold coins are hardened with dissolved silver. White gold is an alloy of this metal with 18 per cent nickel. Nichrome, an alloy of nickel and chromium, which is highly resistant to corrosion at high temperatures, is the basis of electrical heating devices, such as toasters, irons, heaters, and furnaces. Stellite, a cobalt-chromium alloy, is a silver-white, rustproof, stainless metal that can hold a cutting edge. It is used in the manufacture of surgical instruments, etc.

While metals in general do not form compounds with each other, a few hundred are known to exist. The formulas for these compounds, however, do not, in general, follow from the simple valences of the metal atoms involved. Few alloys containing metallic compounds are of any importance since they tend to be hard, brittle, and of very low strength and ductility. The hardness

TABLE 55.—COMPOSITION AND USES OF THE COMMON NONFERROUS ALLOYS

Name	Composition, per cent	Uses and properties
Aluminum brass	Cu, 71–55; Zn, 26–42; Al, 1–6	Marine fittings, propeller blades, etc.
Aluminum bronze	Cu, 99–89; Al, 1–11	Hard, noncorrodible
Babbitt metal	Sn, 89; Sb, 7.3; Cu, 3.7	Bearings
Bell metal	Cu, 75–80; Sn, 25–20	Bells
Brass	Cu, 73–66; Zn, 27–34	For cold working, sheets, tubes, etc.
Britannia metal	Zn, 90–85; Sb, 5–10; Cu, 1–3	Antique tableware, etc. Harder and lighter than pewter
Carboloy	Tungsten carbide and cobalt	Grinding and cutting tools
Constantan	Cu, 60–45; Ni, 40–55; Mn, 0–1.4; C, 0.1; Fe	Electrical temperature-measuring devices. Thermocouples
Delta metal	Cu, 56–54; Zn, 40–44; Fe, 0.9–1.3; Mn, 0.8–1.4; Pb, 0.4–1.8	Marine fittings. Strong as mild steel but not easily corroded
Dow metal	Mg, 90–96; Al, 4–10; Mn	Motor parts. Aircraft
Duralumin	Al; Cu, 3.5–5.5; Mg, 0.5–0.8; Mn, 0.5–0.8; Fe; Si	Light yet of high tensile strength. Metal airplane parts, framework of dirigibles, etc.
German silver	Cu, 55; Zn, 25; Ni, 20	Silver substitute
Green gold	Au, 75; Ag, 11–25; Cd, 13–0	Jewelry, etc.
Gun metal	Cu, 95–71; Sn, 0–11; Pb, 0–13; Zn, 0–5; Fe, 0–1.4	Buttons, badges, trays, gears, etc.
Magnalium	Al, 95–70; Mg, 5–30	Light metal. Scientific instruments, balance beams, etc.
Monel metal	Ni, 68; Cu, 28; Fe, 1.9	Noncorrodible. Counter-tops, sinks
Nichrome	Ni, 80–54; Cr, 10–22; Fe, 4.8–27	Resists corrosion at high temperatures. Wire for electrical heating units
Palau	Au, 80; Pd, 20	Substitute for platinum in crucibles, dishes, etc.
Permalloy	Ni, 78; Fe, 21; Co, 0.4; Mn; Cu; C; S; Si	Telephone cables
Pewter	Sn, 89–74; Pb, 0–20; Sb, 0–7.6; Cu, 0–3.5; Zn	Antique plates, bowls, cups, etc.
Shot metal	Pb, 99; As, 1	Bullets and small shot
Silver (coins)	Ag, 90; Cu, 10	
Silver (sterling)	Ag, 80; Zn, 18; Cu, 2.5	
Solder	Pb, 67; Sn, 33	Plumber's solder
Stellite	Co, 80–55; Cr, 20–35; W, 0–10	Surgical instruments
Tin foil	Sn, 88; Pb, 8; Cu, 4; Sb, 0.5	Wrapping for foodstuffs, tobacco, etc.
Tinsel	Sn, 60; Pb, 40	
Type metal	Pb, 60–56; Sn, 10–40; Sb, 4.5–30	Low melting. Plugs in automatic fire sprinkler systems
Wood's metal	Bi, 50; Pb, 25; Sn, 13; Cd, 13	

of such alloys makes them useful for bearing metals such as Babbitt metal which contains SbSn and Cu_3Sn. Sometimes compounds of metals with nonmetals are important in alloys as in the cases of Cu_3P in phosphor bronze and Fe_3C in steel.

5. The Compositions of the Common Nonferrous Alloys. Thus far, we have said very little of the composition of the common alloys. You will find this information in Tables 55 and 56 together with some of the uses to which these alloys are put.

6. Iron-carbon Alloys.—These alloys are perhaps the most important of all to our civilization since they include steel, cast iron, and wrought iron. When pure melted iron is cooled, a crystalline form, known as δ-iron, freezes from the liquid at 1535°C. This form changes to a second type of crystal, γ-iron, at 1404°C. The latter is stable above 900°C. at which temperature it changes to α-iron, the stable form at room temperature.

$$\text{Liquid iron} \underset{}{\overset{1535°}{\rightleftarrows}} \delta\text{-iron} \overset{1404°}{\rightleftarrows} \gamma\text{-iron} \overset{900°}{\rightleftarrows} \alpha\text{-iron}$$

α- and δ-iron are identical in crystalline form so that there are really only two allotropic modifications of the metal.

Iron and carbon form a compound, Fe_3C, in which the percentage of carbon is 6.67; this is known as *cementite*. This compound forms solid solutions with γ-iron, called *austenite*, but is insoluble in crystals of α-iron. Steel contains 0.5 to 1.5 per cent carbon, so that all this element is in the form of the compound cementite. When molten steel solidifies, solid-solution crystals of austenite are formed. These are soft and malleable and are easily rolled into sheets and bars in a rolling mill or drawn into rods and wire. However, at temperatures between 120 and 115°C., depending on the composition of the austenite, cementite and α-iron crystallize from solid solution. This transition is slow, since it takes place entirely within the solid state. A steel must be cooled very slowly to allow the change to complete itself. The result, a mixture of small crystals of α-iron and cementite, is known as *pearlite*. This mixture is comparatively soft, only fairly tough, and not adequately strong for many purposes.

7. Heat-treatment of Steel.—If the solid solution austenite is cooled rapidly, sufficient time is not given to allow cementite to separate, although no cooling is rapid enough to prevent the transition of γ-iron to α-iron. The result is a greatly supersaturated solution of cementite in α-iron, called *martensite.* At ordinary temperature, molecular motion is too small in this unstable system to permit separation of the excess cementite. Martensite is harder than glass and brittle. The rapid cooling required for its formation is attained by plunging hot steel into water or oil, a process known as *quenching.*

By varying the rate of cooling, more or less of the compound can be permitted to separate and a steel of the desired hardness can be obtained. *Tempering* consists in reheating the quenched steel to permit partial separation of cementite. Such a process reduces the brittleness of the hardened steel and at the same time softens the metal. The effects of tempering are not unlike the effects of quenching at some intermediate rate such as in hot oil or water.

8. The Alloy Steels.—With the advent of the automobile, metallic elements, which had previously been names only even to chemists, were alloyed with steel. Alloy steels to fit not only the requirements of the parts of the automobile engine, but also of the tools necessary for its production at high speed were the result. We have just learned how tool steels are tempered by heating to redness followed by quenching. However, if they are heated again to too high a temperature by the friction that develops when tools are used in high-speed lathes, they soften and lose their cutting edge. The necessity for keeping such tools cool limited the speed at which such machines could run. An accidental discovery by Mushet in 1868, that steel which contained tungsten did not require quenching to harden it, led to the introduction of high-speed tool steels by Taylor about 1890 and revolutionized machine-shop practice. Other metals were soon found which gave to steel many valuable properties. Manganese improves the strength of steel. It also eliminates oxygen, which weakens the steel, and sulfur, which makes it brittle. Nickel increases its strength without increasing its brittleness. Chromium in small amounts hardens steel and increases its resistance to shock. In larger amounts this element improves its resistance to corrosion. Stainless steel contains chromium. Even a metal like steel can become fatigued and break under repeated shock. This tendency is greatly lessened by vanadium. Ford cars have made this type of steel famous. Molybdenum steels are harder and more heat-resistant.

Alloy steels naturally cost more than the straight carbon steels. For example, the increased cost per ton for various alloying metals is as follows:

Vanadium for each 0.1 per cent	$ 8.00
Tungsten for each 1 per cent	24.00
Chromium for each 1 per cent	2.30
Nickel for each 1 per cent	8.00

To give some idea of the extent to which alloy steels are used: between May and December, 1918, 45,500,000 lb. of tungsten steel was produced in the United States, containing some 8,000,000 lb. of tungsten.

TABLE 56.—COMPOSITION AND USES OF THE COMMON FERROUS ALLOYS

Name	Composition, per cent	Uses
Acid-resisting iron	Fe, 86; Cr, 13	
Alkali-resisting iron	Fe, 95; Ni, 5	
Alloy steels:		
Chrome steel	Cr, 3	Projectiles, files, jaws of rock crushers, ball bearings, safes, armor plate
Chromium-tungsten	C, 0.25–1; W, 5–25; Cr, 2–10; V, 0.25–1	High-speed tool steel
Chromium-vanadium	C, 0.25–1; Cr, 0.8–1.1; V, 0.15; Mn, 6–15	Gears and axles, railroad rail curves, switches, steam shovels, etc.
Molybdenum	Mo, 0.3–3	Axles
Nickel	Ni, 3–4	Great tensile strength, resists corrosion. Wire cables, drive shafts and crankshafts, bridge trusses, etc.
	Ni, 25	Electrical resistances
	Ni, 30–40	Rustless for pumps, valves, etc.
	Ni, 36	Invar for clock pendulums, scales, etc.
	Ni, 46	Platinite, same coefficient of expansion as glass. Glass to metal seals
Nickel-chromium	Ni, 1–4; Cr, 0.45–2	Armor plate
Auer metal	Fe, 35; Ce, 35; La, 24; Yb, 3	Pyrophoric, or sparking alloy, gas lighters, cigarette lighters, etc.
Duriron	Fe; Si, 14–15; Mn, 2–2.5; C, 0.8–1.3; S, 0.05–0.2; P, 0.05-1	Acid resisting

EXERCISES

1. What is the nature of the structure of metal crystals?

2. How does this structure explain their high malleability and electrical conductivity?

3. What is an alloy?
4. What types of alloys are known?
5. Discuss the importance of the iron-carbon alloys.
6. What types of physical structures are obtained in steel by quenching and heat-treatment?
7. What desirable properties are associated with these structures?
8. What metals are used in alloys of low density?
9. Why are such alloys so valuable in wartime?
10. What is the composition of stainless steel?

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CHAPTER FORTY-EIGHT

THE ALKALI AND THE ALKALINE-EARTH METALS

These are the two most reactive groups of metals in the periodic table. The alkali metals of Group I are lithium, sodium, potassium, rubidium, and cesium. A report of the discovery of the last alkali metal of atomic number 87 in the lowest place in the group was published by Mlle. Perey in 1939.

TABLE 57.—THE ALKALI METALS (GROUP I)

Metal	Atomic number	Atomic weight	Planetary electrons	Density	Melting point, °C.	Valence
Lithium....	3	6.940	2, 1	0.53	186	+1
Sodium.....	11	22.997	2, 8, 1	0.97	97.5	+1
Potassium..	19	39.096	2, 8, 8, 1	0.86	62.3	+1
Rubidium...	37	85.48	2, 8, 18, 8, 1	1.53	38.5	+1
Cesium.....	55	132.91	2, 8, 18, 18, 8, 1	1.90	26	+1
....	87	....	2, 8, 18, 32, 18, 8, 1	....	.....	+1

The alkaline-earth metals of Group II are calcium, strontium, barium, and radium. Although, strictly speaking, beryllium and magnesium, which head Group II, are not alkaline-earth metals, they are closely related.

1. Sodium.—The most important alkali metals are sodium and potassium. The compound from which sodium and all its compounds are obtained is common salt from which the metal is prepared by electrolysis. The reactions of the free metal are summarized by the following equations:

$$2Na + O_2 \rightarrow Na_2O_2 \qquad 2Na + H_2 \rightarrow 2NaH$$
$$2Na + Cl_2 \rightarrow 2NaCl \qquad 2Na + 2HOH \rightarrow 2NaOH + H_2$$
$$2Na + S \rightarrow Na_2S \qquad 2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$
$$3Na + P \rightarrow Na_3P \qquad 3Na + AlCl_3 \rightarrow 3NaCl + Al$$

2. Sodium Chloride.—Over 75 per cent of the solids dissolved in sea water is sodium chloride. The dissolved salts make up 3 per cent of the weight of the oceans and some 25 per cent of the waters of the Great Salt Lake in Utah. Further, large beds of salt, the remnants of ancient salt lakes, occur beneath the surface. Salt is mined, pumped to the surface from underground brines, or crystallized from salt-lake water by solar evaporation. By allowing the salt to crystallize until the remaining solution approaches saturation with sodium sulfate and then discarding the remaining solution, nearly pure salt is obtained. Table salt is 99.7 per cent pure. Traces of magnesium salts, which are deliquescent, are responsible for the caking of salt in damp weather. The total annual salt production in the United States averages 8,500,000 tons and is valued at over $27,000,000.

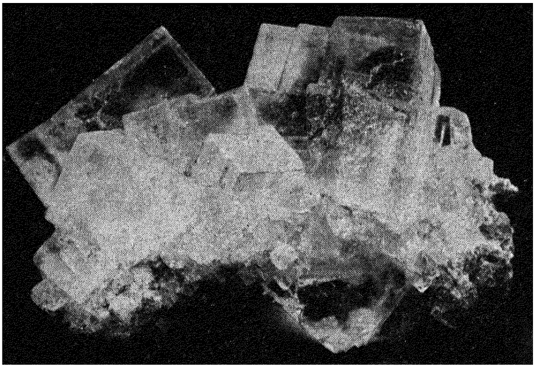


Fig. 176.—Cubic crystals of common salt. (*Courtesy of American Museum of Natural History, New York.*)

Table 58.—Salt Production in the United States

Source	Per cent	Source	Per cent
Michigan	31	Louisiana	6
New York	26	California	5
Ohio	17	Utah	1
Kansas	10	Other states	4

Each adult should obtain 15 to 18 lb. of salt per year from his diet. One-third of the salt produced is converted into sodium carbonate by the Solvay process. Chilled brines are used in refrigeration. Salt is used in the preservation of foods, tanning, ceramics, the manufacture of soap, metallurgy, and in the preparation of chlorine and its compounds.

3. **Sodium carbonate,** next to lime, is the most widely used basic heavy chemical. In the trade, it is known by several names—soda, soda ash, washing soda, and sal soda. It owes its useful basic properties to the carbonate ion, which is a strong base (42-20). Nearly 3,000,000 tons is produced annually from salt by the Solvay process. When crystallized from aqueous solutions below 35°C., sodium carbonate crystals contain water of hydration ($Na_2CO_3.10H_2O$). This hydrate is called sal soda. Above 35°C., its crystals contain less water of hydration ($Na_2CO_3.H_2O$). This monohydrate is used in washing powders. The anhydrous salt is known as soda ash.

A few deposits of sodium carbonate occur in nature in British East Africa, British Columbia, California, and Oregon. The United States has used as much as 110,000 tons of the natural product annually.

TABLE 59.—USES OF SODIUM CARBONATE

Industry	Per cent	Industry	Per cent
Glass	38.49	Paper and pulp	4.46
Chemicals	31.39	Textile	2.23
Soap	8.94	Water softening	1.78
Cleaning powders	6.25	Miscellaneous	6.46

4. **History of the Production of Soda.**—Sodium carbonate is essential to the manufacture of glass and soap. During the Middle Ages, the glass factories of France and Bohemia were dependent on soda, imported by Arabs from the natural deposits in desert places of Asia Minor, or on barilla from Spain, which consisted of soda from the ashes of marine plants. Shortly before the French Revolution, after England had cut France off from her barilla supply, the French Academy of Science offered a prize of 2,400 livres for a method of preparing soda from salt. The problem was solved by Nicolas Leblanc, the physician to the Duke of Orleans. In the Leblanc process, salt was treated with concentrated sulfuric acid.

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

The sodium sulfate, heated with limestone and coke, was converted into the carbonate

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$
$$Na_2S + CaCO_3 \rightarrow CaS + Na_2CO_3$$

which was leached out from the insoluble calcium sulfide with water.

The French Revolution was fatal to the hopes of Leblanc. The Duke of Orleans was guillotined, and Leblanc's daughter fell ill and died. Leblanc committed suicide. The prize was never awarded. During the 75 years that followed, his process grew into a great industry until it was replaced by the more economical Solvay process.

5. The Solvay Process.—Ernest Solvay (1838–1922) was the son of a modest salt refiner of Brabant, Belgium. His childhood was spent in an "atmosphere" of this raw material of his process. In 1860, he went to Schaarbeck to assist his uncle who was the director of a small gas works in that town. Here he came in contact with a by-product of gas manufacture, ammonia, NH_3, which was to be a second chemical essential to the success of his process. One year later, he applied for a patent for the process by which virtually all soda is manufactured today.

A saturated brine (NaCl) solution is further saturated with ammonia and carbon dioxide in gas absorption towers. Whereupon the following reactions take place:

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 + NH_3 \rightarrow NH_4^+ + HCO_3^-$$
$$HCO_3^- + Na^+ \rightarrow NaHCO_3\downarrow$$

The formation of the bicarbonate ion in a solution, in which the sodium-ion concentration is so high, results in the precipitation of sodium bicarbonate. The remaining solution contains ammonium chloride. The precipitate is filtered from the mother liquor in rotary vacuum filters. Some of it is sold as bicarbonate to baking-soda ($NaHCO_3$) and baking-powder manufacturers. Most of it, however, is converted into the normal carbonate, Na_2CO_3, by being heated in closed calciners.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

The success of the process depends on the recovery of the ammonia which is in solution in the form of ammonium chloride.

This is treated with milk of lime to release ammonia gas.

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + 2HOH + CaCl_2$$

It is then used over and over again. Its recovery is practically complete. The advantages of the Solvay over the Leblanc process are obvious. It requires little fuel and offers little wastage of material. The only by-product of this process is calcium chloride, which, because it is hygroscopic, has been used extensively for laying the dust on dirt roads, for killing weeds, and for drying.

6. The Reactions of Sodium Carbonate and Bicarbonate. Since the carbonate ion is such a strong base, aqueous solutions of sodium carbonate are strongly basic owing to hydrolysis

$$CO_3^{=} + HOH \rightleftarrows HCO_3^- + OH^-$$

followed by

$$HCO_3^- + HOH \underset{\longleftarrow}{\overset{\rightarrow}{\longleftarrow}} H_2CO_3 + OH^-$$

The pH of a molar sodium carbonate solution is 11.6. As the second equation shows, solutions of sodium bicarbonate are also basic but less so since the bicarbonate ion is not so strong a base as the carbonate ion. Hence sodium bicarbonate is safe to use internally to correct an acid condition.

The following equations illustrate the basic character of the carbonate and bicarbonate ions:

$$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3,$$

or $$CO_3^{=} + H_3O^+ \rightarrow HCO_3^- + H_2O$$

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2,$$

or $$HCO_3^- + H_3O^+ \rightarrow 2H_2O + CO_2$$

$$Na_2CO_3 + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + NaHCO_3,$$

or $$CO_3^{=} + HC_2H_3O_2 \rightarrow HCO_3^- + C_2H_3O_2^-$$

$$NaHCO_3 + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O + CO_2,$$

or $$HCO_3^- + HC_2H_3O_2 \rightarrow H_2O + CO_2 + C_2H_3O_2^-$$

The reactions of the bicarbonate ions in baking powders were considered earlier (42-21).

7. Sodium Hydroxide.—This very soluble, deliquescent solid is known as caustic soda or lye. Both sodium and potassium hydroxides are classed as *alkalies.* Ionic in crystal structure both hydroxides should be considered as salts, but the common practice is to consider them as bases. This practice is justified because of the high concentration of hydroxyl ions in their aqueous solutions. The hydroxyl ion, you will remember is the strongest base that can exist in water (33-3). Completely ionic, a 0.1*M* solution of sodium hydroxide has a pH of 13. Why?

More expensive than soda, sodium hydroxide is manufactured by the electrolysis of common salt solutions (17-2b). A second commercial preparation treats soda with slaked lime.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + 2NaOH$$

The reaction is carried out in boiling solutions and the insoluble calcium carbonate removed by filtration. About 900,000 tons are produced annually.

Typical reactions of sodium hydroxide are as follows:

$$NaOH + HCl \rightarrow NaCl + HOH,$$

or

$$OH^- + H_2O^+ \rightarrow 2H_2O$$

$$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + HOH,$$

or

$$OH^- + HC_2H_3O_2 \rightarrow HOH + C_2H_3O_2^-$$

$$3NaOH + FeCl_3 \rightarrow 3NaCl + Fe(OH)_3\downarrow,$$

or

$$3OH^- + Fe^{+++} \rightarrow Fe(OH)_3\downarrow$$

TABLE 60.—USES OF SODIUM HYDROXIDE

Industry	Per cent	Industry	Per cent
Rayon, cellophane, etc.	18.3	Rubber reclamation	6.7
Chemical	15.6	Pulp and paper	5.6
Soap	13.9	Textile	5.6
Petroleum	12.8	Lye	4.4
Exports	7.2	Miscellaneous	9.9

The use of caustic soda in the manufacture of soap will be discussed later (55-9).

8. Other Sodium Salts.—Although compounds of sodium are less abundant in nature than those of potassium, common salt is such a readily available, soluble source that sodium compounds are less expensive and, hence, more widely used. Sodium sulfate, or Glauber's salt, $Na_2SO_4\cdot10H_2O$, occurs widely, usually associated with common salt. Its solubility in water varies to a greater extent with the temperature than does sodium chloride. Hence it crystallizes from natural brines in cold weather. Large deposits occur in Siberia, Canada, North Dakota, and in the

Southwest of the United States. It is used in glassmaking, in the manufacture of paper from southern pine, and in the dye industry. Sodium sulfide is made commercially by heating the sulfate with carbon.

$$Na_2SO_4 + 2C \rightarrow Na_2S + CO_2$$

The following sodium salts have been discussed previously: sulfite (36-6), thiosulfate (36-14), nitrate (39-9), nitrite (39-5), cyanide (42-22).

9. Tests for Sodium.—The simplest test is the yellow color of luminous sodium vapor. Any sodium salt, heated in the Bunsen burner flame, gives this delicate test. Indeed, dust particles usually contain sufficient traces of salt to give this test.

Few sodium compounds are insoluble. Among those which are, the pyroantimonate, $Na_2H_2Sb_2O_7$, may be used as a test.

10. Potassium and Its Salts.—The reactions of potassium and of its salts are similar to those of sodium and of the corresponding sodium salts. Because of their value in mixed fertilizers, a source of potassium salts is essential to the economy of any nation.

Feldspar, a constituent of all granitic rocks, is a compound of potassium, but unfortunately it is very insoluble in water. This mineral is abundant everywhere; yet because of this insolubility it is useless as a plant food. Natural waters bearing carbon dioxide in solution slowly convert it into soluble potassium compounds, but this action is too slow to resupply potash to a soil at the rate at which crops remove its compounds. The soluble potash compounds, formed from feldspar, eventually find their way into the ocean; but although the total weight of such compounds in the sea is very large, their concentration is so small in comparison with other salts that their recovery for use as fertilizer seems out of the question. However, what man cannot do, nature has done in certain places on this earth on a large scale. Occasionally, a certain body of salt water is cut off from the ocean by a geologic upheaval of the ocean bottom. An inland salt lake is the result. If this body of water receives less water by drainage from the surrounding terrain than it loses by evaporation, the salts in it become more concentrated until, eventually one after the other, they begin to crystallize out of solution. Such salt beds have been laid down at Stassfurt, Germany. They are in layers as shown in

Fig. 177. The potash occurs in them as sylvite, KCl, and carnallite, $KCl.MgCl_2.6H_2O$. These deposits and those in Alsace gave to Germany practically a world monopoly of potash for fertilizers until the end of the First World War. Then the acquisition of Alsace by France destroyed the monopoly. During that war, our country was in dire need of potash. Prices rose from $40 to $400 per ton. Under these extreme conditions, every possible source of potash in this country was utilized. Potash from wood ashes; from the dust of cement kilns and blast furnaces; from the sugar-beet crop, which alone uses up 18,000 tons of potash annually in this country; from Searles Lake in California and other alkali lakes in Nebraska, Utah, and California; from the mineral alunite, a moderately soluble potassium compound that occurs at Marysvale, Utah; from the Leucite Hills of Wyoming; and even from kelp, that giant seaweed which grows off the coast of California. The result in 1917 was about 32,500 tons of potash, enough to last this country a little more than a month, and at prices too high for peacetime competition with German potash.

In 1928, the domestic production of potash was more than 50,000 tons, about one-sixth of the consumption, most of which came from Searles Lake. In 1912, potassium salts were discovered in the Permian basin of Texas and New Mexico. These deposits proved to be so extensive that they will supply the potash needs of this country for at least several generations. Commercial operations started in 1930, and by 1934 the capacity for potash production became equal to the domestic demand. The plants are located near Carlsbad, New Mexico. They produce potassium chloride of as high as 98 to 99 per cent purity.

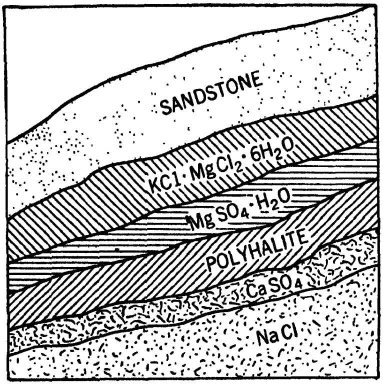


FIG. 177.—Deposits of salts from sea.

11. Tests for Potassium.—The flame color of potassium is violet, but since sodium compounds are so universally present as impurities, the yellow flame of the sodium obscures that of potassium. By looking at the flame through cobalt-blue glass which filters out the yellow light, the potassium flame may be detected.

Among the few insoluble potassium compounds are the yellow chloroplatinate (K_2PtCl_6), the white perchlorate ($KClO_4$), and the yellow cobaltinitrite [$K_2NaCo(NO_2)_6$].

12. Lithium, Rubidium, and Cesium.—The three remaining alkali metals are of lesser importance. Lithium at the top of Group I is the metal of lowest density (0.534). It occurs in the waters of certain mineral springs and in a few rare silicate minerals. Its reactions are, in general, the same as those of sodium. Lithium carbonate and phosphate are only sparingly soluble. Lithium salts give a beautiful crimson flame test.

Rubidium and cesium were the first elements to be discovered by Bunsen with the aid of his newly perfected spectroscope (26-3). They were named after their characteristic flame colors (*rubidus*, dark red, and *coesius*, sky-blue). Cesium is the most active of the known metals, since its single valency electron, remote from the nucleus, is most readily removed. Its use in photoelectric cells depends upon the fact that the quanta (26-6) in visible light possess enough energy to release electrons from cesium atoms.

13. The Alkaline-earth Metals.—The physical properties of these metals, calcium, strontium, barium, and radium, are summarized in Table 61. These together with beryllium and magnesium are in Group II of the periodic table. The latter have been included in Table 61 although they are not alkaline-earth metals.

TABLE 61.—PROPERTIES OF THE METALS OF GROUP II

Element	Atomic number	Atomic weight	Planetary electrons	Valences	Density	Melting point, °C.
Beryllium	4	9.02	2, 2	+2	1.8	1350
Magnesium	12	24.32	2, 8, 2	+2	1.74	651
Calcium	20	40.08	2, 8, 8, 2	+2	1.55	810
Strontium	38	87.63	2, 8, 18, 8, 2	+2	2.6	800
Barium	56	137.36	2, 8, 18, 18, 8, 2	+2	3.5	850
Radium	88	226.05	2, 8, 18, 32, 18, 8, 2	+2	(5)	960

14. Calcium.—The reactions of this metal may be summarized in the following equations:

$$2Ca + O_2 \rightarrow 2CaO$$
$$Ca + H_2 \rightarrow CaH_2$$
$$Ca + Cl_2 \rightarrow CaCl_2$$
$$Ca + S \rightarrow CaS$$
$$3Ca + N_2 \rightarrow Ca_3N_2$$
$$3Ca + 2P \rightarrow Ca_3P_2$$

$$Ca + 2HOH \rightarrow Ca(OH)_2 + H_2$$
$$Ca + 2HCl \rightarrow CaCl_2 + H_2$$
$$2Ca + CO_2 \rightarrow 2CaO + C$$

In general, its reactions and those of the other alkaline-earth metals are similar to but less vigorous than the reactions of the alkali metals.

15. Limestone, or calcium carbonate, is the source of nearly all the calcium compounds that do not occur in nature. Its anion, the strongly basic carbonate ion, is responsible for its reactions with strong acids and even with such weak acids as acetic. These reactions result in the preparation of the calcium salts of the acids used.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$
$$CaCO_3 + 2HC_2H_3O_2 \rightarrow Ca(C_2H_3O_2)_2 + H_2O + CO_2$$

A similar reaction is responsible for the presence of calcium ions in objectionably high concentration in the water of limestone regions. Natural waters with carbon dioxide in solution convert the insoluble limestone into the more soluble bicarbonate.

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

or

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{++} + 2HCO_3^-$$

Calcium carbonate occurs also as marble and chalk and as the principal constituent of sea shells, coral, pearls, and egg shells.

16. Lime, or quicklime, is the oxide of calcium and is prepared by heating limestone. Crushed limestone is fed into the top of vertical shaft kilns, which are upright cylindrical furnaces lined with firebrick. The temperature necessary to decompose the limestone

$$CaCO_3 \rightarrow CaO + CO_2$$

is maintained by burning coal, coke, wood, producer gas, or fuel oil. A good draft is maintained to sweep away the carbon dioxide from the lime. The equilibrium is determined by the carbon dioxide concentration alone, since both limestone and lime are solids. Hence the pressure of carbon dioxide is kept as low as possible to prevent a reversal of the reaction. The process is continuous, since the lime can be withdrawn at intervals from the bottom of the kiln without shutting down the fire.

This basic oxide is the least expensive and most widely used of the basic heavy chemicals. Nearly 4,000,000 tons are manufactured annually. Lime reacts with water to form calcium hydroxide

$$CaO + H_2O \rightarrow Ca(OH)_2$$

a process known as *slaking;* the dry product is known as *slaked lime,* or *hydrated lime.* The reaction is strongly exothermic as anyone who has made whitewash well knows. A typical metal hydroxide, slaked lime is a source of hydroxyl ions. However, it is only slightly soluble in water and hence cannot be used to prepare strongly basic solutions. Its saturated solution is known as *limewater.*

TABLE 62.—USES OF LIME

Applications	Per cent	Applications	Per cent
Construction	28.5	Calcium carbide	5.0
Agriculture	12.0	Sanitation	5.0
Metallurgy	11.6	Tanneries	4.0
Paper and pulp	10.0	Glass	3.0
Refractories	10.0	Bleaching	0.6
Alkalies	6.0	Miscellaneous	4.3

In the construction industry, lime is used in mortar, plaster, concrete, glass, stucco, sand-lime brick, and cold-water paints. In agriculture, lime has many varied uses. Soils that are too acid are neutralized with slaked lime and even ground limestone. Lime is also treated with chemicals to form insecticides and fungicides. Among these, calcium arsenate is used in large quantities by cotton growers to combat the boll weevil. We have already discussed the use of limestone as a flux in metallurgy (46-2), in the preparation of caustic soda from sodium carbonate (48-7), in the manufacture of calcium carbide (42-15), and in bleaching powder (17-4d). When sulfur dioxide is bubbled through limewater, calcium bisulfite is formed.

$$Ca(OH)_2 + 2SO_2 \rightarrow Ca(HSO_3)_2$$

This is used to dissolve the lignin which cements cellulose fibers together in wood, and so to convert the latter into paper pulp.

Calcium oxide is extremely stable toward heat. At the temperature of the oxyhydrogen flame, it glows with an intense white light but does not decompose. This was the intense source of illumination used in lighthouse beacons, in projectors, and in theater spotlights before the use of electricity. This use explains the origin of the phrase "to be in the limelight."

17. Portland Cement.—In 1824, Joseph Aspdin, an English bricklayer, took out a patent for the manufacture of a cement by heating a mixture of limestone and clay. He called this material portland cement, for on setting it resembled an English building stone called portland stone. This is our modern cement. The raw materials limestone and clay are abundant and found in large deposits of uniform composition in many places. They are composed essentially of three oxides: lime, CaO; alumina, Al_2O_3; and silica, SiO_2. These must first be intimately mixed in the proper proportions. The limits for good quality are given in Table 63.

TABLE 63.—COMPOSITION OF CEMENT

Material	Limits, per cent	Average, per cent
Lime, CaO	60–64.5	62.0
Silica, SiO_2	20–24.0	22.0
Alumina, Al_2O_3	5– 9.0	7.5
Magnesia, MgO	1– 4.0	2.5
Iron oxide, Fe_2O_3	2– 4.0	2.5
Sulfur trioxide, SO_3	1– 1.75	1.5

This mixture, either wet or dry, is "burned" in huge, rotary, inclined kilns, 9 to 11 ft. in diameter and 150 to 250 ft. long. The kiln is heated by pulverized coal, natural gas, or oil, which is blown into the lower end by compressed air, producing a flame some 40 ft. in length. Such kilns will burn 1,000 to 1,500 barrels of cement per day. The mixture is charged in the upper end of the rotating kiln and raked down toward the hotter, lower end by rakes set into the walls. First the mixture is dried; then carbon dioxide is given off from the limestone; and finally, at about 1425°C., chemical reactions take place in which compounds are formed between the three oxides which partially fuse. Of these, the formation of a tricalcium silicate, $3CaO.SiO_2$, is most to be desired. The clinker is discharged from the lower end of the kiln, and 2 to 3 per cent of gypsum is added to regulate the setting time of the cement. It is then ground and bagged.

Cement when mixed with sand and water forms a plastic mass that sets after several hours, after which it gradually hardens. These two processes appear to be quite complicated. Water reacts chemically with the silicates and aluminates in cement, forming a gelatinous, colloidal material when it sets and hardens. This is especially true of the tricalcium silicate, which is the most important cementing material. This gelatinous material in time partially crystallizes.

The United States now manufactures well over half the cement produced in the world, or nearly 200,000,000 barrels valued at about $300,000,000.

18. Calcium Salts.—The mineral gypsum, $CaSO_4 \cdot 2H_2O$, is found in large deposits in Michigan, New York, Iowa, and Texas. Over 2,000,000 tons are mined annually, most of which is used in the manufacture of plaster. When this dihydrate is heated at about 125°C., part of the water of crystallization is lost and plaster of Paris is formed.

$$\underset{\text{gypsum}}{2CaSO_4 \cdot 2H_2O} \rightleftarrows \underset{\text{plaster of Paris}}{(CaSO_4)_2 \cdot H_2O} + 3H_2O$$

This reaction is reversible. When plaster of Paris is mixed with enough water to form a creamy paste, the reverse reaction takes place and the crystals of gypsum interlace to form a rigid mass. Commercial plaster contains glue to retard the rate of setting and is used as a finishing coat on plaster walls and for making casts and gypsum wallboard.

Calcium nitrate is made by treating either slaked lime or limestone with nitric acid. Calcium chloride is a by-product of the Solvay process. Calcium fluoride, or fluor spar, occurs in nature and is used as a flux in metallurgy and to make opaque glass.

19. Strontium, Barium, and Radium.—Both strontium and barium occur mainly as sulfates, celestite ($SrSO_4$) and barite ($BaSO_4$), and to a lesser extent as carbonates, strontianite ($SrCO_3$) and witherite ($BaCO_3$). The carbonates may be readily converted into other salts upon treatment with the appropriate acids. The sulfates, however, are insoluble in acids since the sulfate ion is an infinitesimally weak base. They can be readily reduced by heating the sulfates with carbon, *e.g.*,

$$BaSO_4 + 2C \rightarrow BaS + 2CO_2$$

Since the sulfide ion is a strong base, barium sulfide can be readily converted into other barium salts.

Pure white barium sulfate is made by precipitation when the sulfide is treated with sodium sulfate.

$$BaS + Na_2SO_4 \rightarrow Na_2S + BaSO_4\downarrow$$

This material, called blanc fixe, is used as a filler in paints, rubber goods, oilcloth, plastics, and linoleum and in the manufacture of lithograph inks.

The oxides are prepared by heating the carbonates or the nitrates

$$BaCO_3 \rightarrow BaO + CO_2$$
$$2Sr(NO_3)_2 \rightarrow 2SrO + 4NO_2 + O_2$$

or by heating the carbonates with carbon

$$BaCO_3 + C \rightarrow BaO + 2CO$$

Barium peroxide is formed by heating the oxide in air.

$$2BaO + O_2 \rightleftarrows 2BaO_2$$

At a higher temperature the reaction is reversed. Barium peroxide is the commercial source of hydrogen peroxide.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + H_2O_2$$

The hydroxides are formed from the oxides and water.

The radioactivity of radium is such a spectacular property that one seldom stops to consider the chemical properties of this element. These, however, are so similar to those of barium that they need not be considered separately.

The presence of strontium may be readily detected by its brilliant red flame color. Barium salts give a green flame. The nitrates of both strontium and barium mixed with sulfur, carbon, and an oxidizing agent are used to produce colored flares.

20. Magnesium is not an alkaline-earth metal. Its place in the electromotive series is between these metals and aluminum. The following reactions are typical:

$$2Mg + O_2 \rightarrow 2MgO \qquad Mg + H_2O \rightarrow MgO + H_2$$
$$3Mg + N_2 \rightarrow Mg_3N_2 \qquad 2Mg + CO_2 \rightarrow 2MgO + C$$
$$Mg + Cl_2 \rightarrow MgCl_2 \qquad Mg + 2HCl \rightarrow MgCl_2 + H_2$$

Magnesium burns with an intense white light. Hence it is used in flashlight powders, star shells, and tracer bullets. Its strength as a reducing agent is shown by its combustion in an atmosphere of carbon dioxide. It reacts slowly with boiling water, readily with steam.

21. Magnesium Oxide and Hydroxide.—The naturally occurring carbonate magnesite decomposes into the oxide *magnesia* upon heating. As in the case of lime, magnesia is also extremely stable toward heat. Hence it is one of the most widely used refractory materials in lining furnaces of all types. Unlike lime, magnesia does not react readily with water. The hydroxide is prepared by precipitation.

$$Mg^{++} + 2OH^- \rightarrow Mg(OH)_2\downarrow$$

Milk of magnesia is a suspension of the hydroxide in water and may be taken internally as an antacid. Its limited solubility prevents too high a concentration of hydroxyl ions, but as an acid is neutralized more of the hydroxide dissolves. The precipitation of the hydroxide by ammonium hydroxide is prevented by the presence of an ammonium salt. The high concentration of the ammonium ions from the salt so reduces the hydroxyl-ion concentration

$$NH_4^+ + OH^- \overset{\longrightarrow}{\leftarrow} NH_3 + HOH$$

that the solubility product of magnesium hydroxide is not exceeded.

Since magnesium hydroxide has an even smaller solubility product than magnesium carbonate, the addition of sodium carbonate to a solution containing magnesium ions precipitates both the carbonate and the hydroxide. The hydrolysis of the carbonate ion furnishes the hydroxyl ions.

$$\begin{gathered} CO_3^= + HOH \rightleftarrows HCO_3^- + OH^- \\ Mg^{++} + 2OH^- \rightarrow Mg(OH)_2\downarrow \\ Mg^{++} + CO_3^= \rightarrow MgCO_3\downarrow \end{gathered}$$

The mixed precipitate contains approximately three times as much carbonate as hydroxide. This white precipitate is the *magnesia alba* used extensively in tooth powders and in silver polish. Mixed with 15 per cent asbestos, it forms an excellent, heat-insulating pipe covering.

22. Magnesium Salts.—Magnesium sulfate occurs in nature as Epsom salts, $MgSO_4.7H_2O$, and is used in medicine, in dyeing textiles, and in tanning. The chloride, $MgCl_2.6H_2O$, occurs in sea salts and, when heated, is hydrolyzed by its own water of crystallization.

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

This reaction should suggest at least one reason why sea water should not be used in boilers.

Several important silicates of magnesium occur in nature. Asbestos is a double silicate of magnesium and calcium ($3MgSiO_3.CaSiO_3$) and owes its fibrous structure to long chains of silicate ions that share oxygen atoms in common. Talc, or soapstone, is $H_2Mg_3(SiO_3)_4$.

23. Beryllium occurs mainly in the mineral beryl, $Be_3Al_2(SiO_3)_6$. Emeralds and aquamarines are gem varieties of this mineral, the former tinted green with chromic oxide and the latter blue and light green by compounds of iron. The hydroxide of beryllium is amphoteric, which is not surprising in view of the position of this element at the top of Group II.

24. Hard Water.—Natural water, which contains an appreciable concentration of calcium and magnesium ions, is known as hard water. We have learned how water in limestone regions contains calcium bicarbonate in solution (48-15). Sparingly soluble sulfates such as gypsum are leached out of the soil. Hard water is unfit for use in laundering or as a boiler water.

The soaps used in laundering are either sodium or potassium salts of certain organic compounds known as fatty acids (55-7). The formula for a typical soap, sodium oleate, is $NaC_{18}H_{33}O_2$. Soaps react with the soluble compounds of calcium and magnesium found in hard water, forming calcium or magnesium salts of the fatty acids of the soap which are insoluble. The reaction is one of double decomposition, *e.g.*,

$$2NaC_{18}H_{33}O_2 + CaSO_4 \rightarrow Ca(C_{18}H_{33}O_2)_2\downarrow + Na_2SO_4$$

These insoluble compounds are useless in working up a lather with water and represent a waste of soap. Calcium and magnesium compounds are also objectionable in boiler water. When a hard water is vaporized in the boiler, these compounds are deposited as a hard heat-insulating scale in the boiler tubes. Such a scale not only makes the operation of the boiler inefficient, but also renders its use dangerous. Localized superheating and pitting of the inside walls of the boiler tubes result. A scale of ¼ in. in thickness requires 50 per cent more fuel.

25. Water Softening.—Hard waters are classified either as waters of temporary or of permanent hardness. Water of temporary hardness can be softened by heat alone. Such water contains the bicarbonates of calcium and magnesium. When heated, the soluble bicarbonates decompose into the insoluble carbonates which settle to the bottom and can then be removed.

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2$$

Water of permanent hardness contains the sulfates of these metals which cannot be removed by heat alone, although such water can be softened by chemical methods.

An English chemist, Thomas Clark, first introduced the use of lime, CaO, for softening water of temporary hardness. This reagent converts the soluble bicarbonates into the insoluble carbonates.

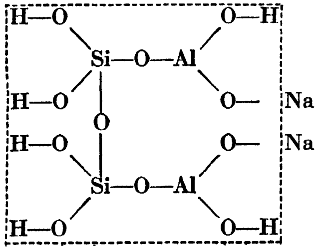
$$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3\downarrow + H_2O$$

Later, Porter introduced the use of soda, or washing soda, to remove the permanent hardness due to calcium sulfate. The calcium is precipitated as its carbonate by this treatment.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$$

A combination of the two the Porter-Clark, or soda-lime, process is used to soften billions of gallons of water annually.

About 1910, Dr. Robert Gans introduced the so-called permutite process of water softening. A compound is used which resembles a certain class of minerals found in nature called zeolites. The molecule of this artificial zeolite is said to have the following structure:



To save ourselves the trouble of writing out this complex structural formula, we shall let the symbol Ze stand for that portion of the molecule which is within the dotted line. This, we see, has a valence of 2 since it is combined with two univalent sodium atoms. When hard water is allowed to filter through a bed of this insoluble compound, the following reactions take place:

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow 2NaHCO_3 + CaZe$$
$$Na_2Ze + CaSO_4 \rightarrow Na_2SO_4 + CaZe$$

When the permutite bed has been exhausted owing to its complete conversion into its calcium or magnesium derivative, a solution of common salt is allowed to flood up into it from below which results in its conversion back into its original form.

$$CaZe + 2NaCl \rightarrow CaCl_2 + Na_2Ze$$

The permutite process produces a water of "zero" hardness.

26. Deionized Water.—Distillation has been the only method for preparing pure water until recent years. Artificial zeolites substitute sodium ions for those of calcium and magnesium and, therefore, substitute one ion for another. In 1935, resinous ion exchangers became available commercially which make possible the removal of both cations and anions from water. The raw water is first passed through a hydrogen-exchange resin HR, which substitutes hydrogen (hydronium) ions for the metal cations of the dissolved salt.

$$HR + Me^+ \rightarrow H^+ + MeR$$

or

$$HR + MeX \rightarrow HX + MeR$$

The salts are thus converted into the corresponding acids. These in turn are absorbed when the water is next passed through an acid absorbent. The latter is a resin of the amine-formaldehyde type which contains amino ($-NH_2$) groups. The acids add to these groups.

$$RNH_2 + HX \rightarrow RNH_2.HX$$

Passing dilute sulfuric acid through the spent hydrogen-exchange resin regenerates it.

$$2MeR + H_2SO_4 \rightarrow 2HR + Me_2SO_4$$

The resulting water compares favorably with distilled water, and its cost is much lower.

Ion-exchange resins are now being used by our armed forces to prepare small quantities of drinking water from sea water. Many lives have been saved on our life rafts by equipment using this principle.

EXERCISES

1. Write equations for the reactions involved in the Solvay process.

2. What is the principal by-product of this process, and for what is it used?

3. Into what reaction does soda enter in the manufacture of glass?

4. Into what reaction does baking soda enter in commercial baking powders?

5. What is the economic importance of potash?

6. Are solutions of the following salts acidic, basic, or neutral: KNO_3, K_2CO_3, $CaSO_4$, $MgCl_2$? Explain.

7. How is cement manufactured?

8. Write equations for the reactions that take place when solutions of magnesium sulfate and sodium carbonate are mixed.

9. Why does the presence of an ammonium salt prevent the precipitation of magnesium hydroxide by ammonia water?

10. Would sodium chloride prevent the precipitation of magnesium hydroxide when sodium hydroxide is added to a solution of magnesium chloride? Explain.

11. What are limestone, slaked lime, quicklime, and hydrated lime?

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CHAPTER FORTY-NINE

COPPER, MERCURY, SILVER AND GOLD

These are the metals below hydrogen in the electromotive series. In terms of the periodic table these metals at first sight seem strange companions. Copper, silver and gold are in Group 1, mercury in Group 2. However, all have the valence of +1 in common and all are relatively difficult to oxidize.

TABLE 64.—PROPERTIES OF COPPER, SILVER, GOLD, AND MERCURY

Metal	Atomic number	Atomic weight	Planetary electrons	Valences	Group	Density	Melting point, °C.
Copper....	29	63.57	2, 8, 18, 1	+1, +2	1	8.92	1083
Silver.....	47	107.880	2, 8, 18, 18, 1	+1	1	10.5	960.5
Gold......	79	197.2	2, 8, 18, 32, 18, 1	+1, +3	1	19.3	1063
Mercury..	80	200.61	2, 8, 18, 32, 18, 2	+1, +2	2	13.55	−38.87

1. **Copper** forms two series of compounds corresponding to its two valences of +1 and +2. In general, the cuprous salts of oxygen acids are unknown and binary cuprous salts are insoluble. Cupric salts of oxygen acids are common, but binary cupric salts tend to be unstable.

When heated in a stream of air or oxygen, the metal is first converted into the red cuprous oxide

$$4Cu + O_2 \rightarrow 2Cu_2O$$

and then into black cupric oxide

$$2Cu_2O + O_2 \rightarrow 4CuO$$

Heated with an excess of sulfur, copper forms cuprous sulfide.

$$2Cu + S \rightarrow Cu_2S$$

It combines directly with chlorine, forming first cuprous then cupric chloride. Under the combined action of the oxygen, water vapor, and carbon dioxide of the atmosphere, the metal slowly becomes covered with the familiar blue-green coating of a basic cupric carbonate.

Copper does not displace hydrogen and hence is not attacked by nonoxidizing acids. Nitric and hot concentrated sulfuric acids convert the metal into the corresponding cupric salts.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$$

2. The Cupric Ion.—Cupric sulfate, or blue vitriol, $CuSO_4 \cdot 5H_2O$, is the commonest salt of divalent copper and is the usual source of the cupric ion. This ion is hydrated in aqueous solution with four molecules of water and is blue in color. The hydrated ion is a very weak acid, and hence solutions of cupric salts are feebly acidic

$$Cu(H_2O)_4^{++} + H_2O \rightleftarrows Cu(H_2O)_3OH^+ + H_3O^+$$

or, more simply,

$$Cu^{++} + HOH \rightleftarrows CuOH^+ + H^+$$

This is another example of the hydrolysis of a cation (33-9).

When an alkali-metal hydroxide is added to a solution containing cupric ions, the light-blue cupric hydroxide precipitates. The latter decomposes at the temperature of boiling water into the black cupric oxide. When ammonia water is added to solutions in which the cupric-ion concentration is appreciable, the solubility product of the hydroxide is exceeded.

$$Cu^{++} + 2OH^- \rightarrow Cu(OH)_2\downarrow$$

Further addition of ammonia causes the formation of the deep purple-blue cupric-ammonia complex ion

$$Cu^{++} + 4NH_3 \rightarrow Cu(NH_3)_4^{++}$$

and so reduces the cupric-ion concentration that the hydroxide precipitate redissolves. When ammonia is added to a solution, in which the concentration of the cupric ion is so low that its color is imperceptible, the deeper color of the ammonia complex becomes readily visible. This serves as a delicate test for the cupric ion.

Hydrogen sulfide precipitates the black cupric sulfide from neutral and from not too acid solutions of the cupric ion.

3. Univalent Copper.—Cuprous chloride is one of the few salts of univalent copper which is even sparingly soluble. Cuprous iodide is precipitated when an iodide is added to a cupric salt, owing to the instability of cupric iodide.

$$Cu^{++} + 2I^- \rightarrow CuI_2$$
$$2CuI_2 \rightarrow 2CuI\downarrow + I_2\downarrow$$

Similarly, the addition of a cyanide to the cupric ion first causes the precipitation of cuprous cyanide

$$Cu^{++} + 2CN^- \rightarrow Cu(CN)_2$$
$$2Cu(CN)_2 \rightarrow 2CuCN\downarrow + (CN)_2$$

with the liberation of the poisonous gas cyanogen. An excess of the cyanide ion redissolves the precipitate, owing to the formation of the complex cuprocyanide ion.

$$CuCN + CN^- \rightarrow Cu(CN)_2^-$$

4. Silver forms only one series of compounds in which the metal is univalent. It is one of the less reactive metals. It is not oxidized by atmospheric oxygen but is slowly tarnished by sulfur and its compounds to the black silver sulfide. It does not replace hydrogen from acids, but oxidizing acids convert the metal into the corresponding silver salts.

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$$

5. The Silver Ion.—Silver nitrate, or lunar caustic, is the most readily available soluble silver salt. When the hydroxyl ion is added to the silver ion, dark-brown silver oxide precipitates

$$Ag^+ + OH^- \rightarrow AgOH$$
$$2AgOH \rightarrow Ag_2O\downarrow + H_2O$$

owing to the instability of the hydroxide. The addition of ammonia water first precipitates the oxide, as above, which redissolves in an excess of ammonia forming the silver-ammonia complex ion.

$$Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+$$

Halide ions precipitate the corresponding silver halides.

$$Ag^+ + Cl^- \rightarrow \underset{\text{white}}{AgCl\downarrow}$$
$$Ag^+ + Br^- \rightarrow \underset{\text{cream}}{AgBr\downarrow}$$
$$Ag^+ + I^- \rightarrow \underset{\substack{\text{light}\\\text{yellow}}}{AgI\downarrow}$$

Of these, the iodide has the smallest solubility product. The chloride precipitate dissolves readily when ammonia is added; the bromide, less readily; and the iodide, practically not at all.

The reaction of the silver ion with the cyanide ion is similar to that of copper. Silver cyanide first precipitates and then redissolves as the addition of more cyanide forms the silver cyanide complex ion.

$$Ag^+ + CN^- \rightarrow AgCN\downarrow$$
$$AgCN + CN^- \rightarrow Ag(CN)_2^-$$

The electrolyte in silver-plating baths is the potassium salt of this complex ion. The article to be plated is made the cathode and silver metal the anode. The complex ion is dissociated to a slight extent so that the low concentration of silver ions, needed to obtain a tenacious coating of silver, is maintained.

$$Ag(CN)_2^- \rightleftarrows Ag^+ + 2CN^-$$

Silver ions are discharged on the cathode

$$Ag^+ + e^- \rightarrow Ag$$

and go into solution from the silver-metal anode

$$Ag \rightarrow Ag^+ + e^-$$

The silver ion is easily reduced to the free metal as one might suspect from its position in the electromotive series. Silver mirrors are made by reducing silver ions with mild organic reducing agents such as glucose or formaldehyde. By adding ammonia to a silver nitrate solution, most of the silver is in the form of the silver-ammonia complex ion. The reducing agent thus acts on a very low concentration of silver ions, and the metal is deposited in very fine crystals on the glass surface.

6. Photography.—A photographic film consists of an emulsion of silver bromide and iodide suspended in gelatin attached to a cellulose acetate sheet. On exposure to light, the silver salts are reduced to the free metal. The extent of this reduction is very slight during the brief period of the exposure, but it is proportional to the intensity of the light in the image focussed on the emulsion. This invisible latent image of grains of silver is developed by organic reducing agents, such as hydroquinone and pyrogallol, which reduce additional grains of silver more readily in those areas of the film where the initial reduction was the greatest. The negative is now blackest with metallic silver where the light in the original image was most intense. The excess silver salts in the negative must now be removed, since exposure to light would reduce them to the metal. This is done by a process known as fixing. The negative is immersed in a solution of hypo, or sodium thiosulfate, which dissolves the silver halides forming complex ions.

$$AgBr + 2S_2O_3^{=} \rightarrow Ag(S_2O_3)_2^{\equiv} + Br^-$$

A positive print is developed and fixed in a similar manner.

7. Gold forms two series of compounds corresponding to the valences of +1 (aurous) and +3 (auric). The metal is not attacked by solutions of acids or alkalies. Nitric acid does not react with it. Aqua regia, a mixture of 3 parts hydrochloric and 1 part nitric acid, converts it to chlorauric acid.

$$Au + 3HCl + HNO_3 \rightarrow AuCl_3 + NO + 2H_2O$$
$$AuCl_3 + HCl \rightarrow HAuCl_4$$

8. Mercury forms two series of compounds in which its valence is +1 or +2. The mercurous ion is peculiar in that it consists of two atoms of mercury linked by an electron pair. Further, each atom has lost an electron which gives this diatomic ion a charge of +2. For the sake of simplicity, we shall write the mercurous ion Hg^+ instead of the more exact Hg_2^{++}. Both the liquid metal and its vapor are poisonous. The free metal reacts only with oxidizing acids. When concentrated nitric acid reacts with an excess of mercury, mercurous nitrate is formed.

$$Hg + 2HNO_3 \rightarrow HgNO_3 + NO_2 + H_2O$$

With an excess of the acid, the mercuric nitrate results.

$$Hg + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

9. Reactions of the Mercurous Ion.—Since mercurous hydroxide is unstable, the oxide is precipitated when hydroxyl ions are added to the solution of a mercurous salt.

$$2Hg^+ + 2OH^- \rightarrow Hg_2O\downarrow + H_2O$$

This oxide decomposes slowly at room temperature and rapidly at 100°C. into mercury and mercuric oxide.

$$Hg_2O \rightarrow Hg + HgO$$

Mercurous chloride is precipitated when the chloride ion is added to a solution of the mercurous ion.

$$Hg^+ + Cl^- \rightarrow HgCl\downarrow$$

The precipitate reacts with ammonia to form the insoluble, white mercuric aminochloride and black metallic mercury.

$$2HgCl + 2NH_3 \rightarrow \underset{\text{white}}{HgNH_2Cl\downarrow} + \underset{\text{black}}{Hg\downarrow} + NH_4Cl$$

This reaction used in conjunction with the initial precipitation of the white mercurous chloride serves as a test for the mercurous ion.

Mercurous chloride, known in medicine as calomel, is used to stimulate the liver. Although the mercurous ion is poisonous, the low solubility of mercurous chloride makes it safe to take internally. It should be kept in brown-glass bottles, however, since the action of light slowly converts this salt into the deadly mercuric chloride and metallic mercury.

10. Reactions of the Mercuric Ion.—When sodium hydroxide is added to a solution of a mercuric salt, the yellow mercuric oxide precipitates.

$$Hg^{++} + 2OH^- \rightarrow HgO\downarrow + H_2O$$

This substance when heated changes into a red variety which can also be prepared by heating mercury in air, at a moderate temperature. At higher temperatures, the oxide decomposes into mercury and oxygen.

The iodide precipitates in a yellow modification

$$Hg^{++} + 2I^- \rightarrow HgI_2\downarrow$$

which changes gradually to a red form. The black sulfide is precipitated by hydrogen sulfide from acid solutions.

The mercuric ion is easily reduced. Indeed mercuric salts may be converted to the corresponding mercurous compounds by warming with metallic mercury.

$$Hg^{++} + Hg \rightarrow 2Hg^+$$

Stannous chloride may be used as a reducing agent to accomplish this change.

$$2HgCl_2 + SnCl_2 \rightarrow \underset{\text{white}}{2HgCl\downarrow} + SnCl_4$$

The reduction does not stop at the mercurous stage, but the white precipitate of mercurous chloride is further reduced to the free metal.

$$2HgCl + SnCl_2 \rightarrow \underset{\text{black}}{2Hg\downarrow} + SnCl_4$$

These reactions serve as a test for the mercuric ion.

Mercuric chloride is often called bichloride of mercury, or corrosive sublimate. This substance is a deadly poison that destroys the cells of the kidneys. White of eggs may be used as an antidote, as the protein in them precipitates the mercury. In dilute solution it is used as an external antiseptic. It is made by heating a mixture of mercuric sulfate and sodium chloride.

$$HgSO_4 + 2NaCl \rightarrow HgCl_2\uparrow + Na_2SO_4$$

The fact that this substance sublimes and that its aqueous solutions are poor conductors of electricity indicate that mercuric chloride is molecular rather than ionic.

EXERCISES

1. Show by means of equations how the following transformations may be accomplished:

$$CuSO_4 \rightarrow Cu \rightarrow Cu(NO_3)_2 \rightarrow CuO \rightarrow CuCl_2 \rightarrow CuI$$

2. Why does the fact that cupric sulfide is precipitated from acid solutions by hydrogen sulfide indicate that its solubility product is small?

3. Draw the formula of the $Cu(NH_3)_4^{++}$ ion in such a way as to show the electrons in the valency shells of each atom.

4. What reactions are used as a test for the mercurous ion?

5. Show by means of equations how the following changes may be brought about:

$$Hg \rightarrow Hg(NO_3)_2 \rightarrow HgNO_3 \rightarrow Hg_2O \rightarrow Hg$$

6. Why does a precipitate of silver chloride darken when exposed to light?

7. Explain in terms of solubility product why silver chloride dissolves in ammonia.

8. How could a mixture of mercuric and sodium chlorides be separated?

9. Why does gold dissolve in aqua regia?

10. What reaction do you predict would take place between stannous and auric chlorides?

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CHAPTER FIFTY

ZINC, ALUMINUM, TIN, AND LEAD

Despite the fact that these metals are not in the same group in the periodic table they resemble one another in that their hydroxides are amphoteric.

TABLE 65.—PROPERTIES OF ZINC, ALUMINUM, TIN, AND LEAD

Metal	Atomic number	Atomic weight	Planetary electrons	Valences	Group	Density	Melting point, °C.
Zinc........	30	65.38	2, 8, 18, 2	+2	2	7.14	419
Aluminum...	13	26.97	2, 8, 3	+3	III	2.70	1380
Tin.........	50	118.7	2, 8, 18, 18, 4	+2, +4	IV	7.31	232
Lead........	82	207.21	2, 8, 18, 32, 18, 4	+2, +4	IV	11.35	328

1. Reactions of Zinc.—Since zinc is placed relatively high in the electromotive series, the metal is active and a strong reducing agent. Powdered zinc, or zinc dust, burns brilliantly in the Bunsen flame, forming the white oxide. This compound finds use as a paint pigment, as a filler in tires, and in the manufacture of oilcloth and surgeon's tape.

The metal replaces hydrogen from dilute acids and alkalies.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$
$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

It is a strong enough reducing agent to reduce dilute nitric acid to ammonia.

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

The metal combines directly with the halogens and with sulfur.

2. Reactions of the Zinc Ion.—When sodium hydroxide is added to the solution of a zinc salt, a white, translucent precipitate of zinc hydroxide is first formed.

$$Zn^{++} + 2OH^- \rightarrow Zn(OH)_2\downarrow$$

or

$$ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2\downarrow + 2NaCl$$

Since this precipitate is amphoteric, it acts as an acid and dissolves in an excess of the hydroxide.

$$H_2ZnO_2 + 2OH^- \rightarrow ZnO_2^= + 2HOH$$

or

$$H_2ZnO_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2HOH$$

The salt formed is sodium zincate. When an acid is added, the hydroxide again precipitates.

$$ZnO_2^= + 2H^+ \rightarrow H_2ZnO_2\downarrow$$

or

$$Na_2ZnO_2 + 2HCl \rightarrow H_2ZnO_2\downarrow + 2NaCl$$

If an excess of the acid is added, the precipitate, acting as a metal hydroxide, redissolves.

$$Zn(OH)_2 + 2H^+ \rightarrow Zn^{++} + 2HOH$$

or

$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2HOH$$

The precipitate, suspended in water, is in equilibrium with two sets of ions.

$$Zn^{++} + 2OH^- \rightleftarrows Zn(OH)_2$$

or

$$H_2ZnO_2 \rightleftarrows 2H^+ + ZnO_2^=$$

Hydrogen sulfide precipitates white zinc sulfide from basic, neutral, and even from feebly acid solutions.

3. Reactions of Aluminum.—Aluminum is a very active metal. The heat liberated in its combustion is high, 133,000 cal. per gram-atom of oxygen consumed. Aluminum powder, blown into the flame of a Bunsen burner, ignites violently. Photoflash bulbs contain aluminum foil in an atmosphere of oxygen. Aluminum rusts rapidly, but the oxide film forms an unbroken coating that protects the metal from further oxidation. The metal reacts violently with the halogens. Aluminum is a strong reducing agent. Its reducing action on ferric oxide liberates so much heat that this reaction is the basis of thermite welding.

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe + 199{,}000 \text{ cal.}$$

A mixture of the reactants is loaded into a crucible with a false bottom over the iron parts that are to be welded together. The reaction is started by setting off an ignition mixture of barium peroxide and magnesium by means of a fuse. A very vigorous reaction ensues, and temperatures between 3000 and 3500°C. are attained. Molten iron runs off through the bottom of the crucible into the space between the ends that are to be welded together. The uses of aluminum as a reducing agent and as an oxygen scavenger in metallurgy have already been discussed (46-12).

Aluminum replaces hydrogen from acids and from metal hydroxides.

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$
$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

4. Reactions of the Aluminum Ion.—Since aluminum hydroxide is amphoteric, the aluminum ion enters into a series of reactions similar to those of the zinc ion when treated with sodium hydroxide.

$$Al^{+++} + 3OH^- \rightarrow Al(OH)_3\downarrow$$

The hydroxide acts as a monoprotic acid toward an excess of hydroxyl ions. Since the precipitate is really an indefinitely hydrated oxide, $Al_2O_3.xH_2O$—$Al(OH)_3$ corresponds to $Al_2O_3.3H_2O$ —we are justified in writing its formula as $HAlO_2$ instead of H_3AlO_3. Hence

$$HAlO_2 + OH^- \rightarrow AlO_2^- + HOH$$
$$\text{or}\qquad HAlO_2 + NaOH \rightarrow NaAlO_2 + HOH$$

When hydrochloric acid is added to this solution of sodium aluminate, the hydroxide precipitates but redissolves when an excess is added.

$$AlO_2^- + H^+ \rightarrow HAlO_2\downarrow$$
$$\text{or}\qquad NaAlO_2 + HCl \rightarrow HAlO_2\downarrow + NaCl$$
$$\text{and}\qquad Al(OH)_3 + 3H^+ \rightarrow Al^{+++} + 3HOH$$
$$\text{or}\qquad Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3HOH$$

When ammonia water is added to solutions containing the aluminum ion, sufficient hydroxyl ion is present to precipitate the hydroxide but not to redissolve it.

Since the aluminum ion is hydrolyzed

$$Al^{+++} + HOH \rightleftarrows AlOH^{++} + H^+$$
$$AlOH^{++} + HOH \rightleftarrows Al(OH)_2^+ + H^+, \text{ etc.}$$

aqueous solutions of aluminum salts are acidic. This fact is made use of in alum baking powders (42-21).

The gelatinous precipitate of the hydroxide will adsorb dyestuffs strongly, forming pigments known as lakes. Precipitated in the fibers of cotton textiles, it acts as a mordant in adsorbing dyes that would not color cotton directly.

When aluminum hydroxide is heated, the oxide (Al_2O_3), or alumina, is formed. This substance occurs in nature as corundum and as the mineral bauxite. Rubies and sapphires are varieties of corundum colored by impurities. Its high melting point makes it a valuable material from which to make crucibles. It is used in abrasives because of its hardness.

5. Aluminum Salts.—Aluminum sulfate, $Al_2(SO_4)_3.18H_2O$, is widely used in industry. It is prepared by heating bauxite, Al_2O_3, or clay, $H_2Al_2(SiO_4)_2.H_2O$, and extracting with sulfuric acid. When relatively small amounts of the sulfate are dissolved in a municipal water supply, enough aluminum hydroxide is formed by hydrolysis to precipitate. This gelatinous solid carries down with it suspended materials which may be easily removed by the sand filter beds. The salt is also used as a mordant in dyeing, in the manufacture of paper, and in baking powders.

The alums are double sulfates of an alkali metal or the ammonium group and of a trivalent metal. All alums crystallize with 24 molecules of water. The following are typical: common alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$; sodium alum, $Na_2SO_4.Al_2(SO_4)_3.24H_2O$; chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$; ferric alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$; and ammonium alum, $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$. All alums are isomorphous.

6. Tin has two valences, +2 and +4. In both valences the hydroxides are amphoteric. *As is the general rule, the higher valence hydroxide is more acidic and less basic than the lower one.* The metal reacts readily with chlorine to form first stannous chloride and then stannic chloride.

$$Sn + Cl_2 \rightarrow SnCl_2$$
$$SnCl_2 + Cl_2 \rightarrow SnCl_4$$

The latter is a liquid and hence a molecular compound. Tin replaces hydrogen from dilute nonoxidizing acids to form the corresponding stannous salts. With dilute nitric acid, stannous nitrate is formed and the nitrogen reduced to the ammonium ion.

$$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

With concentrated nitric acid, insoluble metastannic acid is formed.

7. Reactions of Divalent Tin.—Sodium hydroxide, added to solutions containing the stannous ion, precipitates stannous hydroxide.

$$Sn^{++} + 2OH^- \rightarrow Sn(OH)_2\downarrow$$

or

$$SnCl_2 + 2NaOH \rightarrow Sn(OH)_2\downarrow + 2NaCl$$

The latter, an amphoteric hydroxide, redissolves in an excess of hydroxyl ion, acting as stannous acid and forming the stannite ion.

$$H_2SnO_2 + 2OH^- \rightarrow 2HOH + SnO_2^=$$

Stannous oxide is formed when the hydroxide is heated.

From dilute acid solutions, hydrogen sulfide precipitates the dark-brown stannous sulfide.

$$Sn^{++} + S^= \rightarrow SnS\downarrow$$

This sulfide dissolves in ammonium polysulfide, forming the thiostannate ion

$$SnS + S + S^= \rightarrow SnS_3^=$$

a reaction similar to the formation of the thioarsenate ion discussed previously (41-15).

Both the stannous ion, Sn^{++}, in acid and the stannite ion, $SnO_2^=$, in basic solutions are reducing agents.

8. Reactions of Tetravalent Tin.—The liquid stannic chloride is completely hydrolyzed by water to the insoluble stannic hydroxide.

$$SnCl_4 + 4HOH \rightarrow Sn(OH)_4\downarrow + 4HCl$$

Only in strongly acid solutions are even low concentrations of the stannic ion possible.

$$Sn(OH)_4 + 4H^+ \rightleftharpoons Sn^{++++} + 4HOH$$

This amphoteric hydroxide dissolves in basic solutions to form the stannate ion. In acting as stannic acid in this reaction, its formula is best written H_2SnO_3.

$$H_2SnO_3 + 2OH^- \rightarrow SnO_3^= + 2HOH$$

The hydroxide is converted into stannic oxide, SnO_2, on heating.

Stannic sulfide forms as a yellow precipitate when hydrogen sulfide is passed through an acid solution of a stannic compound. It dissolves in ammonium and alkali sulfides to form the thiostannate ion.

$$SnS_2 + S^= \rightarrow SnS_3^=$$

9. Reactions of Lead.—As is the case with tin, lead forms two series of compounds corresponding to the valences of +2 and +4. However, since lead is below tin in Group IV of the periodic table, it is more metallic.

When the metal is heated in air, lead monoxide, PbO, or litharge, is obtained. This reddish-yellow oxide is used in making flint glass. Although the metal is above hydrogen in the electromotive series, its reactions with dilute hydrochloric and sulfuric acids do not proceed to any extent, since both lead chloride and lead sulfate are insoluble. These salts form protective coatings on the metal surface which prevent further interaction. The use of the metal in the lead-chamber process for making dilute sulfuric acid depends on this property.

Lead dissolves easily in dilute nitric acid and in hot, concentrated sulfuric acid, forming the corresponding salts of divalent lead.

10. Reactions of the Plumbous Ion.—This ion is usually called the lead ion. Addition of hydroxyl ions precipitates the amphoteric lead hydroxide which dissolves in both acids and alkalies forming lead salts and plumbites, respectively.

$$Pb^{++} + 2OH^- \rightarrow Pb(OH)_2\downarrow$$
$$Pb(OH)_2 + 2H^+ \rightarrow Pb^{++} + 2HOH$$
$$H_2PbO_2 + 2OH^- \rightarrow 2HOH + PbO_2^=$$

The lead ion forms precipitates with many anions of which the following are typical:

$$Pb^{++} + 2Cl^- \rightarrow \underset{\text{white}}{PbCl_2\downarrow}$$
$$Pb^{++} + 2I^- \rightarrow \underset{\text{yellow}}{PbI_2\downarrow}$$
$$Pb^{++} + SO_4^= \rightarrow \underset{\text{white}}{PbSO_4\downarrow}$$
$$Pb^{++} + CrO_4^= \rightarrow \underset{\text{yellow}}{PbCrO_4\downarrow}$$
$$Pb^{++} + S^= \rightarrow \underset{\text{black}}{PbS\downarrow}$$

Lead salts are poisonous. Further, their effect is cumulative since small quantities taken into the system accumulate and eventually cause chronic lead poisoning.

11. Compounds of Tetravalent Lead.—These are relatively unimportant. Lead tetrachloride is a yellow liquid that decomposes readily on heating.

$$PbCl_4 \rightarrow PbCl_2 + Cl_2$$

Plumbates, such as Ca_2PbO_4, or calcium orthoplumbate, and K_2PbO_3, or potassium metaplumbate, are known indicating that the unstable hydroxide of tetravalent lead is amphoteric.

The two oxides, red lead, or Pb_3O_4, and the sesquioxide, Pb_2O_3, are really lead orthoplumbate, Pb_2PbO_4, and lead metaplumbate, $PbPbO_3$, respectively. As such they contain both divalent and tetravalent lead.

The dioxide, PbO_2, is a good oxidizing agent. For example, it reacts with sulfur dioxide to form lead sulfate.

$$PbO_2 + SO_2 \rightarrow PbSO_4$$

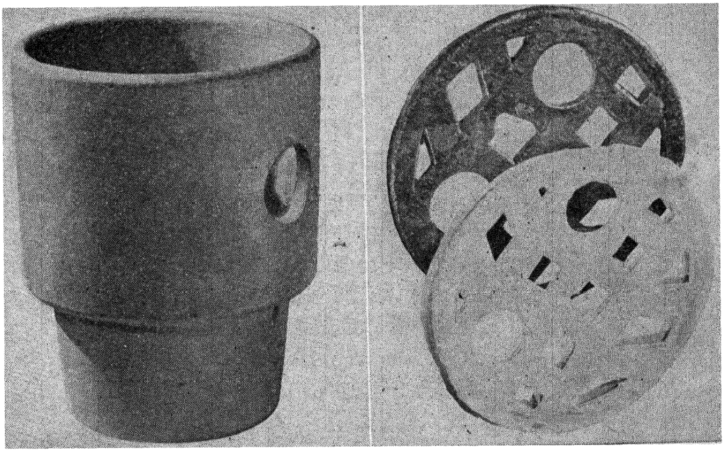
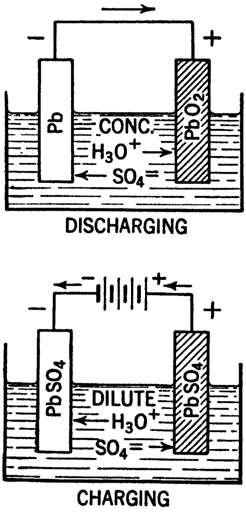


FIG. 178.—Lead buckles and fermenting pot used in the manufacture of white lead by the Dutch process. (*Courtesy of National Lead Company.*)

12. White Lead.—This important paint pigment is a basic carbonate, $(PbCO_3)_2 \cdot Pb(OH)_2$. The Dutch process produces a superior quality of white lead. Lead buckles, shaped somewhat like pretzels, are placed on perforated shelves in earthenware pots over a solution of acetic acid. These pots are stacked in layers covered with planks and resting on fermenting tanbark. The heat of the fermentation raises the temperature, thus evaporating the acetic acid and water. The lead buckles are converted first to a basic lead acetate. Then the carbon dioxide from the fermentation completes the transformation to the basic carbonate.

13. The Lead Storage Cell.—The oxidation-reduction reactions involving lead in its two valences are made use of in the lead storage cell. A storage cell is one capable of storing electrical energy, which is given to it from some external source, as chemical energy and of giving out this energy again when needed. Its operation involves two processes: the charging process, in which electrical energy is supplied to it from some external source and stored as chemical energy; and the discharging process, in which it acts as an electrochemical cell. Since the lead storage cell is the one most widely used today, we shall make it our example of how storage cells in general behave.



DISCHARGING

CHARGING

Fig. 179.—Lead storage cell.

The charging process is one of electrolysis. Both poles of an uncharged cell are composed essentially of insoluble lead sulfate. These are in a dilute solution of sulfuric acid. The pole, which is to be negative in the charged battery, is connected to the negative pole of a source of direct current which must be at a higher voltage than that of the fully charged cell, and the positive pole of the cell is connected to the positive pole of the current source (Fig. 179). The reaction that takes place during the charging process is as follows:

$$E + 2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4 \qquad (1)$$

It is endothermic, absorbing electrical energy and storing it as the chemical energy of the products. The mechanism by which this reaction takes place has not as yet been fully explained, but the following one is simple and logical. At the negative pole

$$PbSO_4 + 2e^- \rightarrow Pb^0 + SO_4^= \qquad (2)$$

The lead is reduced to the free metal, and sulfate ions go into solution. On the other hand, each atom of the divalent lead of the lead sulfate at the positive pole gives up two more electrons, becomes tetravalent, and unites with another sulfate ion.

$$Pb^{+2}SO_4 + SO_4^= \rightarrow Pb^{+4}(SO_4)_2 + 2e^- \qquad (3)$$

The lead persulfate formed is the salt of an exceedingly weak base and is completely hydrolyzed to the insoluble lead dioxide.

$$Pb(SO_4)_2 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4 \qquad (4)$$

Combining equations (2), (3), and (4), we have the complete equation for the charging reaction, (1). The charged cell consists of a negative pole of metallic lead and a positive pole of lead dioxide. Since sulfuric acid is one of the products of this process, the electrolyte becomes more concentrated and hence denser so that the charging process can be followed by a hydrometer which measures the density of the electrolyte.

The charged cell acts as a typical electrochemical cell when it furnishes electrical energy. The cell reaction is the reverse of equation (1):

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O + E \qquad (5)$$

Here again what happens at each pole during discharge is not definitely known. The following mechanism is simple but may not be the correct one. At the negative pole

$$Pb^0 \rightarrow Pb^{++} + 2e^-$$
$$Pb^{++} + SO_4^{=} \rightarrow PbSO_4\downarrow$$

At the positive pole

$$2H_3O^+ + 2e^- \rightarrow 2H^0 + 2H_2O$$
$$2H^0 + PbO_2 \rightarrow PbO + H_2O$$
$$PbO + H_2SO_4 \rightarrow PbSO_4\downarrow + H_2O$$

Both poles are therefore changed to lead sulfate, and sulfuric acid is removed from the solution.

EXERCISES

1. Write equations for reactions that illustrate the amphoteric character of zinc hydroxide.
2. Write equations for the reactions of zinc with each of the following substances: HCl, dilute HNO_3, KOH, $CuSO_4$.
3. Why are solutions of aluminum chloride acidic?
4. Why is carbon dioxide liberated when solutions of aluminum sulfate and sodium bicarbonate are mixed?
5. What are two important uses of aluminum based on its action as a reducing agent?
6. How does the lead storage cell operate?

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CHAPTER FIFTY-ONE

IRON, CHROMIUM, AND MANGANESE

In Group 8 of the periodic table are three triplets of elements: iron, cobalt, and nickel; ruthenium, rhodium, and palladium; osmium, iridium, and platinum. The properties of the first triplet only will be considered in this chapter. Chromium and manganese are in Groups 6 and 7, respectively, and are typical transition-group elements.

TABLE 66.—PROPERTIES OF IRON, COBALT, NICKEL, CHROMIUM, AND MANGANESE

Metal	Atomic number	Atomic weight	Planetary electrons	Valences	Group	Density	Melting point, °C.
Iron.......	26	55.85	2, 8, 14, 2	+2, +3	8	7.86	1535
Cobalt.....	27	58.94	2, 8, 15, 2	+2, +3	8	8.9	1480
Nickel.....	28	58.69	2, 8, 16, 2	+2	8	8.90	1452
Chromium.	24	52.01	2, 8, 13, 1	+2, +3, +6	6	7.1	1615
Manganese.	25	54.93	2, 8, 13, 2	+2, +3, +4, +6, +7	7	7.2	1260

1. The Reactions of Iron.—Iron forms ferrous and ferric compounds in which its valences are +2 and +3, respectively. Three oxides are known: ferrous (FeO), ferric (Fe_2O_3), and magnetic oxide of iron (Fe_3O_4). The latter is a compound of the first two and may be considered as a ferrous ferrite, $Fe(FeO_2)_2$. Although iron in large pieces is incombustible, fine wire, such as is braided together in picture wire, burns brilliantly in oxygen. Indeed finely powdered iron, such as may be prepared by heating ferrous oxalate, is spontaneously combustible. The product of its combustion is the magnetic oxide.

When iron rusts, the final product is ferric hydroxide, the familiar brown scale. Since pure iron is remarkably resistant to corrosion, the rusting of impure iron is probably an electrolytic action. Rain water with carbonic acid in solution serves as the electrolyte, and iron and its impurities serve as electrodes.

The metal combines directly with sulfur, forming ferrous sulfide. With free halogens, ferrous halides are formed first followed by the formation of ferric salts. Above hydrogen in the electromotive series, iron reacts with dilute acids, forming ferrous salts and liberating hydrogen. Its reaction with dilute nitric acid reduces nitrogen to the valence number of −3 in the ammonium ion.

$$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

2. Reactions of the Ferrous Ion.—Ferrous sulfate, or green vitriol, $FeSO_4 \cdot 7H_2O$, is the most important ferrous salt. It may be readily prepared by the action of dilute sulfuric acid on iron. Ferrous ammonium sulfate, or Mohr's salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, is much more resistant to atmospheric oxidation than the ferrous sulfate alone and is commonly used as a source of ferrous ions.

When sodium hydroxide is added to a solution of a ferrous salt in the absence of air, ferrous hydroxide is formed as a white precipitate. In the presence of air, the precipitate is at first green owing to a partial oxidation of the ferrous ion and finally brown when the oxidation to ferric hydroxide is complete. Ferrous hydroxide is entirely basic.

Ferrous salts in solution are slowly oxidized by dissolved oxygen to the corresponding basic ferric salts.

$$4FeSO_4 + 2H_2O + O_2 \rightarrow 4Fe(OH)SO_4$$

Since such basic salts are sparingly soluble, a brown precipitate forms in ferrous salt solutions. This may be prevented to a certain extent by keeping iron nails in such solutions. Ferrous salts are easily converted to ferric salts by adding the corresponding acid and an oxidizing agent.

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

The conversion of ferrous to ferric nitrate requires nitric acid only.

$$3Fe(NO_3)_2 + 4HNO_3 \rightarrow 3Fe(NO_3)_3 + NO + 2H_2O$$

3. Reactions of Ferric Salts.—A reddish-brown, gelatinous precipitate of ferric hydroxide is formed when ammonia water is added to solutions containing the ferric ion.

$$Fe^{+++} + 3OH^- \rightarrow Fe(OH)_3\downarrow$$

This hydroxide is mainly basic. However, when heated with an excess of a strong sodium hydroxide solution, sodium ferrite is formed to a slight extent. This is an indication of feebly acidic properties. The hydroxide in this reaction acts as ferrous acid.

$$NaOH + HFeO_2 \rightleftarrows NaFeO_2 + HOH$$

Aqueous solutions of ferric salts are acidic since the ferric ion is hydrolyzed.

$$\begin{aligned} Fe^{+++} + HOH &\rightleftarrows FeOH^{++} + H^+ \\ FeOH^{++} + HOH &\rightleftarrows Fe(OH)_2^+ + H^+ \\ Fe(OH)_2^+ + HOH &\rightleftarrows Fe(OH)_3 + H^+ \end{aligned}$$

When such solutions are boiled, the hydrolysis is so extensive that ferric hydroxide is formed as a blood-red colloidal precipitate.

4. Complex Cyanides of Iron.—No simple cyanides of iron are stable. When an excess of cyanide ions is added to the solution of a ferrous salt, the complex ferrocyanide ion is formed.

$$Fe^{++} + 6CN^- \rightarrow Fe(CN)_6^{----}$$

or

$$FeCl_2 + 6KCN \rightarrow K_4Fe(CN)_6 + 2KCl$$

Potassium ferrocyanide is a yellow crystalline salt. When chlorine is passed through a solution of a ferrocyanide, the latter is oxidized to the ferricyanide ion.

$$2Fe(CN)_6^{----} + Cl_2 \rightarrow 2Fe(CN)_6^{\equiv} + 2Cl^-$$

or

$$2K_4Fe(CN)_6 + Cl_2 \rightarrow 2K_3Fe(CN)_6 + 2KCl$$

The iron atom in this complex ion is in the ferric stage of oxidation. Potassium ferricyanide forms dark-red crystals.

5. Tests for the Iron Ions.—When solutions of the ferrous and the ferricyanide ions are mixed, a deep-blue precipitate of ferrous ferricyanide, or Turnbull's blue, forms.

$$3Fe^{++} + 2Fe(CN)_6^{\equiv} \rightarrow Fe_3[Fe(CN)_6]_2\downarrow$$

This reaction is the basis of making blueprints. The light-sensitive paper is prepared by immersion in a solution of ferric ammonium citrate and potassium ferricyanide. The ferric ion does not react with a ferricyanide. A drawing in opaque India ink on translucent tracing cloth is clamped in a printing frame over blueprint paper and exposed to light. Where the light penetrates the tracing cloth, the ferric ion is reduced to the ferrous ion. The latter forms Turnbull's blue with the ferricyanide ion when the print is immersed in water.

The ferric ion reacts with the ferrocyanide ion to form a precipitate of Prussian blue.

$$4Fe^{+++} + 3Fe(CN)_6^{==} \rightarrow Fe_4[Fe(CN)_6]_3\downarrow$$

An exceedingly delicate test for the ferric ion is the deep-red color of the solution of ferric thiocyanate that forms when solutions of a thiocyanate and the ferric ion are mixed.

$$Fe^{+++} + 3CNS^- \rightarrow Fe(CNS)_3$$

6. **Cobalt** forms both cobaltous (+2) and cobaltic (+3) compounds of which the former are the more stable. Anhydrous cobaltous salts are blue, whereas aqueous solutions and hydrated salts are pink. This color change has been used to indicate when certain drying agents have absorbed all the water they can. The inexpensive weather indicators, which are blue in dry weather and pink in wet, are another application of this color change. The cobaltic ion forms a great variety of complex ions.

7. **Nickel** forms only one series of salts in which the metal is divalent. The hydroxide is green, insoluble, and entirely basic. The black sulfide is precipitated by hydrogen sulfide from alkaline solutions only. Ammonia forms a blue complex ion, $Ni(NH_3)_6^{++}$.

TABLE 67.—THE CHARACTER OF THE HYDROXIDES OF CHROMIUM

Valence	Hydroxide	Ions	Color
+2	$Cr(OH)_2 \xrightarrow{H^+}$	Cr^{++}, chromous	Blue
+3	$Cr(OH)_3 \xrightarrow{H^+}$	Cr^{+++}, chromic	Green
	or		
	$HCrO_2 \xrightarrow{OH^-}$	CrO_2^-, chromite	Green
+6	$H_2CrO_4 \xrightarrow{OH^-}$	$CrO_4^{=}$, chromate	Yellow

8. **The Reactions of Chromium.**—This element has three valences +2, +3, and +6. In all such cases, *the higher the valence, the less basic and the more acidic are the corresponding hydroxides.* In other words, the higher the valence, the less metallic and the more nonmetallic is the element. Thus the hydroxide of divalent chromium is entirely basic. Chromous salts contain the Cr^{++} ion. The hydroxide of trivalent chromium is amphoteric, acting as chromic hydroxide toward acids but as chromous acid toward alkalies. Hexavalent chromium is nonmetallic. The hydroxide corresponding to this valence is chromic

acid, H_2CrO_4. The chemistry of chromium is summarized in Table 67.

9. Chromous Salts.—The chromous ion is characterized by the ease with which it is oxidized to trivalent chromium by atmospheric oxygen. Chromous salts are, therefore, excellent reducing agents. They may be prepared by the action of acids on the metal or by reducing chromic salts with zinc and hydrochloric acid.

10. Trivalent Chromium.—Chromic salts are usually prepared by reducing dichromates in acid solution (51-11). The hydroxide is precipitated when a solution containing a sufficient concentration of hydroxyl ions is added to a chromic salt.

$$Cr^{+++} + 3OH^- \rightarrow Cr(OH)_3\downarrow$$

This amphoteric hydroxide forms chromic salts with acids and chromites with alkalies.

$$Cr(OH)_3 + 3H^+ \rightarrow Cr^{+++} + 3HOH$$
$$HCrO_2 + OH^- \rightarrow CrO_2^- + HOH$$

Chromic sulfate forms chrome alums with alkali sulfates. Chromic oxide, Cr_2O_3, is obtained as a green powder by heating the hydroxide or by reducing a dichromate with sulfur.

11. Hexavalent Chromium.—Chromium in this valence is nonmetallic, resembling hexavalent sulfur. The red oxide, CrO_3, is deliquescent and a powerful oxidizing agent. A mixture of potassium or sodium dichromate in concentrated sulfuric acid, from which the oxide separates, is known as cleaning solution and, as its name implies, is used to clean glassware in chemistry laboratories.

Chromates are yellow, the color of the chromate ion. When their solutions are acidified, the color changes to the orange of the dichromate ion, $Cr_2O_7^=$. This conversion may involve the formation of an unstable acid chromate ion

$$CrO_4^= + H^+ \rightarrow HCrO_4^-$$

which loses water forming the dichromate ion

$$2HCrO_4^- \rightarrow Cr_2O_7^= + H_2O$$

The two steps combined give the equation

$$\underset{\text{yellow}}{2CrO_4^=} + 2H^+ \rightleftarrows \underset{\text{orange}}{Cr_2O_7^=} + H_2O$$

The reaction is reversible. The addition of hydroxyl ion changes the dichromate to the chromate ion.

Among the more important insoluble chromates are the red silver chromate and the yellow barium and lead chromates.

Dichromates in acid solution are strong oxidizing agents owing to the ease with which the dichromate ion is reduced to the chromic ion.

$$6e^- + Cr_2O_7^{=} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O$$

Thus the iodide ion is easily oxidized to free iodine.

$$2I^- \rightarrow I_2 + 2e^-$$

Multiplying this equation by 3 and adding, we obtain

$$6I^- + Cr_2O_7^{=} + 14H^+ \rightarrow 3I_2 + 2Cr^{+++} + 7H_2O$$

If the substances used in this reaction were potassium iodide, potassium dichromate, and sulfuric acid, the products would be iodine, potassium sulfate, chromic sulfate, and water.

$$\begin{array}{c} 6KI + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3I_2 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O \\ (2I^{-1} \rightarrow I_2 + 2e^-) \times 3 \\ (6e^- + 2Cr^{+6} \rightarrow 2Cr^{+3}) \times 1 \end{array}$$

The equation for the oxidation of ferrous sulfate by potassium dichromate and sulfuric acid may be written as a reaction of ions or with complete formulas.

$$\begin{array}{c} 6e^- + Cr_2O_7^{=} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O \\ 6Fe^{++} \rightarrow 6Fe^{+++} + 6e^- \\ \hline 6Fe^{++} + Cr_2O_7^{=} + 14H^+ \rightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_2O \end{array}$$

$$\begin{array}{c} 6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O \\ (6e^- + 2Cr^{+6} \rightarrow 2Cr^{+3}) \times 1 \\ (Fe^{+2} \rightarrow Fe^{+3} + e^-) \times 6 \end{array}$$

When hydrogen peroxide is added to a cold acid solution of the dichromate ion, the blue, unstable perchromic acid is formed. The exact formula of this acid and the valence of chromium in it have not as yet been definitely established.

12. The Chemistry of Manganese.—This element is in Group 7 of the periodic table and has valence numbers of +2, +3, +4, +6, and +7. Of these the lowest and the highest are found in the most important compounds, the manganous salts and the permanganates.

The free metal reacts readily with dilute acids, liberating hydrogen and forming manganous salts. In many respects its reactions are very similar to those of magnesium.

13. Divalent Manganese.—The Mn^{++} ion is called the manganous ion and is light pink in color. Alkalies precipitate the white manganous hydroxide which oxidizes readily on contact with atmospheric oxygen to the brown manganic hydroxide. Manganous hydroxide is entirely basic. The oxide, MnO, may be obtained as a gray-green powder by heating manganous hydroxide or carbonate out of contact with the air.

Manganous salts may be prepared by the action of the metal on the appropriate acid or by the reduction of the permanganate ion in acid solution.

From feebly basic solutions of the manganous ion, hydrogen sulfide precipitates the pink manganous sulfide.

14. Trivalent Manganese.—In general, salts of trivalent manganese are unstable and are extensively hydrolyzed.

15. Tetravalent Manganese.—The dioxide, pyrolusite MnO_2, is the most important ore of this metal. It exhibits feebly acid properties. It is a strong oxidizing agent in acid solution because of the ease with which manganese is reduced to the divalent condition. Treated with hydrochloric acid, chlorine is liberated.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

In sulfuric acid solution, ferrous sulfate is oxidized to ferric sulfate.

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$$

16. Hexavalent Manganese.—In this valence, manganese is a typical nonmetal existing in the green manganate ion, $MnO_4^{=}$. When manganese dioxide is treated with potassium hydroxide in the presence of air, potassium manganate is formed.

$$4KOH + 2MnO_2 + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

When concentrated green solutions of manganates are poured into an excess of water, the purple color of the permanganate ion appears and brown manganese dioxide precipitates.

$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KOH$$

Thus two atoms of manganese are oxidized from +6 to +7 and one is reduced from +6 to +4, an indication that hexavalent manganese is unstable.

17. The Permanganates.—The purple permanganate ion, MnO_4^-, in which manganese has a valence of +7, is formed by oxidizing the manganate ion with ozone or by passing carbon dioxide through a solution of a manganate.

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + O_2 + 2KOH$$
$$3K_2MnO_4 + 2H_2O + 4CO_2 \rightarrow 2KMnO_4 + MnO_2\downarrow + 4KHCO_3$$

The permanganate ion is a strong oxidizing agent. *In acid solution, it is reduced to the manganous ion.*

$$5e^- + MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O$$

Thus the iodide ion is oxidized to free iodine.

$$2I^- \rightarrow I_2 + 2e^-$$

Multiplying the first equation by 2, the second by 5, and adding, we obtain

$$10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{++} + 5I_2 + 8H_2O$$

Written with complete formulas, the balancing is as follows:

$$10KI + 2KMnO_4 + 8H_2SO_4 \rightarrow 5I_2 + 2MnSO_4 + 6K_2SO_4 + 8H_2O$$
$$(5e^- + Mn^{+7} \rightarrow Mn^{+2}) \times 2$$
$$(2I^{-1} \rightarrow I_2 + 2e^-) \times 5$$

In basic solution the reduction stops at the +4 stage and manganese dioxide is precipitated.

EXERCISES

1. Write balanced equations for the reactions that take place between the following substances:

Iron + sulfuric acid →
Iron + dilute nitric acid →
Ferrous ion + cyanide ion →
Ferric chloride + hydrogen sulfide →

2. Show by means of equations how the following changes may be accomplished:

Ferrous oxide → ferrous chloride → ferric chloride → ferric oxide → iron

3. Using potassium dichromate as the oxidizing agent, write balanced equations for the following transformations:

$$Fe^{++} \rightarrow Fe^{+++}$$
$$H_2S \rightarrow S$$
$$FeSO_4 \rightarrow Fe_2(SO_4)_3$$

4. Write equations for the above transformations, substituting potassium permanganate for the dichromate.

5. Write equations that illustrate the amphoteric character of the hydroxide of trivalent chromium.

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CHAPTER FIFTY-TWO

THE ALIPHATIC HYDROCARBONS

Organic chemistry is one of the most widely applied branches of the science of chemistry. Perhaps no other branch has contributed more toward raising our standard of living. Organic chemistry studies the compounds of which living organisms are composed; and these are invariably compounds of carbon. Atoms of this element, unlike those of practically all other elements, possess the property of uniting directly with one another through covalent bonds to form long chains and ring structures. This unique property makes possible not only the multiplicity of carbon compounds found in living organisms, but also the numerous "organic" compounds that have been synthesized in chemistry laboratories. Nearly 300,000 compounds of carbon are known, more than those of all the other elements combined. Up to within about one hundred years ago, an idea was firmly fixed in the minds of chemists that such compounds could be formed only in living tissue through the agency of some vital force. Then in 1828 Wöhler, a German chemist, synthesized urea, a product of animal metabolism, in his laboratory by heating ammonium cyanate. The bridge connecting the inorganic with the organic is the means by which thousands of tons of organic chemicals are manufactured today.

1. Structural Formulas.—Organic chemists are essentially molecular architects. Molecules of organic compounds are so complex as compared with those which inorganic chemistry studies that information as to the way in which the atoms are joined in such molecules is essential before methods of synthesizing them can be worked out and their reactions correctly interpreted. Structural formulas of molecules are the "blueprints" that guide organic chemists to the solution of problems. In such formulas, each valence bond represents a shared pair of electrons.

Because of the complexity of many organic molecules, students are almost invariably puzzled by them at first. Once familiarity with them has been gained, this confusion disappears and the study of organic chemistry offers no more difficulty than any other branch of the science. Unfortunately, the amount of time that can be allotted to their study in an elementary course is so meager that all that can be hoped for is to give some knowledge of what has been and may yet be attained in this field.

2. The Hydrocarbons.—The simplest class of organic compounds is that of the hydrocarbons—compounds whose molecules contain carbon and hydrogen only. Of these, several hundred are known. They have been classified into two general types—aliphatic and aromatic hydrocarbons. Molecules of aliphatic hydrocarbons are composed of chains of carbon atoms, whereas those of aromatic hydrocarbons contain one or more rings of carbon atoms. Most of the aromatic hydrocarbons are derived from coal tar (42-7), and many of these are the raw materials from which dyes, drugs, and explosives are prepared. The derivatives of the aliphatic hydrocarbons, however, make up the vast majority of the compounds found in plant and animal tissues. The aliphatic hydrocarbons are divided into three series: the paraffin, olefin, and acetylene series. These we shall now study.

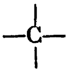
3. The Paraffin Hydrocarbons.—The formulas for the molecules of hydrocarbons of the paraffin series all conform to the type formula C_nH_{2n+2}. Formulas for individual hydrocarbons of this series can be derived by substituting whole numbers for *n* in the type formula. The formulas, names, and physical constants of the first few and several of the higher members of this series are given in Table 68.

TABLE 68.—TYPICAL PARAFFIN HYDROCARBONS

CH_4, methane	B.p. − 164°C.
C_2H_6, ethane	B.p. − 90°C.
C_3H_8, propane	B.p. − 38°C.
C_4H_{10}, butane	B.p. + 1°C.
C_5H_{12}, pentane	B.p. + 37°C.
C_6H_{14}, hexane	B.p. + 69°C.
C_7H_{16}, heptane	B.p. + 98°C.
$C_{15}H_{32}$, pentadecane	M.p. + 10°C.; b.p. 271°C.
$C_{16}H_{34}$, hexadecane	M.p. + 18°C.; b.p. 287°C.
$C_{35}H_{72}$, pentatriacontane	M.p. + 74.7°C.

At room temperature (20°C.), the first four members of this series are gases; from C_5H_{12} to $C_{16}H_{34}$, liquids; and those with more than 16 carbon atoms, solids.

You are, no doubt, puzzled by the fact that tetravalent carbon and univalent hydrogen can form so many compounds. A study of the structural formulas of these compounds, however, will explain how this is possible. Each carbon atom in these formulas we must represent as follows:

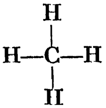


$$\begin{array}{ccc} & | & \\ - & C & - \\ & | & \end{array}$$

the four arms corresponding to its valence of 4. Each univalent hydrogen atom must be written

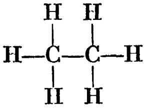
H—

The structural formula for the methane molecule is, therefore,



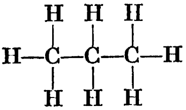
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

Ethane, with an empirical formula C_2H_6, has the following structure:



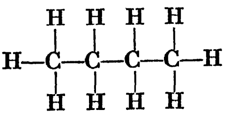
$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H \\ & | & | & \\ & H & H & \end{array}$$

One of the valence bonds serves as a link between the two carbon atoms. The structural formula for propane, C_3H_8, is



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

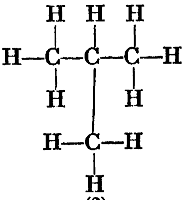
When we consider the formula of butane, C_4H_{10}, we find that there are two possible structures.



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

(1)

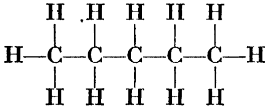
and

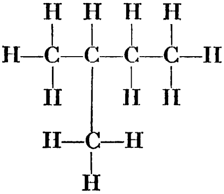


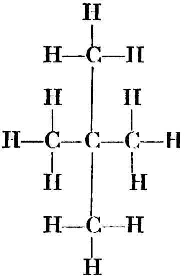
$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H \\ & | & | & | & \\ & H & | & H & \\ & H- & C & -H & \\ & & | & & \\ & & H & & \end{array}$$

(2)

These are molecules of two different substances since, although they are built up of the same number of the same kind of atoms, these atoms are linked together in different ways. Substances resembling each other in this way are called *isomers*. The two isomeric butanes, corresponding to the above formulas, are very similar, but not identical, in their chemical properties. Their physical properties are also different. For example, normal butane (1) has a higher boiling point than isobutane (2). There are three isomeric pentanes.







These hydrocarbons occur in petroleum and in natural gas. All are combustible, burning completely to carbon dioxide and water or partially in the presence of a limited supply of oxygen to water and carbon or carbon monoxide (8-7). They are inert toward the action of acids and bases. Practically insoluble in water, the small amount that does dissolve does not ionize to give hydronium ions. They are not, therefore, acids. Their reactions with the element chlorine yield a number of interesting products in which chlorine atoms are substituted for part or all of the hydrogen atoms. For example, methane can be converted into any one of four such products.

$$CH_4 + Cl_2 \rightarrow \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

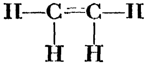
$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow \underset{\text{chloroform}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \rightarrow \underset{\substack{\text{carbon}\\ \text{tetrachloride}}}{CCl_4} + HCl$$

Methyl chloride is used in household refrigerators and as a local anesthetic; chloroform is the well-known general anesthetic; and carbon tetrachloride is an important solvent for fats and grease in dry-cleaning and a fire extinguisher (pyrene).

4. The Unsaturated Hydrocarbons.—Hydrocarbons of the olefin and acetylene series are characterized by the presence of one or more double or triple valence bonds, respectively, between carbon atoms in their molecules. Thus the structural formula for ethylene, C_2H_4, the first member of the olefin series, contains a double bond

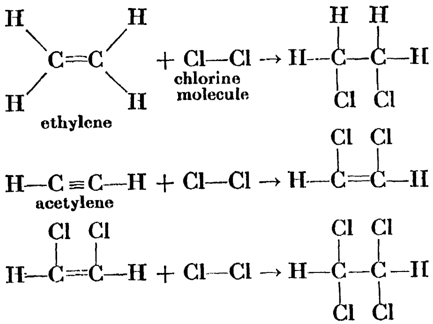


$$\underset{\textstyle H}{H—\overset{}{C}}=\underset{\textstyle H}{C}—H$$

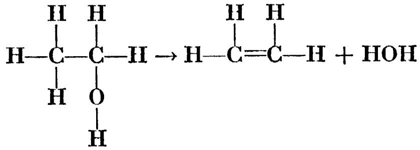
Acetylene, C_2H_2, the first member of acetylene series, has a triple bond in its structure.

$$H—C \equiv C—H$$

Compounds whose molecules contain double or triple bonds are spoken of as *unsaturated.* A single bond is sufficient to hold two carbon atoms together. Multiple bonds represent valences that are not doing their full duty. The extra bonds show a great tendency to open up to add other atoms, such as chlorine or hydrogen, to the molecules. When ethylene or acetylene is treated with chlorine, for example, addition of chlorine takes place at the unsaturated linkages, as follows:



5. Ethylene can be prepared by removing the elements of water from ethyl alcohol.



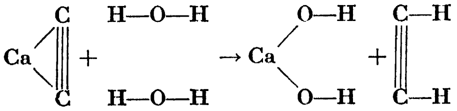
$$CH_3{-}CH_2{-}OH \rightarrow CH_2{=}CH_2 + HOH$$

ethyl alcohol

This dehydration is accomplished by passing alcohol vapor over a catalyst, such as porous kaolin. During the last war, it was used in the manufacture of mustard gas, and means of producing it on a large scale and at a low cost were developed. After the war, it was found to be as good as acetylene in welding and much safer to handle. It is now used extensively to color green oranges and lemons. Citrus fruit becomes ripe before its skin loses the green color. It can be shipped in this condition with little danger of spoilage and then brought to full color by ethylene gas after it has arrived at its destination. In as low a concentration as 1 part of ethylene per 3,000 parts of air, 25 cu. ft. of this gas can color a carload of oranges in 5 days. Ethylene is also used as a general anesthetic in medicine. The story of the discovery of its use for this purpose is interesting. About 1908, a Chicago florist discovered that several shipments of carnations promptly closed up their petals and went to sleep when placed in a certain corner of his greenhouse. He called Dr. Crocker, a botanist at the University of Chicago, into consultation. The latter discovered that a leaky gas pipe was doing the damage. Since illuminating gas is a mixture of various substances, he tried the action of each of these on carnations and found ethylene to be the offender. Finally, in 1922, Prof. Luckhardt, also of the University of Chicago, with the aid of Mr. Carter, found that rats in an atmosphere of 80 per cent ethylene curled up and went to sleep; in this way its anesthetic properties were discovered.

Ethylene is now obtained by cracking (52-11) fuel oils. It has become the raw material from which many organic substances of commercial importance are manufactured. Among these are ethylene glycol, an antifreeze used in automobile radiators, from which many important solvents are made.

6. Acetylene is prepared in large quantity by the action of water on calcium carbide, CaC_2.



$$CaC_2 + 2\,H{-}O{-}H \rightarrow Ca(O{-}H)_2 + HC{\equiv}CH$$

It is used extensively for oxyacetylene welding and cutting and in the synthesis of such important organic compounds as acetic acid (53-5) and acetone (53-4).

7. Petroleum.—With coal, petroleum ranks as our most valuable natural resource for the production of energy. From it we derive the energy to run our automobiles and our oil-burning locomotives and steamships. With it the machines of the world are lubricated. Without it, the machine age probably never would have developed. Petroleum was known to the ancients. The bitumens were used by the Chaldeans as early as 3000 B.C. In ancient Babylon and Nineveh, mosaics and stone tablets were held in place with these substances. Its use is mentioned several times in the Old Testament. In America it was known to the Indians before the coming of the white settlers. During the late 1700's, it was sold as a liniment for aching joints and muscles. In 1854, the Pennsylvania Rock Oil Company sent a sample to Prof. Benjamin Silliman, Jr., of Yale to analyze. He distilled the oil and showed that the various fractions of the distillate could be used as illuminating oils, lubricating oils, and oils for making gas. In 1859, Col. E. L. Drake drilled the first oil well at Titusville, Pa., which yielded 15 barrels a day. During the next few years, the Oil Creek region was the center of an oil boom and literally bristled with oil wells. Pennsylvania was the leading producer for many years. In the decade from 1890 to 1900, the Ohio and Indiana fields were discovered and exploited; and from 1900 to 1910, the Oklahoma and North Texas fields. More recently, the fields of the Gulf Coast of Texas and those of California have been opened up.

8. The Nature and Origin of Petroleum.—Petroleum consists of a large number of hydrocarbons, most of which are liquids, mutually dissolved in one another. The nature of these hydrocarbons is not the same in petroleum from different localities. Pennsylvania crude oil is made up mainly of paraffin hydrocarbons. Petroleum from Texas and Oklahoma contains larger amounts of aromatic hydrocarbons. Compounds of sulfur and other objectionable impurities are also present to a greater or lesser extent.

We have reason to believe that petroleum is of both vegetal and animal origin. The remains of, for the most part, marine plants and animals, imprisoned in rock strata, probably resulted in the production of the hydrocarbons of petroleum. These were stored away in the muddy rocks and the black shales of stagnant waters. In time they were liberated by circulating ground water and stored under high pressure in underground caverns in sandstone deposits. As in the case of coal, nature took hundreds of thousands of years to produce the petroleum that we are using at such an alarming rate today.

9. Petroleum Production.—Since Col. Drake drilled the first oil well, nearly 40,000,000,000 barrels have been brought to the surface in over 26 countries. Of these the United States produces about 1,500,000,000 barrels of the 2,250,000,000-barrels annual world production. The United States supplied 62.5 per cent, Russia 10.8 per cent, Venezuela 9.9 per cent, and Iran 3.5 per cent of the total crude oil produced in 1941. Twenty-two states produce oil with Texas, California, Louisiana, and Illinois the leading producers.

Petroleum is brought to the surface by drilling wells through the overlying strata into the oil-bearing sandstones. The depth of the well may vary from a few hundred feet to 3 miles. If the oil is under high pressure, a gusher results.

Crude petroleum is not, in general, refined at the oil field but is either shipped in tankers or pumped through a gigantic network of pipe lines to the refinery. These pipes connect refineries on the Great Lakes and the Atlantic Coast with all the large fields east of the Rocky Mountains. In some instances, the distance is as great as 1,600 miles, as in the case of oil from an Oklahoma field pumped to the Atlantic seaboard.

10. Refining.—The fundamental process of crude-oil refining is one of distillation to accomplish a separation of hydrocarbons of different boiling points. Until recently, this operation has been carried out in iron stills set in brickwork and heated by burning fuel oils. At first, gaseous hydrocarbons are given off. These consist of hydrocarbons whose molecules contain one to four carbon atoms, *e.g.*, methane, CH_4; ethane, C_2H_6; propane, C_3H_8; and butane, C_4H_{10}. As the temperature rises, vapors of very low boiling liquids pass out of the still into a condenser. These consist of, for example, pentane, C_5H_{12}, and hexane, C_6H_{14}. They are used as solvents by the varnish and rubber industries. The next vapors to condense form the gasoline fraction, which consists of hydrocarbons with 5 to 10 carbon atoms in their molecules. The next fraction is kerosene, which is composed of hydrocarbons with 10 to 15 carbon atoms per molecule. Following the kerosene fraction at higher still temperatures come the oil distillates from which the lubricating and fuel oils are obtained. Some of these contain solid hydrocarbons in solution which are frozen out and sold as "paraffin." There remains in the still a dark, viscous liquid which is sold as a fuel or as asphalt or is heated further and converted into a form of coke. The following table gives the percentages of the various distillates:

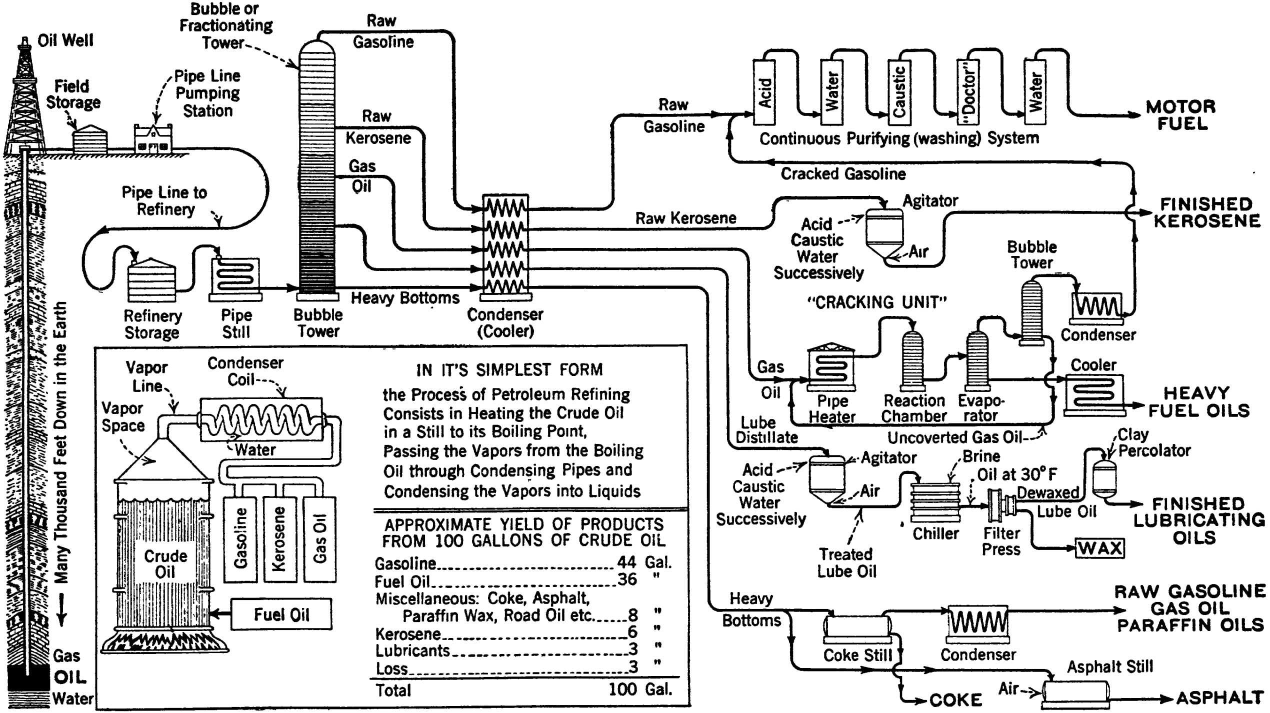
$$\text{Petroleum} \xrightarrow[\text{distillation}]{\text{fractional}}$$

	Per Cent
Gas	4
Gasoline	25
Kerosene	15
Gas oil	40
Lubricating oils and paraffin	12
Coke	4

The operation outlined above is known as "batch" distillation and is necessarily an intermittent process. The batch still has to be cleaned after each run before it can be charged with a fresh supply of crude oil. It has been replaced by modern stills of far greater capacity which operate continuously.

These pipe stills receive a continuous flow of crude petroleum which is vaporized by pipes heated to 370°C. The mixed vapors pass into a fractionating, or "bubble," tower in which they rise through condensed vapors in perforated trays. Condensation of the hydrocarbon fractions takes place in the order of their vapor pressures. The heavy oils condense at the bottom of the tower, hence their name "heavy bottoms." Lube distillate, containing the lubricating oils, gas oil, and raw kerosene, condense in order at higher levels, and raw gasoline vapors pass uncondensed from the top of the tower (Fig. 180). The condensed liquids and the gasoline vapor next pass in separate pipes through a water cooler in which gasoline condenses.

These fractions must be further purified before they can be marketed. Corrosive sulfur compounds and gum-forming substances are removed from raw gasoline by successive treatment with dilute sulfuric acid, water, caustic soda, and, finally, a "doctor" solution of sodium plumbite. A final washing with water leaves it colorless and free from harmful impurities. Raw kerosene is purified in much the same manner. The gas-oil



IN IT'S SIMPLEST FORM
the Process of Petroleum Refining Consists in Heating the Crude Oil in a Still to its Boiling Point, Passing the Vapors from the Boiling Oil through Condensing Pipes and Condensing the Vapors into Liquids

APPROXIMATE YIELD OF PRODUCTS FROM 100 GALLONS OF CRUDE OIL

Gasoline	44 Gal.
Fuel Oil	36 "
Miscellaneous: Coke, Asphalt, Paraffin Wax, Road Oil etc.	8 "
Kerosene	6 "
Lubricants	3 "
Loss	3 "
Total	100 Gal.

FIG. 180.—Flow chart tracing crude oil refining from well to finished products. (*Courtesy of American Petroleum Institute.*)

fraction is converted into more gasoline and into a fuel oil by the cracking process discussed in the next paragraph.

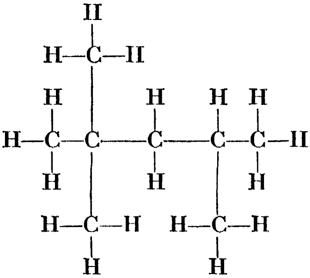
The lube distillate is chilled after treatment with acid and caustic, whereupon solid hydrocarbons known as paraffin wax separate from solution and are filtered from the lubricating oil. The heavy bottoms may be used directly as industrial fuel oils or may be converted into lighter oils and coke by being subjected to high temperatures in the absence of air in coking stills. They may also be converted into asphalt by heat in the presence of air, a process that involves oxidation.

We have merely outlined the most important steps in petroleum refining. Chemical research has added many other improvements to the refining process which make the gasoline and the lubricating oils of today far superior to those of the immediate past.

11. Cracking.—The percentage of gasoline from crude oil has been steadily rising. This has been in part due to improved refinery practice but mainly to the introduction in 1913 of the Burton process for making gasoline by cracking fuel, or gas, oils. These oils, boiling between 225 and 375°C., are heated in stills under a pressure of 4 atm. and at a temperature of 400°C. Under these conditions a breakdown of more complex into simpler molecules, corresponding to lower boiling, more volatile liquids, occurs. These can then be used as gasoline. Today about half the gasoline used is "cracked" gasoline. The cracking process has been of tremendous value as a means of conserving the supply of petroleum. In 1936, nearly 2,000,000,000 additional barrels of crude oil would have been used to supply the world with gasoline had the cracking process been unknown.

12. Increasing the Efficiency of Internal-combustion Engines.—At the present cost of gasoline, the fuel economy of a motorcar is held in less esteem than its performance. With war rationing of gasoline, however, engine efficiency would be a deciding factor in the purchase of a car if new models were being manufactured. The simplest way to obtain fuel economy is to increase the gear ratio in the rear axle so that the driving wheels turn proportionally faster than the engine. A car, so equipped, however, is slow in acceleration and a poor hill climber. Another method is to increase the compression ratio of the engine, *i.e.*, the ratio of the clearance volume, when the piston is at the top of its stroke, to the total cylinder volume. If this ratio is increased too much, the motor will knock. Such engines demand antiknock gasoline. These gasolines invariably contain tetraethyl lead ("ethyl gasoline"). Straight-run gasoline knocks badly in engines of high compression ratio. Cracked and polymer gasolines are much better in this respect. They are, therefore, blended with straight-run gasoline and tetraethyl lead is added.

13. Octane Numbers.—Straight-chain aliphatic hydrocarbons are the worst offenders in respect to knocking. Olefins and branched-chain hydrocarbons have high antiknock properties. A system of rating gasolines as to their antiknock quality has been adopted universally in terms of so-called octane numbers. A pure branched-chain isooctane



2,2,4-trimethylpentane

with excellent antiknock properties was given an octane number of 100, whereas the straight-chain heptane, which knocks badly, was rated at 0. The octane number of a gasoline is equal to the percentage of isooctane in a mixture of the two reference hydrocarbons which gives the same performance in an experimental engine as the gasoline. Commercial gasolines have octane numbers of 81, 74, and 65 for the premium, regular, and third grades, respectively.

14. Polymerization and Alkylation.—The cracking process produces 300 billion cubic feet of waste gases annually in the United States. These contain up to 20 per cent of unsaturated hydrocarbons. By the use of a solid phosphoric acid catalyst, the unsaturated molecules of these gaseous hydrocarbons can be made to combine with one another to form larger molecules of liquid hydrocarbons of high antiknock value. This process is known as *polymerization.* Thus two molecules of gaseous butylene combine to form dibutylene, a liquid. Further, catalysts have been developed which make possible the addition of saturated hydrocarbons to olefins thus forming branched-chain hydrocarbons. This process is *alkylation.* Finally, by using other catalysts, straight-chain hydrocarbon molecules can be persuaded to rearrange their atoms into the more valuable branched-chain structures. The result has been that on Dec. 1, 1941, 40,000 barrels of 100-octane aviation gasoline were being produced daily. The Petroleum Coordinator requested that this daily amount be tripled, which will supply 35,000 airplanes with gasoline for one hour's flight.

15. Other Sources of Gasoline.—Large amounts of gasoline are obtained from the so-called "wet" natural gas. This gas contains the vapors of liquid hydrocarbons which can be condensed out of it by compression. This casing-head gasoline is of a very high grade. In 1935, some 1,600,000,000 gal. were obtained from this source.

We have mentioned the fact that at one stage in nature's production of petroleum, the oil is held in porous shale formations. Many of these oil-shale deposits are to be found today, notably in Colorado, Utah, and Indiana, and in Scotland. It has been estimated that in Indiana there are over 450 billion tons of these deposits. Powdered oil shales can be heated in stills and the volatile oils distilled off from the rocky material. Oil shales represent a natural resource that will be tapped to an increasingly greater extent as the supply of petroleum begins to fail.

16. Hydrogenation of Coal and Carbon Monoxide.—In Germany, a process was developed by Bergius for converting coal into hydrocarbons. Pulverized coal suspended in oil is heated to about 450°C. in an atmosphere of hydrogen. From a metric ton of coal are obtained 40 gal. of motor fuel, 50 gal. of Diesel engine oil, and 35 gal. of fuel oil together with 10,000 cu. ft. of a fuel gas.

At present, the Fischer-Tropsch process holds the brightest promise for the future. This involves the catalytic hydrogenation of carbon monoxide which can be easily prepared from coal. It is estimated that the Bergius-process plants in Germany produced 24 million barrels and the Fischer-Tropsch plants, 35 million barrels in 1940.

17. Hydrogenation of Petroleum.—The tremendous research organization of the I. G. Farbenindustrie extended the Bergius process to the hydrogenation of crude petroleum and distillery residues by hydrogen gas under high pressures and in the presence of catalysts. It developed catalysts for this process which were surprisingly resistant to sulfur poisoning. In 1927, the Standard Oil Company of New Jersey joined research forces with the I.G.F., with the result that today the process is in commercial operation in this country. Phenomenal yields of gasoline and gas oil are claimed. Since the process takes place with an expansion in volume, more than 100 per cent volumetric yields are not only possible, but have been consistently obtained.

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CHAPTER FIFTY-THREE

DERIVATIVES OF THE HYDROCARBONS

Since the hydrocarbons are the simplest types of organic compounds, the classification of more complex types is based on that of the hydrocarbons. The more complex compounds are considered as related to the hydrocarbon of nearest similar structure in that hydrogen atoms of the hydrocarbon have been replaced by other atoms in the compound under consideration.

1. The Alcohols.—An alcohol can be considered as a compound in which one or more of the hydrogen atoms of a hydrocarbon have been replaced by hydroxyl, OH, groups. The simplest and most important alcohols are derivatives of the paraffin hydrocarbons. If we remove one hydrogen atom from a hydrocarbon, a univalent group is the result. Such a group combined with the OH group is found in the molecules of these alcohols, as shown in Table 69.

TABLE 69.—TYPICAL ALCOHOLS

Hydrocarbon	Univalent group	Corresponding alcohol
CH_4, methane	CH_3–, methyl	CH_3OH, methyl alcohol
C_2H_6, ethane	C_2H_5–, ethyl	C_2H_5OH, ethyl alcohol
C_3H_8, propane	C_3H_7–, propyl	C_3H_7OH, propyl alcohol
C_4H_{10}, butane	C_4H_9–, butyl	C_4H_9OH, butyl alcohol

The name of the group is derived from that of the corresponding hydrocarbon by substituting *yl* for *ane*.

The first two alcohols, methyl and ethyl, are the most important of this series. Both have a number of other names. Methyl alcohol is commonly known as wood alcohol. More recently it has appeared on the market as methanol. Ethyl alcohol is otherwise known as grain alcohol or ethanol.

Methyl alcohol, until quite recently, was obtained exclusively as a by-product of the destructive distillation of wood (42-6). About 1923 a process by which wood alcohol can be synthesized from water gas (42-12) was developed in Germany. When water gas, a mixture of carbon monoxide and hydrogen, is brought in contact with a suitable catalyst at a temperature of about 400°C. and under a pressure of 50 atm. or greater, methyl alcohol is synthesized as in the following reaction:

$$CO + 2H_2 \rightarrow CH_3OH$$

The catalysts most frequently used are mixtures of the oxides of zinc and chromium or of zinc and copper. During the first three months of 1925, slightly over 100,000 gal. of synthetic methanol was imported into this country at a cost of less than 50 cents a gallon. The domestic product from wood distillation cost then about 75 cents a gallon. As a result, the wood-distillation industry, which employed 4,000 wage earners and produced $30,000,000 worth of products in 1923, was threatened with extinction. In 1936, 30,000,000 gal. was manufactured in the United States valued at 40 cents a gallon.

Methyl alcohol is used as a solvent for gums and resins in the manufacture of varnish and shellac, for the preparation of formaldehyde (53-3), and as a denaturant for ethyl alcohol to render the latter unfit for internal use. It is a violent poison when taken internally, causing blindness and death.

Ethyl, or grain, alcohol, C_2H_5OH, is prepared by the fermentation of sugars. In this country sugar-cane molasses and corn are the most important raw materials. The molasses is diluted with water and made slightly acid. Then a pure culture of yeast is added and the following reaction takes place:

$$\underset{\text{a sugar}}{C_6H_{12}O_6} \rightarrow 2C_2H_5OH + 2CO_2$$

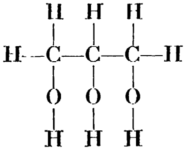
After the fermentation is complete, the mash is distilled with steam. The distillate is redistilled several times to give the pure 95 per cent alcohol of commerce.

The industrial uses of ethyl alcohol are so many and varied that we can only catalogue a few. First of all, it is an important solvent used in the preparation of varnishes, lacquers, shellacs, enamels, and pyroxylin plastics (55-5). Over 4,000 medicines need alcohol in their preparation. It is used as an antifreeze compound in automobile radiators, as a motor fuel, in the preparation of flavoring extracts, in the manufacture of dyes and artificial silk, and in the preparation of ethylene and ether.

Butadiene, a substance used in the manufacture of synthetic rubber, is made from alcohol.

Of the physiological effect of ethyl alcohol taken internally, most of you, no doubt, have heard. The question of the advisability of its use from the standpoint of public and private morals is debatable. But you may be interested in learning of the psychological and physiological effects of its use as reported dispassionately by a scientist. If you are, by all means read a paper by Benedict on "Alcohol and Human Physiology."[1]

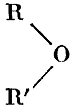
There exist many alcohols with more than one OH group per molecule. Such a polyhydric alcohol is glycerin, $C_3H_5(OH)_3$, or



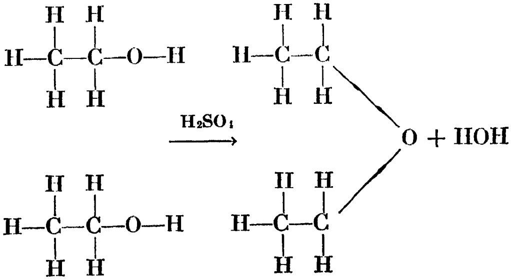
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & O & & O & & O & & \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

This alcohol is a by-product of the manufacture of soap (55-9) and is used mainly in the manufacture of nitroglycerin and dynamite (55-5) and in cosmetics.

2. **Ethers.**—Ethers are organic compounds whose molecules contain two organic groups, such as methyl, ethyl, or propyl, linked together by oxygen. The type formula for an ether is



The most important ether is the well-known anesthetic diethyl ether, $(C_2H_5)_2O$. It is prepared by the dehydration of alcohol by means of sulfuric acid.



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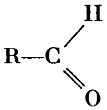
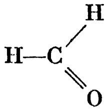
[1] *Ind. Eng. Chem.*, 17, 423 (1925).

3. **Aldehydes** are characterized by the typical formula



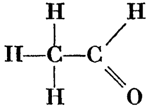
or, more simply, RCHO

in which R may be an organic radical or hydrogen. The names and formulas of the three simplest aldehydes are



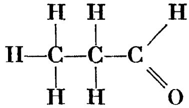
or HCHO

formaldehyde



or CH_3CHO

acetaldehyde



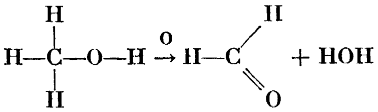
or CH_3CH_2CHO or C_2H_5CHO

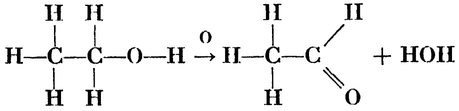
propionaldehyde

These aldehydes result from the oxidation of alcohol molecules that contain the $—CH_2OH$ group.

$$R{-}CH_2OH \xrightarrow[\text{(from an oxidizing agent)}]{O} R{-}CHO + H_2O$$

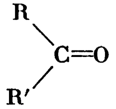
Thus, methyl and ethyl alcohols yield formaldehyde and acetaldehyde, respectively, on oxidation.





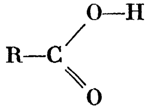
Formaldehyde, a gas, gives the well-known antiseptic and disinfectant formalin, when dissolved in water. Treated with phenol, or carbolic acid (54-2), it forms the synthetic resin bakelite. It is used extensively in the manufacture of dyes and drugs.

4. Ketones.—The molecules of ketones are characterized by the general formula

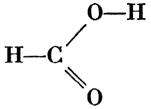


in which R and R′ may be any organic groups. Dimethyl ketone, or acetone, CH_3COCH_3, is the most important of these compounds. It is used extensively as a solvent.

5. Organic Acids.—All organic acids contain the $-COOH$ group.

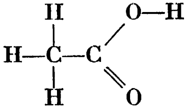


In the above formula, R may be hydrogen or any organic radical. A few of the simpler organic acids are



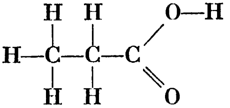
or $HCOOH$

formic acid



or CH_3COOH

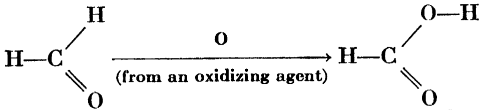
acetic acid



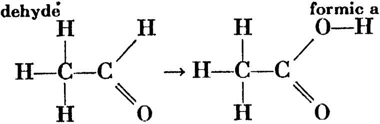
or C_2H_5COOH

propionic acid

These acids result from the oxidation of an aldehyde.

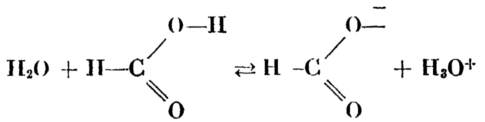


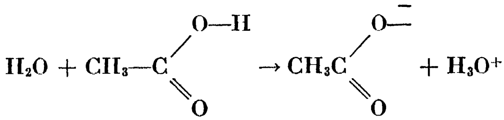
formaldehyde formic acid



acetaldehyde acetic acid

These acids ionize in water to give hydronium ions, the hydrogen of the —COOH group leaving the remainder of the molecule.





They, therefore, enter into neutralization reactions with bases forming salts.

$$\overset{-}{\mathrm{HCOO}}\,\overset{+}{\mathrm{H}} + \overset{+}{\mathrm{Na}}\,\overset{-}{\mathrm{OH}} \rightarrow \underset{\substack{\text{sodium}\\ \text{formate}}}{\overset{-}{\mathrm{HCOO}}\,\overset{+}{\mathrm{Na}}} + \mathrm{HOH}$$

$$\overset{-}{\mathrm{CH_3COO}}\,\overset{+}{\mathrm{H}} + \overset{+}{\mathrm{Na}}\,\overset{-}{\mathrm{OH}} \rightarrow \underset{\substack{\text{sodium}\\ \text{acetate}}}{\overset{-}{\mathrm{CH_3COO}}\,\overset{+}{\mathrm{Na}}} + \mathrm{HOH}$$

6. Esters.—When an alcohol reacts with an acid, an ester is formed. Thus, ethyl alcohol and hydrochloric acid form ethyl chloride.

$$C_2H_5OH + HCl \rightarrow C_2H_5Cl + HOH$$

This type of reaction is called *esterification.* In form, at least, it is analogous to a neutralization reaction between a base and an acid to form a salt and water.

$$NaOH + HCl \rightarrow NaCl + HOH$$

But there is an important difference. Neutralization is a reaction that takes place between substances, each of which is an electrolyte and, therefore, is dissociated into ions. As such it takes place almost instantly. On the other hand, since an alcohol is not an electrolyte, esterification reactions require hours of heating to produce any appreciable yield of the ester.

The acid that reacts with the alcohol may be an organic acid like acetic instead of an inorganic one like hydrochloric, and here again an ester is the product. Thus acetic acid and ethyl alcohol form the ester, ethyl acetate.

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + HOH$$

The esters of organic acids are, in general, sweet-smelling liquids, many of which occur in fruits and flowers in nature. Many of them are important organic solvents.

Esters of polyhydric alcohols are, in several instances, of importance. When glycerin is treated with a mixture of nitric acid and sulfuric acid, glycerin trinitrate, or nitroglycerin, the well-known high explosive is the product.

$$\underset{\text{glycerin}}{C_3H_5(OH)_3} + 3HNO_3 \rightarrow \underset{\text{glycerin trinitrate}}{C_3H_5(NO_3)_3} + 3HOH$$

The sulfuric acid acts as a dehydrating agent (36-11). This substance is a liquid and is extremely difficult to handle with safety. Mixed with a porous substance like sawdust or infusorial earth to soak it up, it is molded into sticks. In this form it is known as dynamite.

7. Amines and amides are both related to ammonia. The amino group, $—NH_2$, which is found in their molecules is a univalent group derived from the ammonia molecule by the removal of a hydrogen atom. An *amine* is composed of this group united to an organic group like methyl, ethyl, or propyl. Methyl amine can be prepared by treating ammonia with methyl chloride.

$$CH_3Cl + 2NH_3 \rightarrow CH_3NH_2 + NH_4Cl$$

An *amide* is related to an organic acid. Its molecules contain the amino group in place of the OH group of the acid.

$$\underset{\text{acetic acid}}{CH_3COOH} \qquad \underset{\text{acetamide}}{CH_3CONH_2}$$

Amides can be prepared from an acid and ammonia.

$$CH_3COOH + HNH_2 \rightarrow CH_3CONH_2 + HOH$$

8. Synthetic Chemicals from Petroleum.—The presence of unsaturated hydrocarbons in the gases from cracking stills has been mentioned before (52-14). Methods have been developed whereby the pure hydrocarbons may be separated from one another by fractional distillation at low temperatures. From such hydrocarbons as ethylene, isopropylene, and isobutylene, obtained in this way, many organic compounds are now being prepared in large quantities and at such a substantial reduction in cost that many new uses have developed for them. Of these we shall mention only a few: ethyl and isopropyl alcohols, ethylene glycol and glycerin, acetone, and a variety of higher alcohols and alcohol ethers which are valuable solvents. In addition, most of the chemicals from which plastics and synthetic rubber are manufactured are made from the hydrocarbon gases of the cracking stills.

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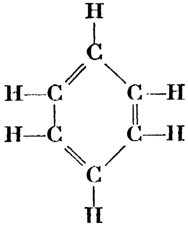
CHAPTER FIFTY-FOUR

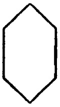
THE AROMATIC HYDROCARBONS

We have already pointed out that the two main classes of hydrocarbons are the aliphatic, or chain, hydrocarbons and the aromatic, or ring, hydrocarbons. The former and their derivatives we have already studied. We shall now consider briefly the aromatic hydrocarbons.

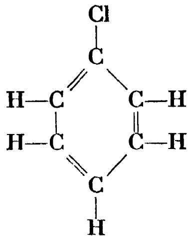
1. The Aromatic Hydrocarbons.—Benzene, the simplest aromatic hydrocarbon, has the empirical formula C_6H_6. Its reactions indicate that its molecular structure is symmetrical; *i.e.*, that each carbon atom is equivalent to every other one and that to each is attached a hydrogen atom. Its structural formula is as follows:



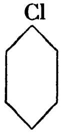
To save time, organic chemists usually use a hexagon



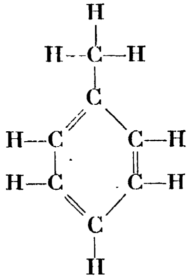
to denote this structure. A derivative of benzene in which one or more of its hydrogen atoms are replaced by other atoms or groups is represented by the hexagon with the substituent group or groups at one or more of its vertices. For example, chlorobenzene, C_6H_5Cl, whose complete structural formula is



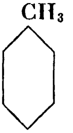
is represented simply as



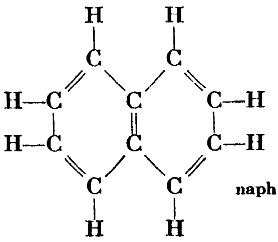
Toluene, $C_6H_5CH_3$, is an important hydrocarbon related to benzene. Its molecule contains the methyl group in place of one of the hydrogen atoms of benzene.



or



Naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, are hydrocarbons whose molecules contain more than one benzene ring.



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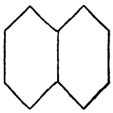
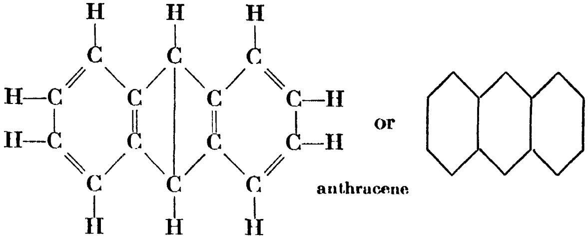
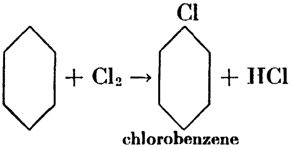


naphthalene



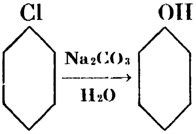
anthracene

2. Derivatives of the Aromatic Hydrocarbons.—When aromatic hydrocarbons are treated with chlorine, substitution reactions take place, *e.g.*,



chlorobenzene

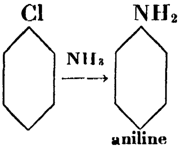
When chlorobenzene is treated with sodium carbonate under suitable conditions, hydroxybenzene is formed.



phenol, or carbolic acid

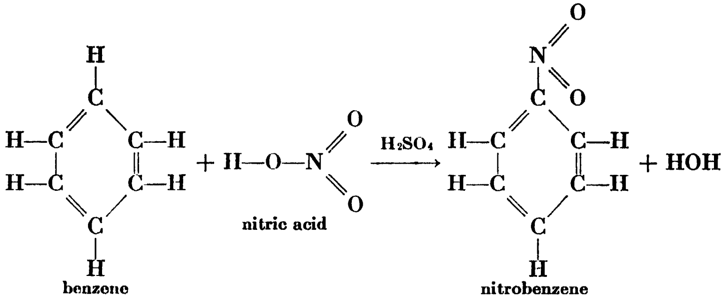
This substance is well known to you as the antiseptic carbolic acid and to chemists as phenol. Large quantities of this substance are used in the drug, dye, and explosives industries; and are condensed with formaldehyde to form the synthetic resin bakelite.

If chlorobenzene is heated under pressure with ammonia, aniline, the raw material from which many dyes and drugs are prepared, is the result.

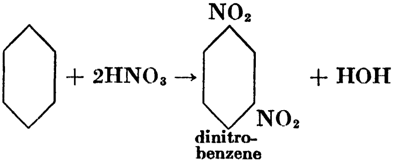


aniline

A very important type of reaction takes place when an aromatic hydrocarbon is treated with a mixture of concentrated nitric and sulfuric acids. To help you follow this reaction, we shall use the structural formula of nitric acid.



The nitro group —NO_2 replaces a hydrogen atom of benzene, and water is removed by the dehydrating action of the concentrated sulfuric acid. Continued action of these mixed acids results in the introduction of two and even three nitro groups in place of other hydrogens of the benzene molecule.



This reaction is of importance in the manufacture of explosives as we shall soon learn.

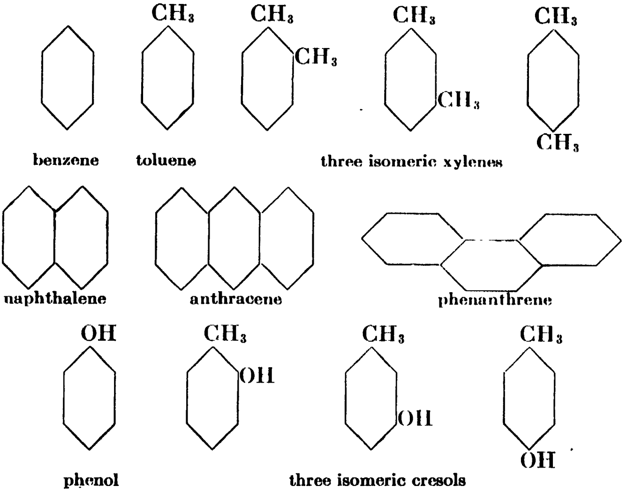
Aldehydes, acids, ketones, ethers, and esters derived from aromatic hydrocarbons are also well known.

3. Coal Tar.—When soft coal is heated in a closed retort (42-8) among the products of the distillate is coal tar, a black, evil-smelling, highly viscous liquid. From this unattractive material, the chemist has prepared dyes which rival the colors of the sunset and perfumes to match the most delicate odors of the flowers. From it also are made drugs to relieve the sufferings of man and cure his diseases and explosives to serve him in peace and add to his troubles in war.

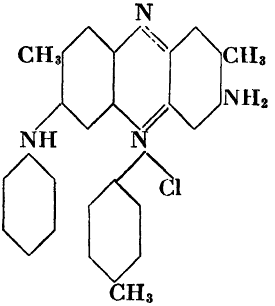
When coal tar is distilled, eight important crudes are obtained in the distillate and pitch is left behind in the retort. These crudes are benzene, toluene, xylene, naphthalene, anthracene, phenanthrene, phenol, and cresol. Some of these we have just been discussing. The others are closely related.

These crudes are the raw materials of the dye, drug, and explosives industries. Some of them are useful in themselves. Benzene is an important liquid fuel and solvent. Naphthalene has been used as a moth repellent in the sometimes too familiar moth balls. The antiseptic properties of phenol, or carbolic acid, are familiar to all of you. The cresols make up the creosote oil that is used extensively as a wood preservative and an antiseptic.

TABLE 70.—CRUDES FROM COAL TAR

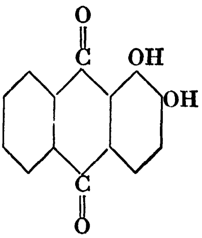


4. The Dye Industry.—Until the middle of the last century, the dyes that were used to color textiles were all of vegetal or animal origin. Logwood for black, cochineal from certain insects and alizarin from the root of the madder plant for red, and indigo and the royal Tyrian purple from a shellfish of the Mediterranean for blue and violet were the tools of the dyer's art. Synthetic dyes were as yet unknown. It is true that as early as 1771 Woulfe had prepared the yellow dyestuff picric acid by the oxidation of indigo, and in 1834 Runge had succeeded in making another yellow dye aurine from phenol; but neither of these was of any great value. Then in 1856 William Perkin, a student of the great organic chemist Hofmann, succeeded in synthesizing mauve, a beautiful purple dye, by accident, while seeking a means of converting aniline into quinine. If he had used pure aniline, the discovery would not have been made at that time. Fortunately the aniline that he used contained toluidine. This mixture, treated with the oxidizing agent sodium dichromate, resulted in the synthesis of the dye.



Illuminating gas from soft coal (42-11) had already gained widespread use at that time so that coal tar was available. Methods of converting benzene from coal tar into aniline had also been worked out. The stage was set for the development of the synthetic-dye industry. Perkin's discovery stimulated research to such an extent that soon many new dyestuffs were synthesized. Nowhere was this research carried on with greater zeal than in Germany. Slowly but surely a gigantic dye industry was developed in that country which became so powerful as to gain a virtual monopoly by forcing competitors out of business.

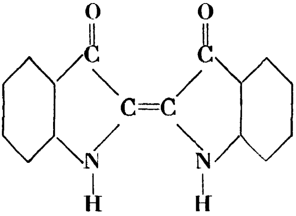
This was a period of rapid development of organic chemistry. Many natural products were analyzed and the structures of their molecules determined. Once their structural formulas were known, methods were soon developed by which they could be synthesized. Ten years after he had discovered mauve, Perkin succeeded in synthesizing alizarin, the natural dyestuff extracted from the roots of the madder plant. Graebe and Liebermann in 1868 proved it to be a derivative of anthracene.



alizarin

In 1869, the commercial production of this dye from anthracene started, and the cultivation of the madder plant, to which 50,000 acres in France alone were devoted, was doomed. In 1870, 750 tons of this dyestuff were extracted from madder roots. Now over 2,000 tons are synthesized annually in chemical plants, and the madder is almost a botanical curiosity.

The same fate threatens the indigo fields of India. The German chemist Baeyer devoted 20 years to the problem of establishing the constitution of the indigo molecule.

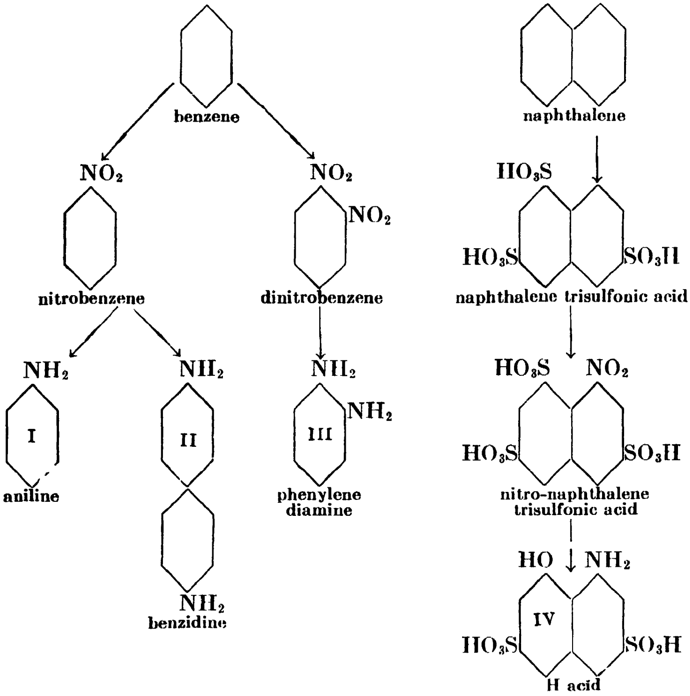


indigo

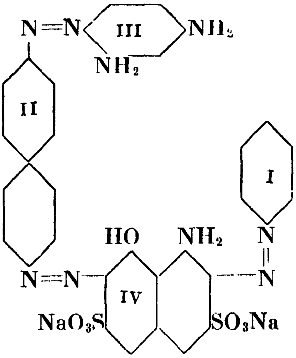
He succeeded in 1884, and the synthesis of indigo in the laboratory soon followed. However, the laboratory method was too expensive to produce the dye commercially in competition with the natural product. Five million dollars and over seventeen years of research were spent by the Badische Anilin und Soda Fabrik before a successful commercial process was worked out. Then the fun started. A million acres of the fields of India were devoted to the culture of the indigo plant in 1897, and these produced $20,000,000 worth of indigo annually. By 1914, India was producing only $300,000 worth. Germany had gained a 96 per cent monopoly of the world's production of this dyestuff.

In 1909, Friedländer succeeded in establishing the structure of Tyrian purple and, oddly enough, found out that it had already been synthesized 5 years before by Sachs but had been rejected as an inferior dyestuff. It was a dibromindigo.

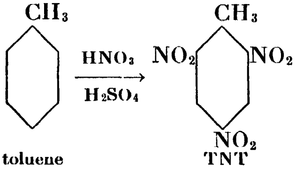
Today the dye industry converts the crudes of coal tar into some three hundred or more dye intermediates from which over a thousand different dyestuffs are made. To give you some idea of the steps involved in the manufacture of a typical dye, let us consider the preparation of a black dye which is used extensively for dyeing hosiery. From the crudes benzene and naphthalene, four intermediates are made.

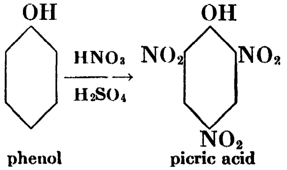


From these four intermediates, the molecule of the dye is synthesized.



5. Explosives.—Our modern high explosives with the exception of nitroglycerin and nitrocellulose are all derived from the same coal-tar crudes. The nitration of toluene and phenol gives two of the most important high explosives—trinitrotoluene (TNT) and picric acid, respectively.

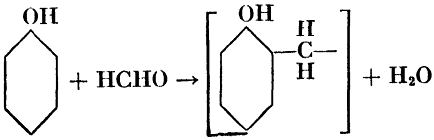




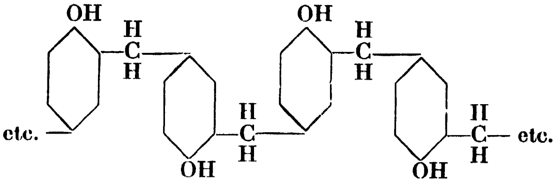
That high explosives can be prepared not only from the same crudes that are used in the manufacture of dyes, but also by the same reactions and in the same chemical apparatus, makes a dye plant readily convertible to the manufacture of explosives in time of war. The monopoly of the dye industry which Germany enjoyed up to the time of the First World War was all to her advantage during the last war. Now, however, the infant dye industry in this country, which had to struggle to keep its head above water in the few years following the armistice, has grown by leaps and bounds until it is competing in the markets of the world with that gigantic chemical trust of Germany—the I. G.

6. Plastics.—The natural resins, *e.g.*, amber, rosin, and shellac, are organic substances whose molecules are large and hence difficult to crystallize. They are, therefore, glassy substances that become less viscous and more plastic on heating. Most modern synthetic plastics are of a similar nature. They are usually formed by the polymerization of relatively simple unsaturated molecules, although some, *e.g.*, celluloid, are manufactured by altering the structure and properties of such naturally occurring substances as cellulose whose molecules are complex to begin with. The latter type will be considered in the next chapter (55-5).

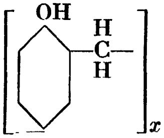
The first commercially successful plastic of the first type is bakelite, introduced by Baekeland nearly 35 years ago. This is prepared from phenol and formaldehyde. The reactions involved are essentially as follows:



This "unit" polymerizes into a long-chain polymer



which may be summarized by



Bakelite is a *condensation polymer* since molecules of water are split off from between phenol and formaldehyde molecules as

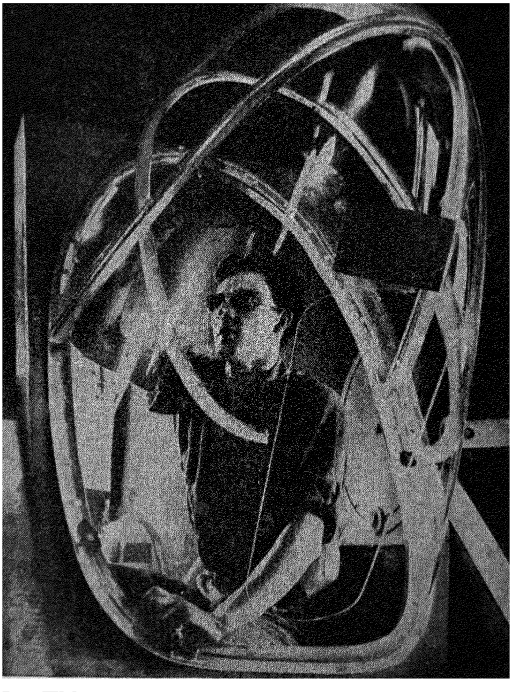
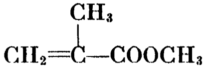


FIG. 181.—This crystal-clear nose for a Martin bomber is made of methyl methacrylate plastic. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

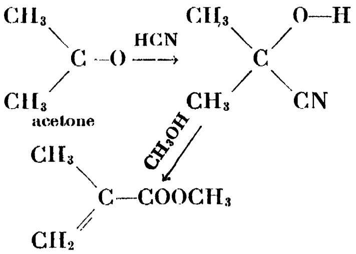
polymerization takes place. It is also a *thermosetting* plastic. The powdered material, when molded into shape by the combined action of heat and pressure, sets permanently and cannot be softened again by heat.

The transparent plastic, so familiar as the material out of which bomber noses are fashioned, is a polymer of methyl methacrylate

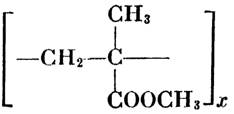


$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}COOCH_3$$

and is known as Lucite or Plexiglas. This ester is prepared from acetone by the following reactions:



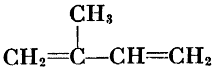
Polymerization results from the opening of the double bond under the influence of a catalyst.



$$\left[-CH_2-\underset{\displaystyle COOCH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\right]_x$$

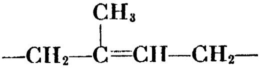
7. Synthetic Rubber.

—Natural rubber is a polymer of isoprene



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2$$

The "unit" in its molecule may be represented by



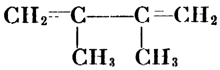
$$-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH-CH_2-$$

The giant molecule of rubber is made up of 800 to 2,500 isoprene units.

During the First World War Germany was cut off from the supply of natural rubber, and isoprene was at that time difficult to synthesize in the large quantities needed. Since isoprene is the methyl derivative of butadiene

$$CH_2{=}CH{-}CH{=}CH_2$$

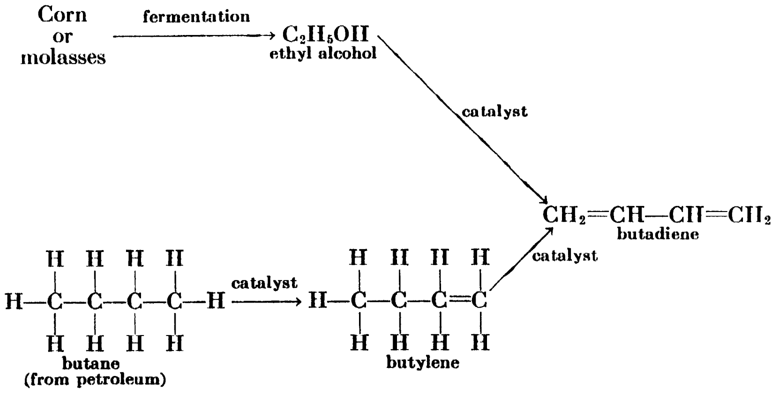
and since this substance can be more readily prepared, German chemists concentrated on the problem of making a synthetic rubber from butadiene and some of its more easily prepared derivatives. The so-called Buna rubbers were the result. The name was derived from butadiene and the symbol for sodium, since this metal was used as a catalyst in the polymerization. A synthetic rubber formed by the polymerization of dimethyl butadiene



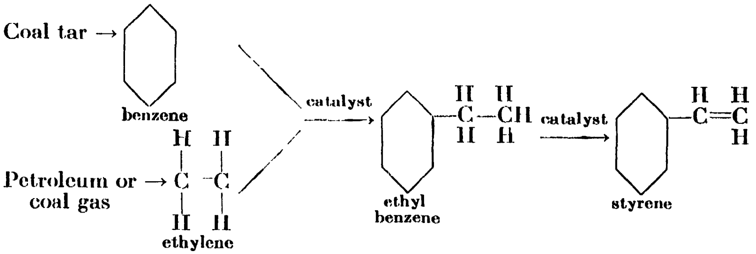
$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

was manufactured in Germany to the extent of 4 million pounds a year during the last war.

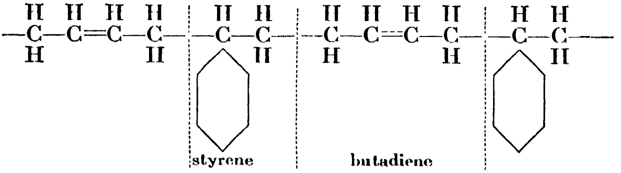
Since that time, research both in the United States and Germany has developed far superior types of synthetic rubber. When the Japanese cut off our supply of natural rubber, the decision was made to embark on a gigantic program for the production of Buna S which is made from butadiene and styrene. The former is made both from alcohol and from petroleum-refinery gases.



Styrene is manufactured from benzene and ethylene.



These two substances, in the proportions of 3 parts butadiene, 1 part styrene, and 7 parts soapy water, are mixed as an emulsion and polymerized by a suitable catalyst. The result is a so-called *copolymer* in which butadiene and styrene units alternate in the giant molecule



The majority of the synthetic rubber plants are now in successful operation, producing well over their rated capacity. The remainder are ready to start. One of the largest of these plants at Institute, W. Va., is producing enough synthetic rubber to make 16 million tires a year. Ordinarily, 7 to 10 years are required from the time a process is developed in the research laboratory until it operates on a full commercial scale. The amazing speed with which the synthetic-rubber program was developed is a tribute to the chemists and chemical engineers of this country.

8. Chemistry and Medicine.—No story of the service of chemistry to mankind would be complete without some reference to the advances that have come through its aid in the field of medicine. A list of the drugs and remedies of the doctor of the seventeenth and eighteenth centuries makes pathetic and even revolting reading. The thought of a leg cut off or an abdomen opened without anesthesia and antiseptics makes us thank our lucky stars that we are fortunate enough to live in the twentieth century. We owe a debt of gratitude to the chemists who have made it possible for us to sleep in blissful ignorance of the explorations of an inquisitive surgeon and have allowed us to wake with the comfortable thought that antiseptics will prevent our wounds from becoming infected. Space is lacking in a book of this kind to give any but the briefest survey of what has been done.

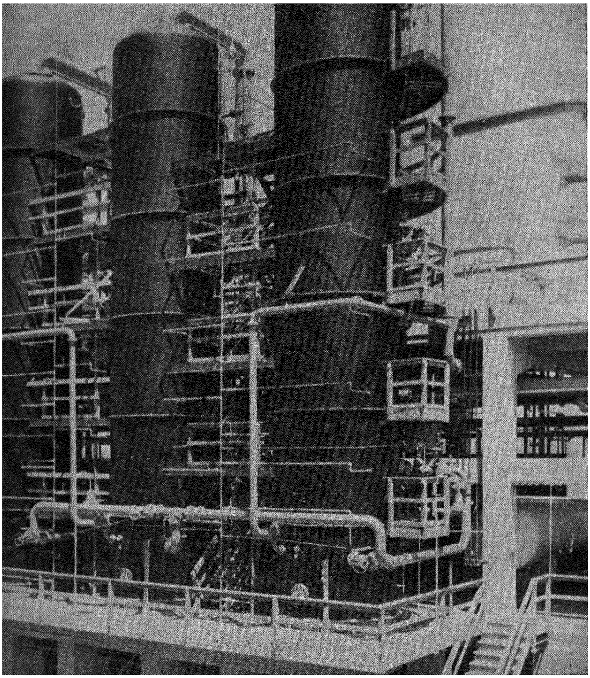
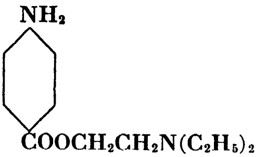


FIG. 182.—Fractionating columns in which unpolymerized reactants are removed from latex for return in the manufacture of synthetic rubber. (*Courtesy of Rubber Reserve Company.*)

In the field of anesthetics we must mention the discovery of nitrous oxide, or laughing gas, by Sir Humphry Davy (39-1) and of chloroform by Liebig in 1832. Ether was discovered in 1544 by Valerius Cordus but was not used to produce anesthesia until 1842 when Dr. Crawford W. Long of Jefferson, Ga., removed a tumor from a patient under its influence. The discovery of the use of ethylene as an anesthetic we have already recorded (52-5).

Cocaine, a vegetable alkaloid, has been used since 1884 as a local anesthetic, but such substances as novocaine



which are synthetic products, are far superior in that they are less toxic, non-habit-forming, and less expensive.

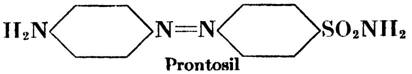
Opium is one of the products that nature offers as a hypnotic, or sleep producer. But you are all familiar with the dangers of its use. Today many synthetic hypnotics, which are less habit-forming, are on the market—veronal, the sulfonals, luminal, to mention only a few.

Practically all the antipyretics (fever reducers) and antiseptics are synthetic chemicals derived from coal tar.

Many chemicals have been prepared to combat specific diseases. Among these are chaulmoogra oil and its derivatives in the treatment of leprosy, carbon tetrachloride in combatting the hookworm, and salvarsan in the treatment of syphilis.

The discovery of the antiseptic properties of sulfanilamide came as the result of a clever example of reasoning by analogy. Dyes with the structure

possess the property of staining vegetable fibers. Since bacteria are one-cell plants, such dyestuffs as the red dye prontosil are germicides. M. and Mme. Tréfouël and their collaborators in France, through their study of the fate of prontosil

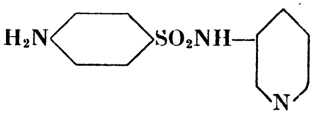


Prontosil

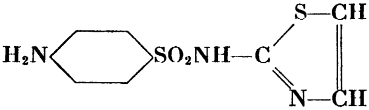
and like dyestuffs in animals, became convinced that all these compounds are broken down to sulfanilamide in the body and that the latter is the active antiseptic. This substance

Sulfanilamide

was tested, and their hypothesis proved to be correct. This anti septic is especially effective against streptococcal infection. A series of analogous compounds have been prepared, a few of which are better than sulfanilamide against other types of infection. Thus sulfapyridine

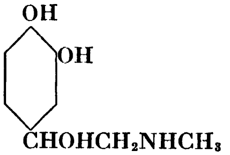


is most effective against certain types of pneumonia; and sulfathiazole,

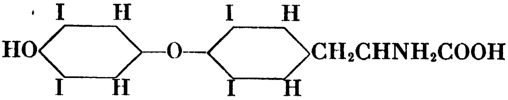


against staphylococci. What prompt treatment with sulfa drugs has done in saving the lives of wounded soldiers is familiar to everyone who reads the newspapers. These drugs must not be used except under the direction of a physician, and preferably in a hospital. Individuals vary in their tolerance, and damage to the kidneys may result.

Finally, many of the secretions of the ductless glands of the body have been investigated by organic chemists to determine their structure and by physiological chemists to ascertain their functions in body metabolism. Among these so-called hormones, adrenaline, the secretion of the suprarenal glands, has been synthesized and is now prepared commercially.



In times of danger, this substance is secreted into the blood stream and produces a contraction of the blood vessels and thus increases the blood pressure. By injecting small quantities of pure adrenaline under the skin, the arterial walls are so violently contracted that the blood is driven out of them and "bloodless" surgery is made possible. Thyroxin, the hormone of the thyroid gland, has been recently proven to be



Insulin, the hormone of the pancreas, is being investigated, but its structure has not yet been determined. Chemists, however, have made possible its extraction in a pure and active form and its use in the treatment of diabetes.

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CHAPTER FIFTY-FIVE

THE CHEMISTRY OF LIFE

We have somewhat unceremoniously hurried you through an introduction to some of the more fundamental types of organic compounds in order to be able to show you something of the complexity of the compounds of which living organisms are composed. Then too, some knowledge of such compounds is necessary before we can discuss any of the problems of animal nutrition. When we examine some of the simplest forms of life, which exist as single-celled organisms visible to us only with the aid of a microscope, with a view to finding something of the nature of the chemical compounds of which they are composed, we find these to be of almost the same complexity as those found in higher organisms. The problem of how such compounds came into existence from inorganic matter is as much a mystery to the chemist as the origin of life is to the biologist. Nowhere do chemists find any evidence of the synthesis of even simple organic substances from inorganic compounds in nature other than in the cells of living organisms. Protoplasm, the physical medium in which the processes of life take place, is mainly a mixture of such complex substances as carbohydrates, fats, and proteins with the molecules of these substances in a structure in which colloidal aggregates play an important part. We shall try to give you some idea of the chemical nature of these types of substances and of their importance both as the raw materials of certain chemical industries and as the foodstuffs from which we derive the energy of our own life processes.

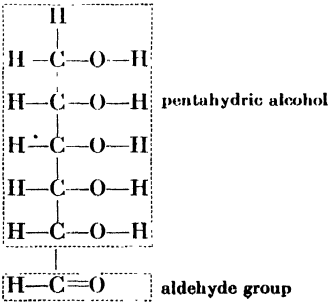
1. Photosynthesis.—In the green leaves of plants are found tiny globular bodies of about 0.002 mm. in diameter. These are the chloroplasts. They are the most important bodies on the whole earth from the point of view of all living organisms, for within them in some mysterious way the radiant energy which comes to the earth from the sun is stored as chemical energy. If these bodies were to stop functioning permanently, all life would soon disappear from the earth. Within them is the substance, chlorophyll, which is probably a mixture of four complex compounds in a colloidal suspension together with some fats, waxes, and mineral salts. The names of these four compounds, their empirical formulas, and the extent to which they are present in chlorophyll are as follows:

	Per Cent
Chlorophyll A ($C_{55}H_{72}O_5N_4Mg$)	61
Chlorophyll B ($C_{55}H_{70}O_6N_4Mg$)	22
Xanthophyll ($C_{40}H_{56}O_2$)	10
Carotin ($C_{40}H_{56}$)	5.9

The large number of atoms in the formulas of these substances is an indication of the complex structures of their molecules. The molecular structures of these complex compounds are fairly well known and it is an interesting fact that the chlorophyll pigments are related to hematin, a derivative of hemoglobin found in the blood of animals. The iron atom in the hematin molecules corresponds to that of magnesium in chlorophyll.

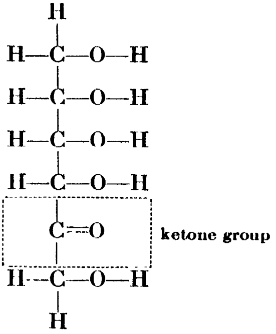
Carbon dioxide and water are the main foodstuffs of the plant. In the chloroplasts, these are in some way converted into carbohydrates, and the radiant energy of the sun is stored as chemical energy in their molecules. In this process oxygen is liberated. The mechanism, by which this synthesis is accomplished, is being studied, using radioactive carbon atoms in carbon dioxide molecules.

2. The Structure of Carbohydrates.—A carbohydrate is an organic compound composed of the elements carbon, hydrogen and oxygen. Further, the hydrogen and oxygen atoms are present in the same ratio as they are in the water molecule, *i.e.*, in the ratio of 2 to 1. The general formula of a carbohydrate is $C_xH_{2y}O_y$. The carbohydrates found in nature are the sugars, dextrins, starches, and cellulose. The structural formula of one of the simplest sugars, glucose, reveals the fact that it is both a pentahydric alcohol and an aldehyde.



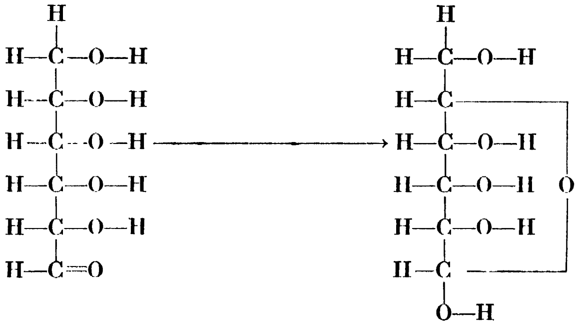
glucose

A slightly different type of sugar is the isomer of glucose, fructose. The structural formula of this sugar



fructose

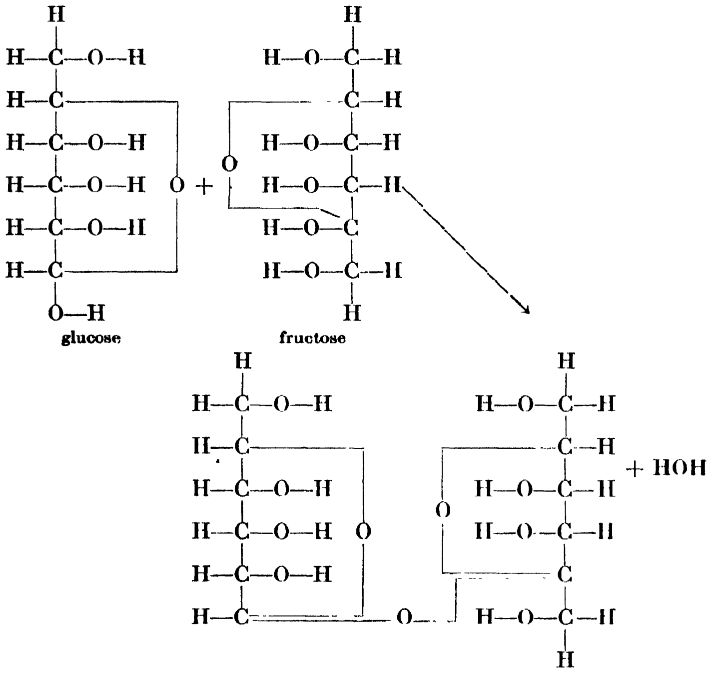
shows it be both a polyhydric alcohol and a ketone. These sugars exist also in another form which results from the molecular rearrangement of the type shown below. In each case a hydrogen atom wanders from a hydroxyl group on the third or fourth carbon removed from the CO group which results in the formation of an oxygen bridge, or lactone structure, between these carbon atoms.


aldehyde form

lactone form

The Two Forms of Glucose

The more complex sugars result from the condensation of two or more simple sugar molecules by the splitting off of water between them. For example, sucrose, or common cane sugar, is formed by the condensation of glucose and fructose.



Starch and cellulose are probably formed by a similar condensation of glucose molecules. Using empirical formulas only, we can represent the synthesis of either cellulose or starch from glucose as follows:

$$xC_6H_{12}O_6 \rightarrow (C_6H_{10}O_5)_x + xH_2O$$

All the reactions that represent the formation of the more complex from the simple carbohydrates by the splitting off of water from between their molecules are reversible. Sucrose, for example, can be readily hydrolyzed into glucose and fructose. Starch and cellulose can be quantitatively hydrolyzed back into glucose. This change actually takes place when starches are digested in our bodies. Cellulose, on the other hand, is indigestible. However, if sawdust (mainly cellulose) is warmed with a dilute solution of hydrochloric acid, it is converted into digestible sugars which have been used successfully as foods in cattle-feeding experiments.

3. The Sugar Industry.—The only sugar that John Doe knows about is the one which chemists call sucrose. This sugar, as you all know, is extracted from sugar cane and from sugar beets. The sugar crop from these two sources in the 1924–1925 season amounted to nearly twenty-five million tons. This was produced in the following countries and amounts:

TABLE 71.—THE SUGAR CROP

Country	Tons of sugar		Source
Cuba	5,100,000		Cane
United States and colonies	2,757,837	1,783,652	Cane
		974,185	Beet
British India	2,537,000		Cane
Java	1,977,490		Cane
Germany	1,600,000		Beet
Czechoslovakia	1,460,000		Beet
France	830,000		Beet
Brazil	500,000		Cane
Poland	495,000		Beet
Japan and Formosa	460,000		Cane

The methods by which sugar cane or sugar beets are cultivated and harvested are beyond the scope of this book. The extraction of the sugar from them involves first the maceration of the cane between rollers or the cutting of the beets into small slices by revolving knives. The sugar is then extracted with water, the acidity of the resulting solution reduced and certain of its impurities precipitated by lime, and finally the water removed and the sugar crystallized in evaporators and vacuum pans.

In the Western Hemisphere, corn is the source of many sugars. The kernel of corn consists of three parts—the hull, the germ, and the white body part which is mainly starch and makes up over half the weight of the kernel. When this is heated with a very dilute acid, the starch is hydrolyzed into various products among which are the dextrins which are used as the "gum" on the back of postage stamps and the flaps of envelopes, and corn syrup, a mixture of maltose (45 per cent) and glucose (20 per cent), both of which are sugars, and dextrin (35 per cent). Cornstarch can be quantitatively hydrolyzed into glucose which is used extensively in candymaking. It has the advantage over cane sugar for this purpose that it is extremely difficult to crystallize. The corn crop in this country of over 3,000,000,000 bushels annually is valued at more than the wheat, cotton, potato, and rye crops put together. Fifty million bushels of corn are converted into corn products which include 800,000,000 lb. of corn syrup, 600,000,000 lb. of starch, and 230,000,000 lb. of glucose.

4. The Cellulose Industries.—Cellulose is the carbohydrate that forms the cell walls and woody structure of plants. Cotton is practically pure cellulose. Its empirical formula $(C_6H_{10}O_5)_x$ tells us nothing of its structure and, therefore, of its chemical properties. Cellulose is formed by the condensation of several glucose molecules

$$xC_6H_{12}O_6 \rightleftarrows (C_6H_{10}O_5)_x + xH_2O$$

and cellulose can be quantitatively hydrolyzed back into glucose. Further there are three OH groups per $C_6H_{10}O_5$ in the cellulose molecule. It, therefore, acts like a "poly"-trihydric alcohol which we can show by writing its formula

$$[C_6H_7O_2(OH)_3]_x$$

Many industries use cellulose as such and do not alter it chemically. Among these are the cotton textile and the lumber industries. The production of paper from wood involves chemistry only in the removal of the impurities with which cellulose is mixed in wood. Lignin is the most important of these. In the manufacture of paper, logs of spruce or hemlock are cut up by disk choppers and the chips are digested for several hours under pressure with a solution of sodium or calcium bisulfite. This treatment dissolves out the lignin and leaves the almost pure cellulose fibers of paper pulp. The pulp is bleached with chlorine, mixed with sizing materials, such as glue or rosin, to prevent ink from running on the finished product, and finally made up into paper by a mechanical process in a paper machine. Paper made from linen or rag stock lasts longer than that from wood pulp. Wood is being used up at an alarming rate by our newspapers and periodicals. One New York paper uses up nearly 2,000 acres of forest annually.

5. The Cellulose Esters.—Certain other industries use cellulose as a raw material, changing its chemical nature in the process of the manufacture of their finished products. We have pointed out that cellulose is an alcohol. As such it can be converted into esters when treated with acids. The most important of these are the cellulose nitrates which are formed when cellulose is treated with a mixture of concentrated nitric and sulfuric acids

$$\underset{\text{cellulose}}{[C_6H_7O_2(OH)_3]_x} + 3xHNO_3 \rightarrow \underset{\text{cellulose nitrate}}{[C_6H_7O_2(NO_3)_3]_x} + 3xHOH$$

The trinitrate of cellulose is the well-known high explosive nitrocellulose, or guncotton. This substance is insoluble in water but dissolves in a solution of ether and alcohol which is called collodion. The story goes that Alfred Nobel, a Swedish chemist, once cut his finger while working in his laboratory. He coated the cut with this ether-alcohol solution and, while waiting for the solvents to evaporate, conceived the idea of using this substance as an absorbent for the liquid high explosive nitroglycerin. When he mixed the collodion solution with nitroglycerin, it set to a jelly. This was the discovery of blasting gelatin, the first of a series of high explosives which are so little sensitive to shock that they can be fired from a cannon with safety to the gunners. This was in 1878. Nobel made a fortune from this discovery, part of which he bequeathed to establish a fund from which the prizes that bear his name are awarded annually to those who have made outstanding discoveries in medicine, chemistry, and physics, who have created idealistic literature of great merit, and who have made significant contributions to the promotion of peace.

If cellulose is treated under milder conditions with mixed nitric and sulfuric acids, a mixture of the mono- and the di-nitrate is obtained.

$$[C_6H_7O_2(OH)_3]_x + 2xHNO_3 \rightarrow [C_6H_7O_2(OH)(NO_3)_2]_x + 2xHOH$$

$$[C_6H_7O_2(OH)_3]_x + xHNO_3 \rightarrow [C_6H_7O_2(OH)_2NO_3]_x + xHOH$$

This mixture is called *pyroxylin*. While not explosive, it is extremely inflammable. From it many useful materials are made.

In 1870, John Wesley Hyatt discovered celluloid while trying to find a substitute for ivory out of which to make billiard balls. This material is made by molding together under alcohol pyroxylin with half its weight of camphor and then subjecting the mixture to heat and pressure in molds. Hyatt began manufacturing this substance in 1872 in Newark, N. J. Its use in photography is well known to all of you.

A great variety of the so-called pyroxylin plastics are derived from celluloid, for this material can be colored with many dyes and can be made transparent by bleaching or opaque by the addition of the oxides or chlorides of certain metals. Ivory, tortoise shell, coral, amber, and many other natural products can be imitated in celluloid. A slow-burning celluloid is now made for safety films from the acetate instead of the nitrate of cellulose. Another use of pyroxylin is in the manufacture of artificial leather. This is made by impregnating canvas with a castor-oil solution of pyroxylin. Spray and brushing lacquers consist of pyroxylin dispersed colloidally in such a solvent as butyl acetate or a mixture of ethyl and amyl acetates. Camphor is used as a plasticizer and some light-fast and light-impenetrable pigment is added together with resins to give luster and hardness to the finished lacquer surface.

6. **Artificial silk,** or rayon, is also a cellulose derivative. There are four processes by which this important textile is manufactured. In 1889, the first samples of artificial silk were exhibited at the Paris Exposition. They were made by the nitrate process discovered by Count Hilaire de Chardonnet. This process involves the extrusion of a solution of cellulose nitrate through a tiny orifice into a solution of calcium sulfide. This removes the nitrate groups from the cellulose molecule and precipitates what is practically the original cellulose as an artificial fiber that has the luster of silk.

Today most of the rayon is made by the viscose process which was discovered by Cross and Bevan, two English chemists, in 1892. In this process, cotton or wood pulp is treated with a strong sodium hydroxide solution and with carbon disulfide, converting it into the water-soluble sodium cellulose xanthate, or viscose. This solution is precipitated as a lustrous cellulose fiber in a sulfuric acid solution. Increasing amounts of rayon are being made by the acetate process. In 1936, 22 per cent of the total production of 258,000,000 lb. was produced by this process. In addition 60,000,000 lb. of wrapping film (cellophane) were made by either the viscose or the acetate process.

7. **Fats** constitute a second important class of organic compounds that are found in living organisms. They are all esters of the trihydric alcohol glycerin and some fatty acid, *i.e.*, an organic acid, similar to acetic acid, but of much greater molecular weight.

The most important fatty acids are as follows:

Saturated fatty acids	Unsaturated fatty acids
$C_{15}H_{31}COOH$, palmitic acid	$C_{17}H_{33}COOH$, oleic acid
$C_{17}H_{35}COOH$, stearic acid	$C_{17}H_{31}COOH$, linoleic acid

A fat can be synthesized by an esterification reaction between glycerin and a fatty acid (53-6).

$$\underset{\text{glycerin}}{C_3H_5(OH)_3} + \underset{\text{stearic acid}}{3C_{17}H_{35}COOH} \rightarrow \underset{\substack{\text{glyceryl stearate,}\\ \text{or stearin}}}{(C_{17}H_{35}COO)_3C_3H_5} + 3HOH$$

The fats that are esters of the saturated fatty acids are solids, whereas the liquid fats, like cottonseed and olive oils, are derived from fatty acids that have double bonds in their molecules and are, therefore, unsaturated. All the fats found in nature are mixtures usually of both solid and liquid fats. Beef suet, for example, is about three-quarters palmitin and stearin and one-quarter olein. Hog lard is 40 per cent palmitin and stearin and 60 per cent olein. Butter is an emulsion containing 14 per cent water with palmitin, stearin, and olein and in addition about 8 per cent butyrin, $(C_3H_7COO)_3C_3H_5$. Cottonseed and olive oils contain 75 per cent olein, an unsaturated liquid fat. Linseed oil, used so extensively in paints, contains linolein, an ester of glycerin and linoleic acid. This acid is highly unsaturated.

8. Hydrogenation of Fats.—The conversion of liquid unsaturated fats into solid saturated ones is an industry of great importance. This can be accomplished by adding hydrogen to the double bonds in the molecules of the unsaturated fat, using finely divided nickel as a catalyst, *e.g.*,

$$\underset{\text{olein, a liquid fat}}{[CH_3(CH_2)_7CH{=}CH(CH_2)_7COO]_3C_3H_5} \xrightarrow[\text{at } 200^{\circ}\text{C.}]{\text{H} \quad \text{Ni}} \underset{\text{stearin, a solid fat}}{[CH_3(CH_2)_7CH_2CH_2(CH_2)_7COO]_3C_3H_5}$$

This process of hydrogenating double bonds using nickel as a catalyst was worked out by Paul Sabatier, a French chemist, and won for him the Nobel Prize in 1912. By means of this process, such liquid fats as cottonseed oil are partially hydrogenated to the semisolid vegetable shortenings which are so popular today. Complete hydrogenation results in a hard, brittle product.

Hydrogenated fats are also extensively used in the manufacture of soap.

9. A soap is a salt of a fatty acid. Its preparation involves the treatment of a fat with either sodium or potassium hydroxide.

$$\underset{\text{stearin a fat}}{(C_{17}H_{35}COO)_3C_3H_5} + 3NaOH \rightarrow \underset{\text{sodium stearate, a soap}}{3C_{17}H_{35}COONa} + \underset{\text{glycerin}}{C_3H_5(OH)_3}$$

Glycerin is always obtained as a by-product. Sodium and potassium soaps are used for laundry purposes. Soaps of some of the heavier metals are used as emulsifying agents in the preparation of greases (44-9).

10. The Proteins.—The proteins are more complex than either the carbohydrates or the fats. When proteins are hydrolyzed, a mixture of various amino acids is obtained—substances that are both amines (53-7) and acids (53-5). The simplest of

TABLE 72.—AMINO ACIDS DERIVED FROM PROTEINS BY HYDROLYSIS

CH_2NH_2COOH, glycine

CH_3CHNH_2COOH, alanine

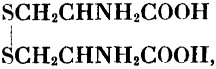
$(CH_3)_2CHCHNH_2COOH$, valine

$(CH_3)_2CHCH_2CHNH_2COOH$, leucine

$C_6H_5CH_2CHNH_2COOH$, phenyl alanine

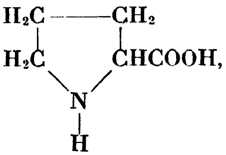
$HOC_6H_4CH_2CHNH_2COOH$, tyrosine

$CH_2OHCHNH_2COOH$, serine



$$\begin{array}{l} SCH_2CHNH_2COOH \\ | \\ SCH_2CHNH_2COOH \end{array}$$

cystine



proline

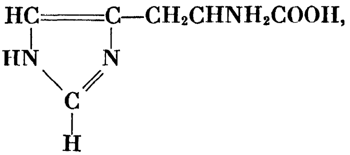
$HOOCCH_2CHNH_2COOH$, aspartic acid

$HOOCCH_2CH_2CHNH_2COOH$, glutamic acid

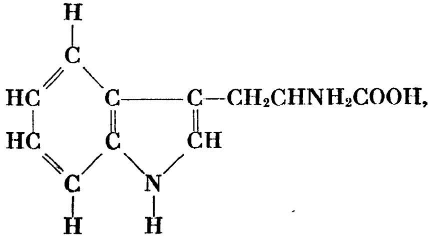
$CH_2NH_2CH_2CH_2CHNH_2COOH$, ornithine

$NH_2C(=NH)NHCH_2CH_2CH_2—CHNH_2COOH$, arginine

$CH_2NH_2CH_2CH_2CH_2CHNH_2—COOH$, lysine



histidine



tryptophane

these is glycine, or amino acetic acid,

$$CH_2NH_2COOH$$

A more or less complete list of the amino acids that have been isolated as products of protein hydrolysis is given in Table 72.

We do not need to caution you not to memorize their formulas. No one protein will hydrolyze to give all these acids. The following table shows the percentages of the various amino acids that are obtained by the hydrolyses of four typical proteins:

Table 73.—Percentages of Various Amino Acids Obtained from Four Different Proteins

Amino acid	Casein	Gelatin	Gliadin	Zein
Glycine	0.45	25.50	0.00	0.00
Alanine	1.85	8.70	2.00	13.39
Valine	7.93	1.00	3.34	1.88
Leucine	9.70	7.10	6.62	19.55
Proline	7.63	9.50	13.22	9.04
Oxyproline	0.23	14.10	?	?
Phenylalanine	3.88	1.40	2.35	6.55
Glutamic acid	21.77	5.80	43.66	26.17
Oxyglutamic acid	10.50	0.00	2.40	2.50
Aspartic acid	4.10	3.50	0.58	1.80
Serine	0.50	0.40	0.13	1.02
Tyrosine	6.50	0.01	3.50	3.55
Cystine	0.50	0.31	2.32	0.85
Histidine	2.84	0.90	3.35	0.82
Arginine	3.81	8.22	3.14	1.82
Lysine	7.62	5.92	0.92	0.00
Tryptophane	2.20	0.00	1.14	0.00
Ammonia	1.61	0.49	5.22	3.64
Total	93.62	92.85	93.89	92.58

Our knowledge of the way in which these amino acids are linked together in the molecule of a protein we owe mainly to the great German chemist Emil Fischer. An amine will react with an organic acid in a similar manner to ammonia to form a substituted amide.

$$\underset{\substack{\text{acetic}\\ \text{acid}}}{CH_3COOH} + \underset{\substack{\text{methyl}\\ \text{amine}}}{HNHCH_3} \rightarrow \underset{\text{methyl acetamide}}{CH_3CONHCH_3} + HOH$$

Since an amino acid is both an amine and an acid, two of its molecules can react together in the above manner, one functioning as an acid and the other as an amine.

$$\underset{\substack{\text{glycine as}\\ \text{an acid}}}{CH_2NH_2COOH} + \underset{\substack{\text{glycine as}\\ \text{an amine}}}{HNHCH_2COOH} \rightarrow \underset{\text{glycyl glycine}}{CH_2NH_2COHNCH_2COOH} + HOH$$

In this way, long chains of amino acids can be linked together by amide linkages. By uniting 7 to 19 amino-acid molecules, Emil Fischer produced synthetic polypeptides which closely resembled the peptones, the simplest of the proteins.

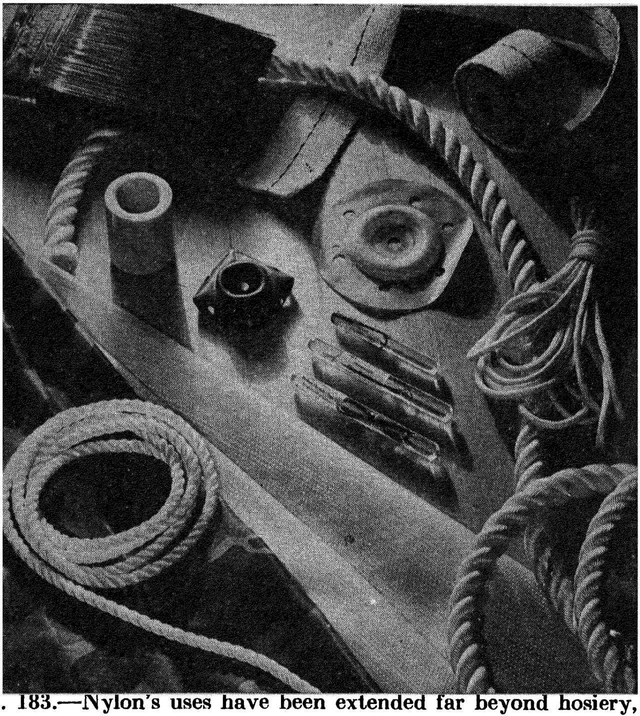


FIG. 183.—Nylon's uses have been extended far beyond hosiery, toothbrush bristles, and tennis racket strings since the war began. Arranged clockwise, beginning at the paintbrush with tapered bristles, are parachute harness webbing, parachute shroud lines, rope for military gliders, cargo parachute cloth, camouflaged Army Air Force escape parachute cloth, and light rope. In the center are experimental molded plastic bearing, carburetor diaphragms, and surgical sutures. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

11. Nylon.—The synthesis of a protein, like wool or silk, on a commercial scale is still beyond the dreams of even such optimists as the organic chemists. Recently, however, an artificial fiber called nylon has come on the market. This is a condensation polymer of hexamethylene diamine

$$NH_2CH_2CH_2CH_2CH_2CH_2CH_2NH_2$$

and adipic acid

$$HOOCCH_2CH_2CH_2CH_2COOH$$

both of which are prepared from benzene and hence from coal. The units combine by splitting off water and forming amide linkages.

$$—\underbrace{NH(CH_2)_6NH}_{\text{hexamethylene diamine}}—\underbrace{CO(CH_2)_4CO}_{\text{adipic acid}}—NH(CH_2)_6NH—CO(CH_2)_4CO—$$

The resulting giant molecule has in it the typical amide linkages found in proteins.

THE CHEMISTRY OF FOOD AND NUTRITION

12. Enzymes and Digestion.—The digestion of the foodstuffs in the bodies of animals is accomplished by secretions of the mouth, stomach, and intestines. These contain enzymes—organic catalysts, as someone has aptly named them—which break down the complex, insoluble molecules in our food into simpler, soluble substances which can then either be built up into our tissues or oxidized to furnish the energy of life processes. The most important digestive enzymes are given in Table 74.

Table 74.—Chief Digestive Enzymes

Act on	Enzymes	Where found	Action
Carbohydrates	Ptyalin	Saliva	Starch to maltose
	Amylopsin	Pancreas	Starch to maltose
	Invertase	Intestine	Sucrose to glucose and fructose
	Maltase	Intestine	Maltose to glucose
	Lactose	Intestine	Lactose to glucose and galactose
Fats	Lipases	Stomach and pancreas	Fats to fatty acids and glycerin
Proteins	Pepsin	Stomach	Proteins to peptones and amino acids
	Trypsin	Intestine	Proteins to peptones and amino acids

During digestion the carbohydrates, which consist mainly of starch, are hydrolyzed to simple sugars. The combined action of ptyalin, amylopsin, and maltase results in a quantitative hydrolysis of starch into glucose. The sugars are stored in the liver to be secreted in small quantities from time to time into the blood to be carried to the tissues. The glucose content of the blood never rises much above 0.1 per cent except in diabetic individuals. The oxidation of glucose to carbon dioxide and water to furnish the energy requirements of the muscles is accomplished by the hormone insulin, a secretion of the ductless glands of the islands of Langerhans of the pancreas. If these glands stop functioning, the sugar is not completely oxidized and diabetes is the result. Carbohydrates can also be converted into fats in the body.

Fats are split up by the lipase enzymes into fatty acids and glycerin which recombine as they pass through the intestinal walls and into the blood. Here they are oxidized as fuel, stored for future use, or enter the tissues.

Proteins are hydrolyzed to the soluble peptones and to amino acids and distributed in these forms to be recombined into the proteins of the tissues or oxidized for muscular work.

13. The Fuel Value of Foods.—One of the simplest methods of measuring the energy that our bodies can obtain from the oxidation of foods is by burning these in a calorimeter and measuring the number of calories of heat evolved. Typical results of such measurements are given in Table 75.

TABLE 75.—HEATS OF COMBUSTION AND APPROXIMATE COMPOSITION OF TYPICAL FOOD ELEMENTS[1]

Substance	Heat of combustion, kcal./g.	Composition, per cent				
		Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur
Glucose	3.75	40.0	6.7	53.3		
Sucrose	3.96	42.1	6.4	51.5		
Starch	4.22	44.4	6.2	49.4		
Butterfat	9.30	75.0	11.7	13.3		
Albumin	5.80	52.5	7.0	23.0	16.0	1.5

[1] SHERMAN, "Chemistry of Food and Nutrition," The Macmillan Company.

The combustion products, carbon dioxide and water, of fats and carbohydrates are the same in our bodies as they are in the calorimeter. Hence the energy emitted is the same. Proteins, however, burn to carbon dioxide, water, and nitrogen in the calorimeter, but in our bodies the nitrogen is excreted as urea and other nitrogenous organic compounds. The body, therefore, does not obtain as much energy from this oxidation as is given off in the complete combustion in the calorimeter. The actual loss is about 1.3 kcal./g. of protein so that the average energy per gram of protein obtained by the body is 4.35 kcal. Sherman gives the following approximate physiological fuel values of the food constituents:

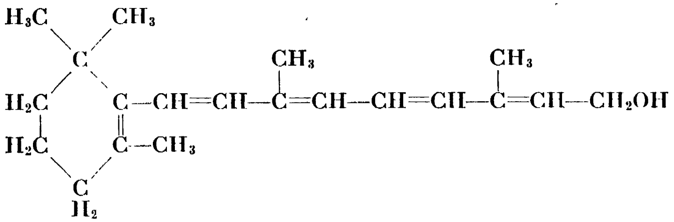
Carbohydrates	4 kcal./g.
Fats	9 kcal./g.
Proteins	4 kcal./g.

The daily energy requirement varies with the body weight of the individual and with the work in which he is engaged. On the average, a man will require about 2200 kcal. per day if he does no strenuous muscular work and upward to 3000 kcal. if he does.

14. The Vitamins.—Before the beginning of this century, dietitians were agreed that the food requirements of an animal consisted in a sufficient quantity of fats, carbohydrates, and proteins together with small amounts of inorganic compounds. Milk was considered, as it is today, as a foodstuff that contains all the essential food consituents. In 1906, Hopkins of Cambridge University showed that when young rats were fed on a diet that consisted of a mixture of *pure* fats, carbohydrates, and proteins together with mineral salts, made up to simulate the proportions of these food constituents in milk, growth ceased and the animals soon died. However, if a little milk was added to the diet, growth was resumed. Some food factor that had hitherto escaped detection was, therefore, present in milk. In 1912, Osborne and Mendel obtained similar results at Yale. At this time the oriental disease beriberi was shown to be due to the lack of a substance that was removed in the polishings of rice in the diet of rice-eating people. Funk proposed the name *vitamin* for such food substances the lack of which produced "deficiency diseases" or prevented normal growth. Within recent years, extremely important research in this field of biochemistry has been rewarded with success nothing short of spectacular. The majority of the known vitamins have been isolated as pure compounds from the complex mixtures in which they are found in nature. The structural formulas for many vitamins have been established. To organic chemists these molecular "blueprints" are of great importance as they suggest means by which such molecules can be prepared synthetically in pure form and in comparatively large quantity. A few of the vitamins are actually being made today on a commercial scale.

The following vitamins are now recognized.

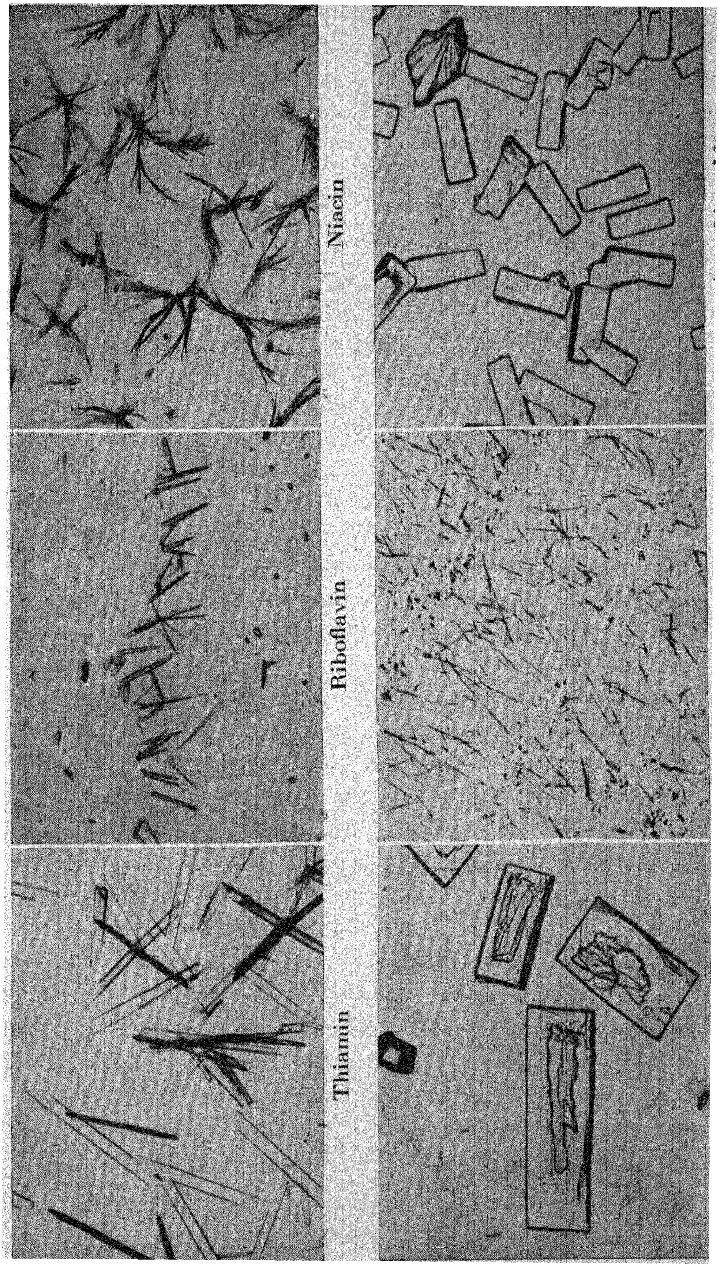
15. Vitamin A, the antixerophthalmic vitamin, prevents night blindness and a disease known as xerophthalmia, which causes a drying out of the outer covering of the eyes. It is essential for normal growth and helps keep the tissues of the respiratory tract healthy. To this extent it increases resistance to infections that enter by way of the nose and throat. Its structural formula was established by Paul Karrer of Zürich in 1933.



This will give you some idea of the molecular complexity of the vitamin and of the necessary labor and skill of many investigators who contributed to its successful formulation. It is closely related to carotene and its isomers, which are found widespread in nature as plant pigments. Carrots, for example, owe their color to the carotenes. These are easily converted in the animal organism into vitamin A. Carotenes or the vitamin itself are found in halibut- and cod-liver oils; in escarole, spinach, and carrots; in mangoes, prunes, and bananas; and in dairy products. The daily requirement of an adult of this vitamin is 4,000 international units.

16. Vitamins of the B Complex.—Before 1920 this group of vitamins, which occur in rice bran, yeast, liver and other materials, was considered to be one substance. It is now known to contain at least the five major vitamins thiamin (B_1), riboflavin (B_2), niacin, pyridoxine (B_6), and pantothenic acid.

Vitamin B_1, or *thiamin*, is called the antineuritic vitamin since its absence in the diet produces the symptoms of neuritis. An enzyme cocarboxylase, which serves a vital function in the oxidation of glucose to carbon dioxide and water, is derived from

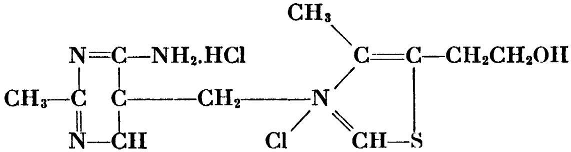


Thiamin Riboflavin Niacin

Pyridoxine Pantothenic acid Ascorbic acid

FIG. 184.—Vitamin crystals. (*Courtesy of Merck and Co., Inc.*)

this vitamin. If the supply is inadequate, the energy derived from this oxidation is insufficient for the needs of nerve tissues. Hence loss of appetite, fatigue, fear, and nervousness are the result. The structure of its molecule was established and the vitamin synthesized by R. R. Williams in 1936.

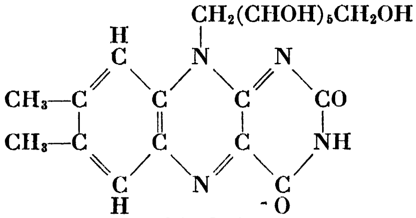


thiamin hydrochloride

The vitamin is now being manufactured, and its price has dropped from $300 per gram for the natural vitamin in 1937 to 53 cents in 1942. At this low price, its use in enriching flour is widespread. At least 66 mg./lb. of flour are required. About 30 tons are made annually. Whole cereals, milk, egg yolk, tomatoes, figs, and grapes are important natural sources.

The international unit of this vitamin is that of 3 micrograms (3×10^{-6} g.) of pure thiamin. The daily adult requirement is 250 to 625 units.

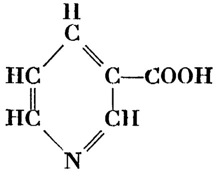
Vitamin B_2, or *riboflavin*, forms part of the molecule of an enzyme that plays an essential role in the oxidation reactions associated with cell respiration. It stimulates the growth of young animals and tends to prevent cracked lips, dermatitis, and baldness. Its structure was established by Kuhn who was also able to synthesize the vitamin in 1935.



Riboflavin

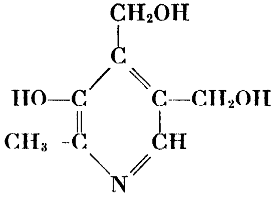
Its commercial production has been somewhat delayed because of the war. In normal times, 1.2 mg. of the vitamin will be required in a pound of enriched flour. It occurs in milk, egg white, yeast, green vegetables, kidney, liver, and other meats.

Niacin, or nicotinic acid,



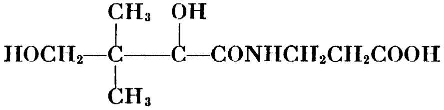
is the antipellagra vitamin. It also prevents a similar disease called blacktongue in dogs. As in the case of other vitamins, nicotinic acid is found in respiratory coenzymes. It is probable that it plays a role in keeping tissue metabolism normal. Niacin is available commercially and is added to enriched flour.

Pyridoxine, or vitamin B_6, was isolated from rice bran by Keresztesy and Stevens in 1938. It has the following structure:



This vitamin prevents a type of pellagra in rats and may be helpful in treating certain cases of muscular rigidity. It also is available commercially.

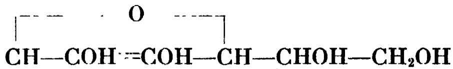
In 1940, the structure and synthesis of *pantothenic acid*



$$\mathrm{HOCH_2{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}\overset{\overset{OH}{|}}{C}{-}CONHCH_2CH_2COOH}$$

was reported by Williams and Major and by Stiller, Harris, Finkelstein, Keresztesy, and Folkers, all of the Merck research laboratories. Liver is a rich source of this vitamin. It prevents dermatitis in chicks. It is just possible that this vitamin may prevent and even cure gray hair in humans as it has in the cases of several fortunate rats.

17. Vitamin C, or ascorbic acid, prevents scurvy.

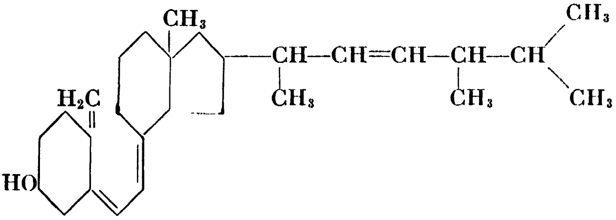


$$\mathrm{\overbrace{CH{-}COH{=}COH{-}CH}^{O}{-}CHOH{-}CH_2OH}$$

ascorbic acid

The vitamin also plays an important role in keeping teeth and gums healthy and in the healing of wounds. Since cooking destroys this vitamin, outbreaks of scurvy among sailors were the rule when cooked food alone was eaten. Fresh fruit in the diet effectively prevents this disease. It is found in citrus fruits, raw vegetables, and tomatoes. In 1937, synthetic ascorbic acid became available in the United States.

18. Vitamin D, the antirachitic vitamin, prevents rickets by regulating the bone-forming processes of the body. It is known to be a mixture of at least two vitamins D_2, or calciferol, and D_3, or dehydrocholesterol.



calciferol

Ergosterol, a compound of similar structure, is converted by ultraviolet light into calciferol. The role of sunlight in preventing rickets is at least partially explained by this conversion. It is abundant in eggs and dairy products and in halibut- and cod-liver oils from which latter it may be concentrated by vacuum distillation.

19. Vitamin E, or α-tocopherol, essential for successful reproduction in rats, is plentiful in the wheat germ. Its structure is known, and it has been synthesized.

20. Vitamin K_1 aids in the clotting of blood and in the prevention of hemorrhages. Its structure and synthesis were reported by Fieser in 1939. It is abundant in green leaves. The vitamin has been used successfully in surgery in preventing serious hemorrhage which is likely to occur in patients suffering from jaundice.

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APPENDIX

I. UNITS

The metric system is a decimal system in which the names of larger and smaller units of length and weight are derived from those of the standard units by the use of the following prefixes:

deci = $\frac{1}{10}$ ×
centi = $\frac{1}{100}$ ×
milli = $\frac{1}{1000}$ ×
micro = 1/1,000,000 ×
deka = 10 ×
hecto = 100 ×
kilo = 1000 ×
mega = 1,000,000 ×

The unit of length is the meter.

1 meter (m.) = 39.37 inches
1 m. = 10 decimeters (dm.) =
100 centimeters (cm.) = 1,000 millimeters (mm.)
1,000 m. = 1 kilometer (km.) = 0.6214 mile
1 angstrom unit (Å.) = 10^{-7} mm. = 10^{-8} cm. = 10^{-10} m.
1 micron (μ) = 10^{-3} mm. = 10^{-4} cm. = 10^{-6} m.
1 millimicron ($\mu\mu$) = 10^{-6} mm. = 10^{-7} cm. = 10^{-9} m.

Volume.

1 liter (l.) = 1.057 quarts
1 l. = 1,000 milliliters (ml.)
1 l. = 1,000.027 cubic centimeters (cc.)
1 ml. = 1.000027 cc.

Weight.

1 gram (g.) = mass of 1 cc. water at 4°C.
1 kilogram (kg.) = 1,000 g. = 2.205 lb.
1,000 kg. = 1 metric ton = 2,205 lb.

Electricity.

Electrostatic unit, e.s.u., is defined as that quantity of electricity which, when placed at a distance of one centimeter from a charge of equal quantity and like sign, will repel it with a force of one dyne. This quantity is exceedingly small.

Electronic charge e, the quantity of charge on an electron.

Coulomb, the quantity of electricity required to deposit 0.0011180 g. of silver on the cathode by electrolysis of a silver salt solution.

Faraday, the quantity of electricity required to deposit 1 gram-equivalent weight of an element by electrolysis.

$$\begin{aligned} e &= 4.8025 \times 10^{-10} \text{ e.s.u.} \\ 1 \text{ coulomb} &= 6.281 \times 10^{18}\, e \\ 1 \text{ faraday} &= 96{,}500 \text{ coulombs} \end{aligned}$$

Ampere, a current of 1 coulomb/sec.

Ohm, the resistance to a current of electricity offered by 14.4521 g. of mercury in a column 106.300 cm. long at 0°C.

Volt, the potential difference required to maintain a current of 1 amp. through a resistance of 1 ohm.

II. VARIATIONS

The mathematical expression

$$x \propto y$$

means that x varies as y. It signifies that if the value of x is doubled, that of y is doubled also or, in general, if the value of x is multiplied or divided by any factor, that of y is multiplied or divided by the same factor. For example, if x is a certain number of apples and y, their cost, the cost will vary with the number. Thus if 5 apples cost 10 cents, 10 apples will cost 20 cents, or 1 apple, 2 cents.

It is obvious that the cost is *not equal* to the number. However, the introduction of a constant into a variation converts the latter into an equation. Thus, if

$$\begin{aligned} x &\propto y \\ x &= ky \end{aligned}$$

The value of the constant may be determined, if a corresponding set of values of x and y are known. In the above example, 5 apples cost 10 cents. Thus

$$\begin{aligned} 5 \text{ apples} &= k \times 10 \text{ cents} \\ k &= \frac{5 \text{ apples}}{10 \text{ cents}} = \frac{1 \text{ apple}}{2 \text{ cents}} \end{aligned}$$

or 1 apple per 2 cents.

If the value of x depends upon two variables y and z and if y and z may be varied independently, then if z is kept constant x will vary as y.

$$(x)_z \propto y$$

On the other hand, if y is constant, x will vary as z.

$$(x)_y \propto z$$

The letter, placed below and to the right of the parenthesis enclosing x, indicates the variable that must be kept constant if the variation is true.

An example will help you to understand the last paragraph. The area of a triangle a depends upon its base b and its altitude h. If the length of the base is kept constant, the area will vary directly as the altitude.

$$(a)_b \propto h$$

On the other hand, the areas of triangles with the same altitude will vary as their bases.

$$(a)_h \propto b$$

If both the base and the altitude are varied, the area will be proportional to the product of the base and the altitude.

$$a \propto bh$$

or

$$a = kbh$$

The value of k may be determined if the area corresponding to a given base and altitude is known. Thus the area of a triangle, whose base is 10 cm. and whose altitude is 5 cm., is 25 sq. cm.

$$25 \text{ sq. cm.} = k \times 10 \text{ cm.} \times 5 \text{ cm.}$$

$$k = \frac{25 \text{ sq. cm.}}{50 \text{ sq. cm.}} = \frac{1}{2}$$

In other words, the area of a triangle is one-half the product of its base and its altitude.

In general, if

$$(x)_z \propto y$$

and

$$(x)_y \propto z$$

then

$$x \propto y \times z$$

and

$$x = kyz$$

The expression

$$x \propto \frac{1}{y}$$

means that x varies inversely as y. Thus, if the value of y is tripled, that of x is one-third as great. In this case

$$x = \frac{k}{y}$$

A variation may be readily changed to a proportion. If

$$s \propto t$$

then

$$s = kt$$

If s_1 and t_1, and s_2 and t_2 are corresponding values of these variables, then

$$s_1 = kt_1$$

and

$$s_2 = kt_2$$

Dividing,

$$\frac{s_1}{s_2} = \frac{t_1}{t_2}$$

Thus corresponding values are in the numerators and in the denominators of each fraction.

An inverse variation leads to a different result.

$$V \propto \frac{1}{P}$$

$$V = \frac{k}{P}$$

$$V_1 = \frac{k}{P_1}$$

$$V_2 = \frac{k}{P_2}$$

$$\frac{V_1}{V_2} = \frac{P_2}{P_1}$$

III. LARGE AND SMALL NUMBERS

Very large numbers and very small fractions are most conveniently expressed by multiplying the significant figures in the number by 10 raised to proper power. The number of molecules in a mole of a substance is 602,000,000,000,000,000,000,000. When written out it is impressive but rather a waste of printer's ink. A decimal point is placed after the first of the three significant numbers (6.02) and these are multiplied by 10 to the twenty-third power.

$$6.02 \times 10^{23}$$

The charge on an electron is 0.000000000480 e.s.u. By using a negative power of 10, this small fraction may be expressed as

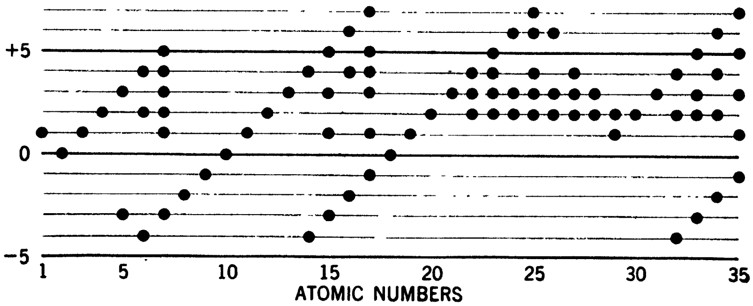
$$4.80 \times 10^{-10} \text{ e.s.u.}$$

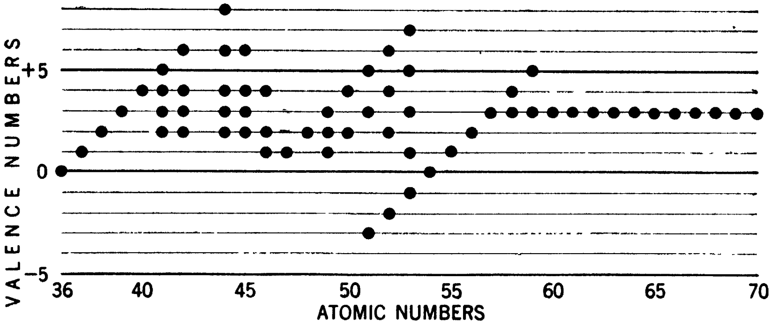
The exponent tells the number of times that 10 must be multiplied by itself. Thus 10^6 is equal to a million. Ten raised to a negative power is equal to the reciprocal of 10 to the same positive power. Thus

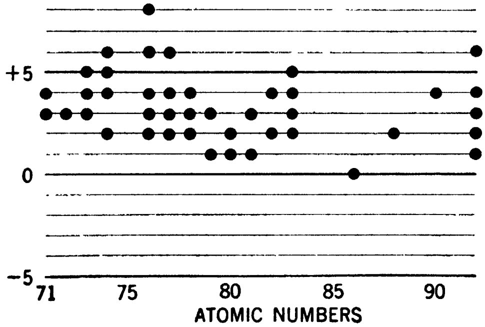
$$10^{-6} = \frac{1}{10^6} = \frac{1}{1{,}000{,}000} = 0.000001$$

The custom of placing the decimal point after the first significant figure makes the process of finding the logarithm of such numbers easier. The power of 10 gives the characteristic directly. Thus the logarithm of 6.02×10^{23} is 23.7796 and that of 4.80×10^{-10}, $\overline{10}.6812$.

IV. VALENCE NUMBERS OF THE ELEMENTS







V. THE COMMON IONS

Cations	Anions
	Charge of One
Li^+, lithium	F^-, fluoride
Na^+, sodium	Cl^-, chloride
K^+, potassium	Br^-, bromide
Rb^+, rubidium	I^-, iodide
Cs^+, cesium	NO_2^-, nitrite
Cu^+, cuprous	NO_3^-, nitrate
Ag^+, silver	ClO^-, hypochlorite
$Hg^+(Hg_2^{++})$, mercurous	ClO_2^-, chlorite
H_3O^+, hydronium	ClO_3^-, chlorate
NH_4^+, ammonium	ClO_4^-, perchlorate
	$C_2H_3O_2^-$, acetate
	CN^-, cyanide
	Charge of Two
Be^{++}, beryllium	$S^=$, sulfide
Mg^{++}, magnesium	$SO_3^=$, sulfite
Ca^{++}, calcium	$SO_4^=$, sulfate
Sr^{++}, strontium	$CO_3^=$, carbonate
Ba^{++}, barium	$SiO_3^=$, silicate
Zn^{++}, zinc	$CrO_4^=$, chromate
Cd^{++}, cadmium	$Cr_2O_7^=$, dichromate
Hg^{++}, mercuric	
Cu^{++}, cupric	
Fe^{++}, ferrous	
Co^{++}, cobaltous	
Ni^{++}, nickel	
Sn^{++}, stannous	
Pb^{++}, lead	
Mn^{++}, manganous	
	Charge of Three
Al^{+++}, aluminum	$PO_3^{\equiv}$, phosphite
Fe^{+++}, ferric	$PO_4^{\equiv}$, phosphate
Cr^{+++}, chromic	$AsO_3^{\equiv}$, arsenite
Sb^{+++}, antimony	$AsO_4^{\equiv}$, arsenate
Bi^{+++}, bismuth	$Fe(CN)_6^{\equiv}$, ferricyanide
	Charge of Four
	$Fe(CN)_6^{==}$, ferrocyanide

VI. VAPOR PRESSURE OF WATER

t, °C.	*p*, mm.	*t*, °C.	*p*, mm.	*t*, °C.	*p*, mm.	*t*, °C.	*p*, mm.
0	4.58	16	13.63	40	55.32	96	657.6
1	4.93	17	14.53	45	71.88	97	682.1
2	5.29	18	15.48	50	92.51	98	707.3
3	5.69	19	16.48	55	118.0	99	733.2
4	6.10	20	17.54	60	149.4	100	760.0
5	6.54	21	18.65	65	187.5	102	815.9
6	7.01	22	19.83	70	233.7	104	875.1
7	7.51	23	21.07	75	289.1	106	937.9
8	8.05	24	22.38	80	355.1	108	1004.4
9	8.61	25	23.76	85	433.6	110	1074.6
10	9.21	26	25.21	90	525.8	112	1148.7
11	9.84	27	26.74	91	546.1	114	1227.2
12	10.52	28	28.35	92	567.0	116	1309.9
13	11.23	29	30.04	93	588.6	118	1397.2
14	11.99	30	31.82	94	610.9	374	1.65×10^6
15	12.79	35	42.18	95	633.9		

VII. SOLUBILITIES OF SALTS

Solubilities are in grams of anhydrous salt per 100 g. of water at 20°C. (upper figure) and 100°C. (lower figure). Where quantitative data are lacking, *s*, soluble; *i*, insoluble; *h*, extensively hydrolyzed; *u*, unstable.

Salt	Acetate	Bromide	Carbonate	Chloride	Chromate	Hydroxide	Iodide	Nitrate	Phosphate	Sulfate	Sulfide
Aluminum	*s* *h*	*s*	*h*	70		*i* *i*	*s* *s*	*s* *s*	*i* *i*	36.4 89.0	*h* *h*
Ammonium	*s* *h*	75.5 145.6	*h*	37.3 77.3	36		*s* 250	*s* *s*		*s* 103.3	*s* *h*
Barium	71 75	104 149	0.0022 0.0065	35.7 58.8	0.00037 0.00046	3.89 > 100	203.1 396	9.2 34.2	*i*	0.00024	*h* *h*
Calcium	34.7 29.7	143 *s*	0.001 0.002	74.5 159	*s*	0.165 0.077	208.8 426.3	129.3 *s*	0.0025	0.21 0.16	*h* *h*
Cupric	*s* *s*	*s* *u*		77.0 107.9		*i* *u*	1.107 *u*	125.1 *s*	*i*	20.7 75.4	3.3×10^{-5} *i*
Ferric	*h*	*s* *s*	*h*	91.8 535.7		*i* *i*		*s* *s*	*i* 0.67	*i* *h*	*h*
Ferrous	*s* *s*	115.1 177.8	0.0065 *i*	69 105.8		0.0007 *i*	*s*	84.5		26.5	0.00062
Lead	55 *s*	0.85 4.75	0.00011 *u*	0.99 3.34	7×10^{-6} *i*	0.016 *i*	0.068 0.436	56.5 38.8	10^{-5} *i*	0.0041 *i*	8.6×10^{-5} *i*

Magnesium	*s* *s*	96.5 120.2	0.01 *i*	54.5 73.0	212 *s*	0.0009	139.8 *s*	*s* *s*	*i*	35.5 74.0	*h*
Manganous	*s* *s*	146.9 228.0	0.0065	73.9 115.3		0.002 *i*	*s* *s*	142.7	*s* *s*	62.9 34.0	0.00062
Mercuric	30 100	0.5 25		6.5 61.3		*i*	0.006 *i*	*s* *u*	*i*		10^{-6}
Mercurous	0.75 *u*	*i* *i*	*i* *u*	0.0002 *i*	*i*	*u*	2×10^{-8}	*s* *u*	*i*	0.06 0.09	*i*
Nickel	16.6 *s*	130.9 155.1	0.009 *i*	64.2 87.6		*i* *i*	148.1 189	*s* *s*	*i* *i*	40 76.7	0.0004
Potassium	255.6 410	65.2 104.0	110.5 155.7	34.0 56.7	61.7 75.6	112 178	144 208	31.6 246	*s* *s*	11.1 24.1	
Silver	1.04 *s*	8.4×10^{-6} 3.7×10^{-4}	0.0032 0.05	1.5×10^{-4} 0.002	*i* 0.011	*u*	3×10^{-7} *i*	222 952	0.0007 *i*	0.796 1.41	1.4×10^{-5} *i*
Sodium	46.5 170	90.5 121.2	21.5 45.5	36.0 39.8	88.7 125.9	109 347	178.7 302	88 180	11 108	19.4 42.5	18.8 *h*
Stannous		*s* *h*		270		*i* *u*	1.3 4.0			1.0 4.0	$2 \times 10^{-}$ *i*
Zinc	39 66.6	446.4 672.2	0.001 *i*	430 615	*i*	0.0004 *i*	484.8 510.5	117.7 *s*	*i* *i*	54.4 80.8	

VIII. SOLUBILITY PRODUCTS

Substance	Solubility product	Substance	Solubility product
$Al(OH)_3$	10^{-33}	CoS	10^{-26}
$Cu(OH)_2$	10^{-19}	CuS	10^{-44}
$Fe(OH)_2$	10^{-14}	PbS	10^{-29}
$Fe(OH)_3$	10^{-37}	MnS	10^{-15}
$Pb(OH)_2$	10^{-16}	HgS	$\sim 10^{-50}$
$Mg(OH)_2$	10^{-11}	NiS	10^{-23}
$Mn(OH)_2$	10^{-14}	Ag_2S	$\sim 10^{-50}$
$Ni(OH)_2$	10^{-14}	SnS	10^{-28}
$Zn(OH)_2$	10^{-17}	ZnS	1.2×10^{-23}
AgCl	1.6×10^{-10}	$BaCO_3$	8×10^{-9}
$PbCl_2$	1.8×10^{-4}	$CaCO_3$	5×10^{-9}
$HgCl(Hg_2Cl_2)$	3×10^{-18}	$MgCO_3$	2.6×10^{-5}
AgBr	5×10^{-13}	$SrCO_3$	1.6×10^{-9}
AgI	1.5×10^{-16}	$BaCrO_4$	2×10^{-10}
CdS	10^{-29}	$CaCrO_4$	2×10^{-2}
Bi_2S_3	10^{-70}	$SrCrO_4$	4×10^{-5}

IX. ACIDS AND THEIR CONJUGATE BASES

Acid	Conjugate base	Ionization constant		*pK*	
		Exact	Approximate	Exact	Approximate
HCl	Cl^-	....	10^7	......	-7
HNO_3	NO_3^-	....	Large	......	Small
H_2SO_4	HSO_4^-	....	Large	......	Small
H_3O^+	H_2O	55.5	10^2	-1.74	-2
HSO_4^-	$SO_4^=$	2×10^{-2}	10^{-2}	$+1.70$	$+2$
H_2SO_3	HSO_3^-	1.7×10^{-2}	10^{-2}	1.77	2
H_3PO_4	$H_2PO_4^-$	7×10^{-3}	10^{-2}	2.16	2
$HC_2H_3O_2$	$C_2H_3O_2^-$	1.8×10^{-5}	10^{-5}	4.74	5
HSO_3^-	$SO_3^=$	5.0×10^{-6}	10^{-5}	5.30	5
H_2CO_3	HCO_3^-	3.1×10^{-7}	10^{-7}	6.51	7
H_2S	HS^-	7.9×10^{-8}	10^{-7}	7.10	7
$H_2PO_4^-$	$HPO_4^=$	7.5×10^{-8}	10^{-7}	7.13	7
HClO	ClO^-	....	10^{-8}	......	8
HCN	CN^-	7×10^{-10}	10^{-9}	9.14	9
H_3BO_3	$H_2BO_3^-$	6.5×10^{-10}	10^{-9}	9.19	9
NH_4^+	NH_3	5.5×10^{-10}	10^{-9}	9.26	9
HCO_3^-	$CO_3^=$	4.5×10^{-11}	10^{-10}	10.35	10
$HPO_4^=$	$PO_4^{\equiv}$	5×10^{-13}	10^{-12}	12.30	12
HS^-	$S^=$	2×10^{-15}	10^{-15}	14.70	15
HOH	OH^-	1.78×10^{-16}	10^{-16}	15.75	16
OH^-	$O^=$	....	10^{-24}	......	24

X. THE RELATIVE STRENGTH OF OXIDIZING AND REDUCING AGENTS

	Reducing Agents		Oxidizing Agents
Strong	K		K^+
	Na		Na^+
	Mg	Weak	Mg^{++}
	Al		Al^{+++}
	Zn		Zn^{++}
	Fe		Fe^{++}
	Sn		Sn^{++}
	Pb		Pb^{++}
	H_2		H^+
	H_2S		S
	Cu		Cu^{++}
	I^-		I_2
	Fe^{++}		Fe^{+++}
	Ag		Ag^+
	Br^-		Br_2
	SO_2		H_2SO_4 (conc.)
	Cl^-		Cl_2
Weak	NO		HNO_3
	Cr^{+++}		$Cr_2O_7^{=}$
	Mn^{++}	Strong	MnO_4^-

XI. ABBREVIATIONS OF PERIODICALS

Chemical and Engineering News	*Chem. Eng. News*
Chemical & Metallurgical Engineering	*Chem. & Met. Eng.*
Chemical News and Journal of Industrial Science, The	*Chem. News*
Industrial and Engineering Chemistry	*Ind. Eng. Chem.*
Journal of the American Chemical Society	*J. Am. Chem. Soc.*
Journal of Applied Physics	*J. Applied Phys.*
Journal of Chemical Education	*J. Chem. Education*
Metals & Alloys	*Metals & Alloys*

XII. TABLE OF LOGARITHMS

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
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	5345	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

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
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
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	2	3	3	4

INDEX

THE PERIODIC TABLE

ATOMIC NUMBERS
IN RED

PERIODS	GROUPS										
	I	II	3		4	5	6	7	8		
	VALENCES										
	+1	+2	+3		Variable						
1	1 H 1.0080										
2	3 Li 6.940	4 Be 9.02									
3	11 Na 22.997	12 Mg 24.32									
4	19 K 39.096	20 Ca 40.08	21 Sc 45.10		22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69
5	37 Rb 85.48	38 Sr 87.63	39 Y 88.92		40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43 Ma	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
6	55 Cs 132.91	56 Ba 137.36	57 La 138.92	58 to 71 RARE EARTHS	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23
7	87	88 Ra 226.05	89 Ac		90 Th 232.12	91 Pa 231	92 U 238.07				

RARE

58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il