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Actinium	Ac	89	227
Aluminum	Al	13	26.98
Americium	Am	95	243
Antimony	Sb	51	121.76
Argon	Ar	18	39.944
Arsenic	As	33	74.91
Astatine	At	85	210
Barium	Ba	56	137.36
Berkelium	Bk	97	249
Beryllium	Be	4	9.013
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Californium	Cf	98	249
Carbon	C	6	12.011
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Copper	Cu	29	63.54
Curium	Cm	96	245
Dysprosium	Dy	66	162.51
Einsteinium	E	99	253

ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Erbium	Er	68	167.27
Europium	Eu	63	152.0
Fermium	Fm	100	254
Fluorine	F	9	19.00
Francium	Fr	87	223.0
Gadolinium	Gd	64	157.26
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.0
Hafnium	Hf	72	178.50
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.008(
Indium	In	49	114.82
Iodine	I	53	126.91
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutetium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.94
Mendelevium	Mv	101	256
Mercury	Hg	80	200.61

ATOMIC WEIGHTS, 1959

ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Neptunium	Np	93	237
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.008
Nobelium	No	102	253
Osmium	Os	76	190.2
Oxygen	O	8	16.0000
Palladium	Pd	46	106.4
Phosphorus	P	15	30.975
Platinum	Pt	78	195.09
Plutonium	Pu	94	242
Polonium	Po	84	210
Potassium	K	19	39.100
Praseodymium	Pr	59	140.92
Promethium	Pm	61	145
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.22
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.1

ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.880
Sodium	Na	11	22.991
Strontium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.95
Technetium	Tc	43	99
Tellurium	Te	52	127.61
Terbium	Tb	65	158.93
Thallium	Tl	81	204.39
Thorium	Th	90	232.05
Thulium	Tm	69	168.94
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.86
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

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the Fundamentals of

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Third Edition

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PREFACE

In revising a textbook, a primary objective is to enhance its usefulness by improving the clarity and accuracy of presentation. In preparing the third edition of *Fundamentals of College Chemistry*, the authors have been guided by suggestions from many teachers who have been using the book in their classes. Although the reader will find many changes, the basic framework and organizational structure of the previous editions have been retained. This edition, like the others, aims to present the fundamentals of chemistry in a concise and orderly manner which can be covered in the nine-months academic year.

A few chapters have been completely rewritten; others have been modified in accordance with newer developments or interpretations. The concept of oxidation numbers is developed and used more extensively than formerly, and oxidation and reduction are described in terms of these oxidation numbers. The section on nuclear changes has been considerably revised and expanded to keep pace with the ever-increasing developments in that area.

As an aid to the instructor, some sections of an advanced or historical nature have been set in small type; if the instructor wishes to omit these, he may do so without loss of continuity. The attempt is made to strike an effective balance between theory and descriptive matter. Use is made of examples from daily life contacts or from industrial situations when these add to the chemical knowledge of a substance or to the understanding of a chemical theory.

The authors wish to acknowledge the aid of their colleagues at Oregon State College and the State College of Washington in making many helpful suggestions. We are especially indebted also to Drs. A. S. Ihde of the University of Wisconsin; F. E. Crane of Douglass College; H. H. Rowley of the University of Oklahoma; and O. F. Steinbach of Queens College for their suggestions and critical reviews of the manuscript.

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SCIENCE IS A TREE OF MANY BRANCHES, BOUNTIFUL ARE ITS FRUITS TO MAN IN MORE COMPLETE HEALTHFUL LIVING

one INTRODUCTION

Man is constantly searching for a clearer understanding of the world in which he lives. Through the ages, many facts about nature have been observed and much knowledge has been accumulated. The beginning chemistry student has access to much more knowledge concerning the nature of things than did Aristotle, Socrates, or Pliny; nearly two thousand years of accumulated facts, and the records of man's constructive thinking pertaining to these facts, are available to him. Science is concerned with man's need to understand, but the mere accumulation of facts is not science. Science is systematized knowledge—facts must be classified and analyzed in such a way that general laws or conclusions may be drawn.

There are many subdivisions of science. Physics, chemistry, geology, and astronomy, which have to do with inanimate things, are called *physical* sciences. The *biological* sciences—such as zoology, botany, bacteriology—are concerned with living organisms. The study of man as an individual and in his group relationships and activities is the work of the *social* sciences, including psychology, anthropology, sociology, and economics.

The scientific method Myth and folklore preceded science in explaining nature and natural processes. Unlike myth and folklore, science is knowledge based on critical observation and experimental tests. The value of experimentation cannot be overemphasized. Aristotle, without benefit of experiments, had said that bodies fall with a speed proportional to their weight. The word of the great Greek was respected, and when he said an object weighing ten pounds will fall ten times as fast as one weighing only one pound, no further proof was deemed necessary. This idea was accepted generally until late in the sixteenth century,

when it was proved false by Galileo, a young lecturer at the University of Pisa. Galileo dropped bronze balls of different sizes from different levels of balconies in the Leaning Tower of Pisa. The assembled crowds could see clearly that two balls of very different weight, dropped simultaneously from the same height in the tower, fell at the same speed and reached the ground at the same instant

Each branch of science now progresses by a pattern of procedure known as the *scientific method.* First, factual knowledge is attained on a given project by reading recorded information on the subject, by observation, and by experimentation which increases normal observational limits. The attainment of data is limited by man's perceptive senses, which he, through ingenuity, expands by his use of instruments and apparatus The laboratory was a tremendous step forward in natural science research, since it permits the manipulation of small quantities of matter under safe and well-controlled conditions. After facts have been obtained, they must be organized and classified Studying these facts to discover relationships between them is the second step. A precise statement which describes a mode of behavior or a pattern of action concerning a group of related facts is a *scientific law*

After facts, and laws concerning the facts, have been made a part of knowledge, a third logical step is to use imagination or speculation regarding particular phenomena and their behavior The why, how, or what pertaining to a group of related facts about things or occurrences may point toward a reasoned generalization called a *hypothesis* In other words, a hypothesis may be a provisional conjecture or an attempt at an explanation for certain laws of nature. The hypothesis then is tested by experimentation, and more facts are obtained, which lead to a verification of the hypothesis or to its modification and correction. A *theory* is a verified hypothesis. A theory is not a permanent conclusion, however, but is changed and modified as experimental results are obtained which are not readily explained by the theory. Theories are useful in that they allow the scientist to anticipate the results of further experiments and aid in the discovery of new phenomena. As Shenstone has said, theories are "searchlights which cast light into dark places and enable us to see, sometimes plainly, sometimes only in dim outline, much that would remain hidden if we were denied their aid."

What is chemistry? Chemistry is concerned with the *properties* of matter, *changes* in matter, and the *laws* or *principles* which govern these changes.

Every substance has properties or characteristics of its own. For example, cane sugar is a white crystalline solid with a sweet taste; iron

is a gray solid which has a certain density and which may be magnetized. Substances may be classified on the basis of their properties.

All of us daily observe many transformations or changes in matter taking place about us: water may be frozen to ice or converted into steam; coal is burned, leaving ashes; wood rots; tools and articles made of metal rust and corrode; plants utilize carbon dioxide, air, water, and soil minerals to build up plant tissue. The chemist is interested in these processes and in thousands more; and he is concerned with the principles which govern the behavior of substances.

Man lives longer and in greater comfort today than he did a few generations ago because he knows more about changes in natural substances and has learned how to utilize these changes in producing thousands of modern-day conveniences and health aids. For example, coal, through chemical processes, may be converted into coke, coal gas, coal tar, and condensible liquids each having commercial value. Ammonia and fuel gas may be obtained from coal gas; coal tar may be converted into antiseptics, therapeutics, dyes, plastics, explosives, and numerous other useful things.

Early history of chemistry Man has always had a lively curiosity concerning natural phenomena. Through the ages he has puzzled over why an apple falls down instead of up, and why sunlight is needed for green plant growth; he has wondered why the moon turns dark at times of eclipse, why certain elements emit tiny bits of energy, and why people act the way they do. From time to time, he has invented hypotheses or theories to explain these natural phenomena.

Thinking men of ancient Greece gave us some of our first chemical hypotheses. Several of these philosophers, among them Empedocles, claimed that the world and all that is in it is composed of the "four elements"—earth, air, fire, and water. Robert Boyle in his book, *The Skeptical Chemist*, published in 1661, suggests how they may have reasoned:

> For if you but consider a piece of green wood burning in a chimney, you will readily discern in the disbanded parts of it the four elements, of which we teach it and other mixt bodies to be composed. The fire discovers itself in the flame by its own light, the smoke by ascending to the top of the chimney, and there readily vanishes into air, like a river losing itself in the sea, sufficiently manifests to what element it belongs and gladly returns. The water in its own form boiling and hissing at the ends of the burning wood betrays itself to more than one of our senses; and the ashes by their weight, their firmness, and their dryness, put it past doubt they belong to the element of earth.

About 400 B.C. Leucippus and Democritus conceived the idea that all matter is made up of minute, discrete particles called *atoms*. Observation and experimentation since have shown them to be correct in their

thinking. This atomic theory is still accepted, if we add the modern theory that the atoms themselves are composed of smaller units—that is, protons, electrons, and neutrons.

The Greek thinkers had the genius to develop hypotheses, but they did not have the equipment or the technical skill to verify them. Imagine, if you will, how difficult it was to make a precise measurement of time, when the most accurate timing device was a sundial. The Greeks could rely to some extent upon observation, but when their limited means of observation failed, they filled unknown gaps with speculations.

In Egypt, chemistry had taken a more practical turn. The Egyptians had attained real skill in the working of gold, silver, copper, iron, lead, tin, and mercury. They knew something of the manufacture of glass, soap, turpentine, sugar, blue vitriol, alum, natural dyes, and pigments. When the Arabs swept into Egypt in the seventh century A.D., they took over the practical skills of the Egyptians and the theories of the Greeks. Adding skills and ideas of their own, they made many advances in science, particularly in mathematics and astronomy. They developed Arabic numerals (1, 2, 3, 4, and so on) and the science of algebra.

The age of alchemy The speculation of the Greek philosopher, Aristotle, that metals could be converted into one another fascinated the alchemists. If this theory proved correct, they reasoned, tin or lead or any base metal could be converted into gold. The wealth-making possibilities of such a transmutation of metals absorbed the energetic interest of alchemists for many centuries. In the courts of many kings, the "gold cooks" (alchemists) held an important place. One emperor built a half-dozen small houses with huge stone fireplaces close to his own palace for alchemical experimentation. King Henry VI of England recommended the study of alchemy to all noblemen, theologians, and scholars. Though some of the alchemists were earnest men with scientific interests, others turned alchemy into one of the greatest frauds in history. Their public demonstrations of would-be transmutations were often clever enough to fool the most cautious.

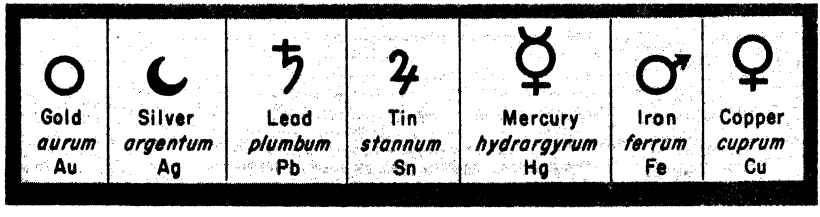


Figure 1–1 Symbols of the seven common metals known to the ancients.

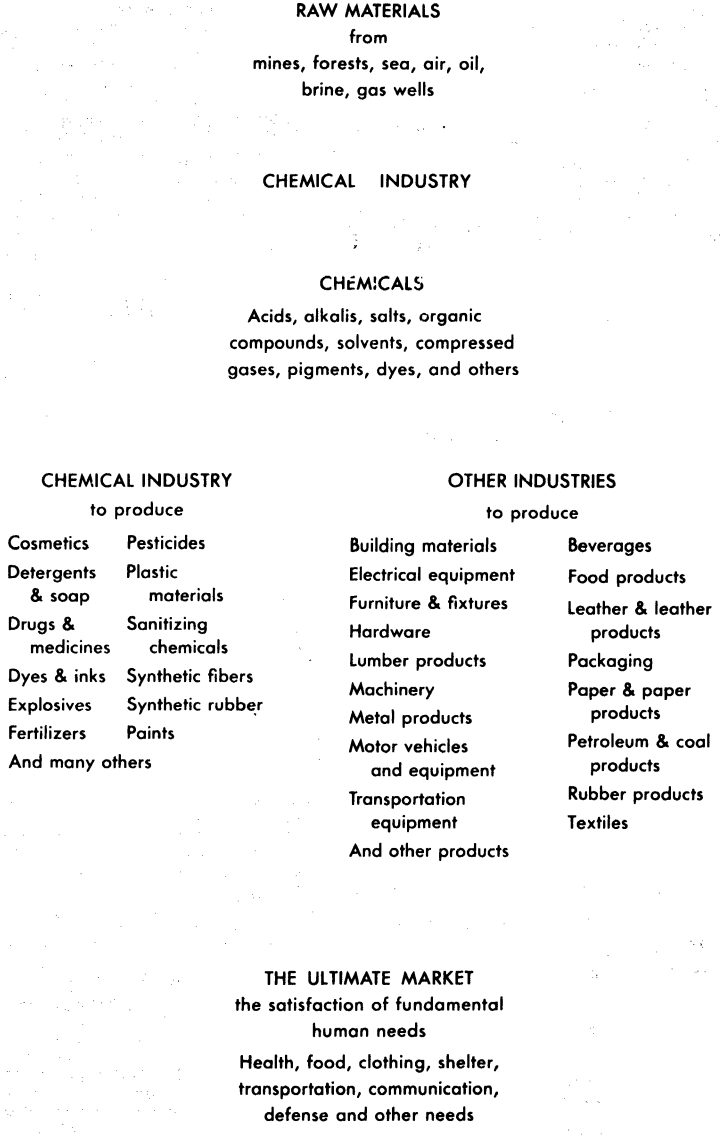


Figure 1–2 Key position of the chemical industry today. In more than 11,000 plants operated by hundreds of chemical manufacturers, raw materials are converted into more than 8,000 compounds.

In their enthusiastic and elaborate attempts to find the secret of changing lead and other metals into gold, the alchemists discovered many new chemical substances and recorded some information about them. They developed new chemical techniques and methods, and designed new and useful equipment. Incidentally, transmutation, the dream of the alchemists, has been attained in recent years. A new subject, nuclear chemistry, considers the transmutation of one kind of atom to another (see Chapter 31).

The alchemists pursued two other particularly enticing goals. (1) They tried to find a "universal solvent" which would dissolve any material—though they apparently overlooked the fact that if such a solvent were found, there would be no container in which it might be kept. (2) They hoped to concoct an "elixir of life" which, when drunk, would restore youth, or at least generally lessen the ills of the human body. We now know of the complexity of the human body, and that no simple drink can be a cure-all or can restore youth.

As man sought medicines or concoctions to cure his ills, he learned and recorded many facts which can be considered as part of chemical knowledge. Some early investigators who tried to apply chemicals to cure disease were called *iatrochemists.*

The early mineralogists in their study of earth rocks, and the metallurgists in their work with the extraction and winning of metals from ores, also contributed to the growing science of chemistry.

Importance of chemistry Aside from its cultural value as a part of a general education, the application of chemical principles has done much to give man control over nature, to alleviate human suffering, and to enhance the comforts of modern living. Chemical industrial processes convert raw materials furnished by nature into products more usable to man (see Figure 1–2).

Today, man has access to two thousand years of observationally and experimentally attained facts, and to the record of man's constructive thinking concerning the processes of nature which these facts reveal. This text will limit itself to the presentation of fundamental knowledge and thinking that has come to be known as the Science of Chemistry.

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In general, for references on various topics, consult the index of Chemical Abstracts or the yearly index of such magazines as Journal of Chemical Education, Industrial and Engineering Journal, Chemical Engineering.

two FUNDAMENTAL PRINCIPLES

Matter and energy *Chemistry is concerned with matter and the changes which it undergoes.* *Matter* may be defined as anything which possesses *weight* or *mass*[1] and occupies space. Rocks, soil, water, and the air we breathe are examples. Any matter which is homogeneous (uniform throughout), such as sugar, table salt, iron, or baking soda, is called a *substance.*

Matter appears in any one of three physical states: *solid, liquid,* or *gas.* Solids are characterized by rigidity and a definite form; liquids flow; gases diffuse and fill any container in which they may be placed. Most substances can be made to appear in all three of these states; for example, water may exist as a solid (ice), a liquid, or a gas (steam). By adding heat, a liquid may be changed to a gas; by subtracting heat, a liquid may be changed to a solid.

Changes in matter are accompanied by changes in energy. *Energy is the ability to do work* and manifests itself in many forms. The more familiar forms of energy are *heat, mechanical, radiant, electrical,* and *chemical.* Though it may pass from one form to another, *energy may be neither created nor destroyed.* This law of nature is known as the Law of Conservation of Energy.

When coal is burned, heat is given up or evolved. This heat, termed heat energy, may be made to do useful work. For example, the heat from the burning coal might be used to generate steam, which in turn could operate a steam engine. The moving parts of a steam engine yield

[1] The *mass* of a body is the quantity of matter it contains. Mass is determined by the body's inertia—that is, the resistance offered to a change in its motion. *Weight,* on the other hand, is the attraction between the earth and the body. Since the attraction between two bodies is inversely proportional to the square of the distance between the centers of the bodies, the masses of two bodies will be proportional to their weights, as long as the weights are measured at the same distance from the earth's center. Consequently, we may compare masses of objects by weighing them. The attraction of the earth for an object is counterbalanced against arbitrarily chosen units of weight. While the mass of an object is constant, its weight varies with its distance from the center of the earth. We shall use the terms "mass" and "weight" interchangeably.

mechanical energy,[2] which may be transformed into electrical energy by means of a dynamo. Electrical energy may be converted into light energy in a light bulb or into heat energy in an electric toaster.

Another form of energy is potential energy, in which matter has position or other factors that can quickly translate mass into motion. Examples are water behind a dam and a coiled spring.

Chemists are more interested in *chemical energy*, which is "stored energy" —the energy possessed by a substance that allows it to be changed into a new substance. Thus when coal is burned, the chemical energy possessed by the coal is transformed into heat energy and light energy. Various forms of energy may also be transformed into chemical energy. This occurs, for example, when plants absorb radiant energy from the sun, a process which induces changes in the plants resulting in the production of plant tissue.

UNITS OF MEASUREMENT

Metric system The metric system of measurement is used in all scientific work. The standard unit of linear measurement is the *meter*, the distance between two marks on a platinum-iridium alloy bar kept in the International Bureau of Weights and Measures in Paris, France. This distance originally was supposed to be one ten-millionth of the distance from the North Pole to the Equator, but this relationship is only approximate. One meter is equivalent to 39.37 inches.

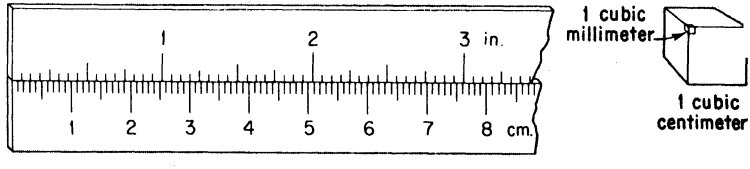


Figure 2–1 Comparison scale of inches and centimeters.

The standard unit of weight is the *gram*, which is one-thousandth of the weight of a piece of alloy metal called the standard *kilogram*.

The standard unit in the measurement of volume is the *liter*, the volume of one kilogram of water at 4° C., the temperature at which

[2] Energy of motion is also called "kinetic energy"; it is a function of both mass (M) and velocity (V) as given by the equation:

$$\text{Kinetic energy} = \tfrac{1}{2}MV^2$$

water has its maximum density.[1] For the measurement of small quantities, the standard units may be divided into smaller units. The commonly used units of the metric system are shown in Table 2–1.

TABLE 2–1 Metric Units

LINEAR

1 millimeter*	(mm)	=	.001 meter (m)
1 centimeter	(cm)	=	.01 m
1 decimeter	(dm)	=	1 m
1 kilometer	(km)	=	1000 m
1 micron	(μ)	=	.001 mm
1 millimicron	(mμ)	=	.000001
1 angstrom	(Å)	=	.0000001 mm

WEIGHT

1 milligram	(mg)	=	.001 gram (g)
1 centigram	(cg)	=	.01 g
1 decigram	(dg)	=	1 g
1 kilogram	(kg)	=	1000 g

VOLUME

1 liter (l) = 1000 milliliters (ml) = 1000.027 cubic centimeters (cc)

* The prefix *milli-* stands for one-thousandth, *centi-*, for one-hundredth, *deci-*, for one-tenth, and *kilo-*, for one thousand

Weights are usually expressed decimally in grams. Thus, 10 grams and 150 milligrams is written as 10.15 g. The relationship between units of measurement in the English and metric systems is shown in Table 2–2. (See also the Appendix.)

TABLE 2–2 English-Metric Equivalents

1 inch	=	2.54 centimeters
1 meter	=	39.37 inches
1 pound	=	453.6 grams
1 liter	=	1.06 quarts
1 kilogram	=	2.2 pounds

Measurement of temperature *Centigrade* and *absolute* scales of temperature, rather than the *Fahrenheit* scale, are employed in scientific work. The student must understand the relationship between these three temperature scales and be able to make conversions from one scale to another. The relationship may be seen in Table 2–3. The horizontal lines *A* and *B* denote the boiling point and the freezing point of water. Note that there are 100 degrees between the freezing and boiling points

[1] It was originally intended that the kilogram weight be the weight of 1000 cubic centimeters of water at 4° C. However, because of errors in measurement, 1000 grams of water actually occupies 1000.027 cc. Thus, one liter = 1000.027 cc.

TABLE 2–3 Comparison of Temperature Scales

		°F.	°C.	°A.
A	Boiling temperature of water	212°	100°	373°
		180°	100°	100°
B	Freezing temperature of water	32°	0°	273°
	Lowest temperature of the universe	−459°	−273°	0

of water on *both* the centigrade and absolute scales of temperature. However, a reading on the absolute scale will always be 273 degrees higher than on the centigrade scale, since 273 on the absolute scale corresponds to 0 on the centigrade scale. To convert centigrade temperature to absolute temperature, we simply add 273 to the centigrade reading; thus

$$^\circ \text{A.} = {}^\circ \text{C.} + 273.$$

The absolute scale of temperature is based on the fact that when a gas is cooled it contracts (decreases in volume) $\frac{1}{273}$ of its volume at 0° C. for every degree the temperature is lowered. Theoretically, then, a gas would possess no volume at a temperature of −273° C. Actually this condition is never realized, since all substances become solids before this temperature is reached. This theoretical temperature is termed absolute zero and is the lowest possible temperature of the universe.

Again referring to Table 2–3, we note that the freezing point of water on the Fahrenheit scale is 32° and the boiling point, 212°. Between the freezing and boiling points there are 212 − 32 = 180 degrees or divisions; on the centigrade scale there are only 100 such divisions. One division on the centigrade scale, then, is equal to $\frac{180}{100} = 1.8$ or $\frac{9}{5}$ divisions on the Fahrenheit scale; conversely, one Fahrenheit degree is equal to $\frac{5}{9}$ of a centigrade degree.

Suppose we have a temperature of 20° C. What temperature does this correspond to on the Fahrenheit scale?

$$20 \text{ divisions C} = \tfrac{9}{5} \times 20 = 36 \text{ divisions F}$$

But these 36 divisions are measured above the freezing point of water, which is 32° F. To get the actual Fahrenheit temperature, then, we must add the 32 to the 36, which gives 68°. Therefore

$$20° \text{ C} = 68° \text{ F}$$

In converting the centigrade temperature to Fahrenheit temperature, we multiplied the centigrade temperature by $\frac{9}{5}$ and then added 32. Expressed mathematically:

$$\text{F} = \tfrac{9}{5}\text{C} + 32$$

To convert Fahrenheit degrees to centigrade degrees, we may solve this expression for C:

$$\text{C} = \tfrac{5}{9}(\text{F} - 32)$$

To obtain the centigrade temperature from Fahrenheit temperature, first subtract 32 from the Fahrenheit temperature, and then multiply the result by $\frac{5}{9}$.

Density The density of a substance is its *mass in relation to its volume*—in other words, mass per unit volume. A piece of iron has a greater density than a piece of wood because the mass of a given volume of iron is greater than the mass of the same volume of wood. Expressed mathematically:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \text{ or } D = \frac{M}{V}$$

In chemical work, the density of a substance is usually expressed in grams per milliliter (g. per ml.).

MATTER AND ITS CHANGES

Changes in matter We can hardly fail to notice the many changes in matter which are continually taking place about us. Nature plays an important role in bringing about many familiar changes. Ice melts to liquid water, which in turn may be converted into water vapor by the application of sufficient heat. Liquid water may be changed into ice, or steam may be condensed to a liquid by a lowering of the temperature. In these processes by which water is changed from one physical state to another, its chemical composition remains the same. Similarly,

no change in chemical composition occurs in the magnetization of iron, melting of lead, or stretching of rubber. Changes which take place without modifying the chemical composition of matter are called *physical changes*.

In contrast to physical changes are processes which take place with a modification of composition. When a piece of iron rusts, a brittle reddish deposit is formed on the surface; the iron is converted into a new substance with a new set of properties. Such changes, which involve alteration of composition, are called *chemical changes*. Decay of animal and vegetable matter, digestion of food, and action of acids on metals are further examples of chemical changes.

Chemical changes are always accompanied by either the liberation or the absorption of heat energy. If heat energy is liberated the change is said to be *exothermic*, if heat energy is absorbed the change is *endothermic*.

The unit of heat energy is the *calorie*, which is defined as the *quantity of heat necessary to raise the temperature of one gram of water one degree centigrade*.[4] A *kilocalorie* (kc.) is 1000 calories and would be the quantity of heat necessary to raise the temperature of one kilogram of water one degree.

Properties of matter Every substance possesses qualities or characteristics by which we are able to identify it. Sugar is a white solid, dissolves in water, and tastes sweet; iron has a metallic luster, may be magnetized, melts at a certain temperature, and rusts with the formation of a reddish deposit. These qualities or characteristics are called *properties*.

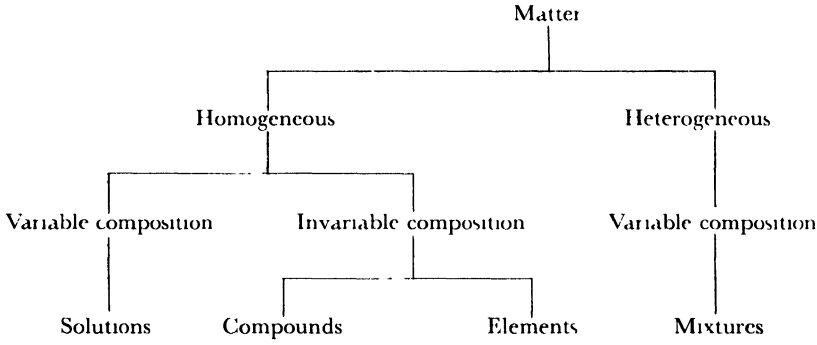
Properties which are associated with physical changes are termed *physical properties*. The melting point (temperature at which a substance changes from the solid state to the liquid state) of a substance is a physical property, since the liquid has the same composition as the solid. Properties which may be perceived by the senses, such as color, odor, and taste, are physical properties. Other common physical properties of a substance are boiling point, density, and solubility in water and other solvents. Less common physical properties of a substance include thermal or electrical conductivity, heat of fusion or vaporization, coefficient of thermal expansion, hardness, malleability, ductility, and crystalline form.

Chemical properties are involved only when matter undergoes chemical change. The rusting of iron is a chemical property of iron, since a change in composition occurs and a new substance is formed. Similarly, as coal burns it combines with oxygen, and new gaseous substances

[4] Unless otherwise designated, all temperatures will hereafter be given in ° C.

are formed. Water, soil minerals, and carbon dioxide are converted by growing plants to many chemical substances The fact that acids will act on most metals is a general chemical property of acids. In chemical changes, the substance undergoing change is nearly always associated with at least one other substance, whereas physical change involves only a single substance.

The classification of matter On the basis of its chemical composition, matter may be classified as follows



A *homogeneous* material is one which is perfectly uniform in composition—every part is exactly like every other part. Every minute bit of sugar is exactly like every other minute bit of sugar Materials which are homogeneous are sometimes termed *pure* substances. Salt, soda, aspirin, and gold are further examples of pure or homogeneous substances

Mixtures Materials which are not uniform in composition are said to be *impure* or *heterogeneous* and are called *mixtures*.[1] Most of the materials which we encounter in everyday life are of this type. Food products, rocks, soil, wood, and cement are examples These materials are mixtures of pure substances.

The constituents of a mixture may be present in different proportions. For example, various cements contain variable proportions of calcium and aluminum silicates. Bread is a mixture of ingredients which may be present in different proportions.

The constituents of a mixture retain their identity as their physical and chemical properties have not been changed by simple mixing—for example, a mixture of powdered iron and sulfur retains the properties

[1] The term "mixture" as used here refers to particles of matter which are at least of microscopic size (can be seen with a microscope) Solutions are sometimes referred to as mixtures, but there the particles we shall find are very much smaller than can be observed with a microscope

of both iron and sulfur. The sulfur, which dissolves in carbon disulfide, may be separated from the iron by extraction with that solvent; the iron, which attracted to a magnet, may be separated from the sulfur by magnetic attraction.

Compounds and elements A *compound* is a pure substance which may be broken down or decomposed by chemical means into two or more simpler substances. Water, for example, is a compound substance, since it may be decomposed into hydrogen and oxygen by means of an electric current. Sugar may be decomposed by heat into carbon and water Baking soda, alum, and table salt are also compound substances.

There are a number of substances, however, which have not been decomposed into simpler substances by ordinary chemical means.[6] For example, such familiar substances as iron, copper, gold, sulfur, oxygen, hydrogen, and tin have not been decomposed These substances are called *elements*. More than one hundred elementary substances have been discovered up to the present time, a list of these will be found inside the front cover of this text. Several of these elements were known in ancient times, though they were not then considered elementary substances

The distribution of the elements in the earth's crust is shown in Figure 2–2 Note that ten elements comprise over 98 per cent of the earth's crust, which includes the atmosphere. Oxygen alone makes up nearly 50 per cent of all matter.

Compounds are made up of various combinations of two or more of

[6] Certain elements (termed "radioactive") are spontaneously decomposing into simpler elements For a more complete discussion, see Chapter 31

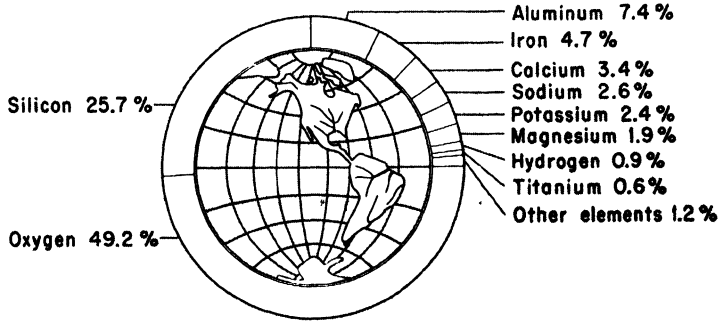


Figure 2–2 Distribution of elements in the earth's crust.

these elements. Sugar, for example, is a combination of the elements carbon, hydrogen, and oxygen; water is composed of the elements hydrogen and oxygen.

Compounds are characterized by their definite or invariable composition All samples of a given compound contain the same elements in a fixed proportion. For example, the proportion of hydrogen to oxygen by weight in water is 1.008:8 Sodium chloride (table salt), no matter what the source of it may be, always contains sodium and chlorine in the proportion of 22 997 parts by weight of sodium to 35.46 parts by weight of chlorine This principle of the constancy of composition is termed the Law of Definite Composition For further discussion of this law, see page 18

Contrasting the properties of mixtures and compounds The characteristics of mixtures and compounds are summarized as follows

MIXTURES	COMPOUNDS
1 Heterogeneous—nonuniform	1 Homogeneous—uniform
2 Constituents retain original identity and properties	2 Compounds have characteristic properties which are not those of the constituents
3 Constituents may be present in any proportion by weight	3 Constituent elements are present in fixed and invariable ratio by weight
4 Constituents usually may be separated by mechanical means	4 Not readily broken down into constituent elements

Metals and nonmetals Elements may be conveniently classified as metals and nonmetals. We are probably more familiar with the properties of metals than those of nonmetals For example, we know that the elements iron, copper, tin, and other metals have, in general, properties of ductility (may be drawn into a wire), malleability (may be hammered or rolled into shape), and a metallic luster. In addition, metals usually have high melting points and a high density, and are good conductors of heat and electricity Nonmetals, on the other hand, have, in general, low melting points, low densities, and are brittle, nonductile, and poor conductors of heat and electricity. Typical nonmetals are sulfur, phosphorus, and carbon. It should be pointed out at this time, however, that there is no sharp line of distinction between many metals and nonmetals.

The only metals that are found as uncombined elements in naturally occurring rocks are gold, silver, copper, platinum, and rare platinum-like metals, plus small, unimportant quantities of mercury, antimony, bismuth, and arsenic. The ancients had very little metal to fashion into

coins or trinkets. Practically all of our zinc, nickel, copper, lead, and arsenic are mined from deposits in which these elements are chemically combined with the nonmetal sulfur. The main ores of iron and of aluminum are oxygen-containing compounds.

There are a number of metallic elements which, though not in common use as metals, are widely used in compounds with nonmetals. For example, most people never see or use metallic sodium; yet the compound sodium chloride (common salt) is an essential food item. The metal calcium has little use, but its compounds are important in bone matter, glass, cement, marble, and other innumerable industrial substances.

Some types of compounds Compounds are many and varied, and we shall mention at this point only three important types—salts, acids, and bases. Most metals unite with most nonmetals, and the resulting compounds are called salts. A *salt* is a compound of a metal with a nonmetal other than hydrogen or oxygen. Lead sulfide, magnesium bromide, and zinc phosphide are salts. Many salts consist of a metal combined with more than one nonmetal (including oxygen); for example, calcium carbonate, a salt, is composed of calcium, carbon, and oxygen.

Many nonmetals will combine with hydrogen, and most of these compounds are *acids*. Chlorine, bromine, or sulfur, for example, react with hydrogen to form acids.

Compounds of metals with both oxygen and hydrogen are called *bases*, or sometimes *hydroxide bases*, since the oxygen-hydrogen grouping is termed "hydroxide." Sodium hydroxide and calcium hydroxide are bases.

Salts, acids, and bases comprise the principal classes of compounds which we shall study in this course. They will be considered in detail in Chapter 10.

Solutions We have all observed that sugar dissolves in water to form a clear solution. The sugar distributes itself uniformly throughout the liquid so that every part of the solution is exactly like every other part. In other words, a solution is homogeneous. We know, too, that the amount of sugar which will dissolve in a given weight of water is variable; we may dissolve a teaspoonful or a cup of sugar in a pint of water. Solutions, then, are like compounds in that they are homogeneous, but they are unlike compounds in that the proportion of constituents is variable.

Although the solution of a solid in a liquid is the most common type of solution we shall encounter, many other types exist. We shall study this subject in more detail later (Chapter 15).

LAWS OF CHEMICAL CHANGE

Law of conservation of mass The French chemist Lavoisier showed in 1785 that *there is no detectable*[1] *gain or loss of mass in a chemical change*; in other words, the total weight of the substances entering into a chemical change is equal to the total weight of the substances produced as a result of the change. Since that time much evidence has accumulated in support of this statement, which is now known as the Law of Conservation of Mass. The law may be demonstrated, within the limits of the accuracy of our weighing devices, by measuring carefully the masses of the reactants and products of a chemical change.

In certain chemical reactions it may seem that the reactants weigh more than the products. For example, if we burn a piece of wood, ashes are the only visible evidence of any product of the reaction. However, in the burning process the wood combines with the oxygen of the air and forms two invisible gases, carbon dioxide and water vapor, which pass into the atmosphere. If the carbon dioxide and water vapor are collected and added to the mineral matter (ashes) which remains, the total weight is found to be equal to the weight of the wood with which we started plus the weight of oxygen which has been taken from the atmosphere. Thus, if we take into account *all* of the reactants and products, we find no change in total mass during the reaction.

In other cases the reactants seem to weigh less than the products. Iron rust, for example, weighs more than the iron from which it is formed. However, if we take into account the weight of the oxygen which combines with the iron during the rusting process, we find that the weight of iron plus oxygen equals the weight of iron rust (iron oxide) produced in the chemical change.

Law of definite proportions The law of definite composition which was stated on page 16 is sometimes referred to as the Law of Definite Proportions. It may also be stated in the following form: *When elements combine to form a given compound, they do so in a fixed and invariable ratio by weight.* This law may be readily demonstrated in the laboratory by determining the ratio in which elements combine with one another. For example, exactly 55.85 g. of iron, no more and no less, will combine with 32.066 g. of sulfur to form the compound ferrous sulfide. It

[1] Einstein and others have demonstrated experimentally that mass and energy are interchangeable under certain conditions according to the Einstein equation $e = mc^2$ (where e = energy, m = mass, and c = velocity of light). A small mass change conceivably accompanies every chemical change, thus accounting for the energy change. However, in ordinary chemical changes the mass loss is so small that it is not detected by our most sensitive balances. The law of conservation of mass thus is a special case of the law of conservation of energy. See Chapter 31 for a more complete discussion of the equivalence of mass and energy.

makes no difference what ratio of weights of iron and sulfur we start with; we find that this ratio (55.85 to 32.066) is always the exact ratio in which iron and sulfur combine to form ferrous sulfide. Naturally, if a fixed ratio is maintained when these elements react, then the compound formed, ferrous sulfide, must have a fixed and definite composition.

Law of multiple proportions Although elements always combine in a definite proportion to yield a given compound, we should point out that they may also combine in a different proportion to yield a different compound. For example, carbon and oxygen may combine to form two oxides of carbon: carbon monoxide and carbon dioxide. Chemical analysis of these compounds will show that in carbon monoxide, 6 g. of carbon combines with 8 g. of oxygen; in carbon dioxide, 3 g. of carbon combines with 8 g. of oxygen. Note that the ratio of the weights of carbon combining with 8 g. of oxygen in the two compounds (6:3) is in small whole numbers—that is, 2 to 1.

The weights of oxygen combining with a fixed weight of nitrogen (14 g.) to form a series of oxides are shown in the following list:

In nitrous oxide	14 g. nitrogen + 8 g. oxygen
In nitric oxide	14 g. nitrogen + 16 g. oxygen
In nitrogen trioxide	14 g. nitrogen + 24 g. oxygen
In nitrogen dioxide	14 g. nitrogen + 32 g. oxygen
In nitrogen pentoxide	14 g. nitrogen + 40 g. oxygen

Again note that the ratios of the weights of one element (oxygen) 8:16:24:32:40 which combine with a fixed weight of the second element (nitrogen, 14 g.) are in small whole numbers (1, 2, 3, 4, 5). The relationship shown here is termed the Law of Multiple Proportions. It may be stated: *The weights of an element which combine with a fixed weight of a second element in different compounds of the two elements are in the ratio of small whole numbers.*

There are many other examples of a series of compounds between two elements where this law holds. We should keep in mind, however, that for any one compound the proportion in which the elements combine is *fixed* and *invariable.*

Equivalent or combining weights The law of definite proportions tells us that there is a definite relationship between the weights of elements in any one compound. A question is immediately suggested: Is there any simple relationship between the weights of two elements each of which combine with a fixed weight of a third element? To answer this question, let us study the combining proportions of elements in two compounds, water and hydrogen chloride. Experiments show that

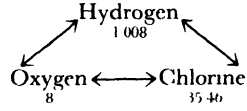
hydrogen combines with oxygen to form water in a ratio of 1.008 parts by weight of hydrogen to 8 parts by weight of oxygen.

Hydrogen (1.008) ⟷ Oxygen (8)

In hydrogen chloride 1.008 parts by weight of hydrogen combines with 35.46 parts by weight of chlorine.

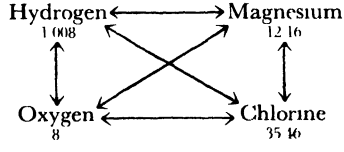
Hydrogen (1.008) ⟷ Chlorine (35.46)

Does it logically follow, then, that oxygen and chlorine will combine in a ratio of 8 to 35.46?



The answer is yes, *the weights of two elements which combine with a fixed weight of a third element are equivalent to one another.* Thus 8 g. of oxygen is equivalent to 35.46 g. of chlorine.

To illustrate further, in the formation of magnesium oxide, 8 parts by weight of oxygen combine with 12.16 parts by weight of magnesium. From the generalization stated above, we should expect 12.16 parts



by weight of magnesium to combine with 35.46 parts by weight of chlorine. This is confirmed by experiments. We might also expect magnesium and hydrogen to combine in a ratio of 12.16 to 1.008. Although magnesium does not combine with hydrogen, it does displace hydrogen from an acid, and experiments show that 12.16 g. of magnesium displaces exactly 1.008 g. of hydrogen.

In order to arrive at a system of related numbers to express equivalent or combining weights, it is necessary arbitrarily to choose some element as a standard for comparison. Because oxygen combines with most other elements, it has been chosen as a standard of comparison and has been assigned an equivalent weight of 8. The weight of an element which combines with 8 parts by weight of oxygen is termed its *equivalent* or *combining weight.* The equivalent weight expressed in grams is termed a *gram equivalent.* Thus 12.16 g. of magnesium and 35.46 g. of chlorine each represent a gram equivalent of these elements.

It was stated in the preceding section that carbon and oxygen may combine in two different proportions to form two different compounds. In carbon monoxide 6 parts by weight of carbon are combined with 8 parts by weight of oxygen, whereas in carbon dioxide 3 parts by weight of carbon are combined with 8 parts by weight of oxygen. While carbon exhibits two combining weights, 6 and 3, in these two compounds, these combining weights stand to each other as small whole numbers, 2 to 1. Chemists were led to conclude: *To each element may be assigned a number, its combining weight, which in itself, or when multiplied by a small whole number, expresses the weight of that element that combines with the combining weight of another element.* This generalization is known as the Law of Combining Weights.

It should be emphasized that though an element may exhibit more than one equivalent or combining weight, these weights are always related as small whole numbers.

Atoms and molecules The fact that elements combine in fixed ratios by weight suggests that elements may be made up of particles or chunks of matter which act as units in chemical change. Much evidence has accumulated in recent years to indicate that such units of matter do exist, and the term *atom* is used to designate them. An atom may be defined as *the smallest particle of an element which can enter into chemical change.*

Let us imagine subdividing a piece of iron into smaller and smaller particles. Eventually we would obtain a piece of iron which could no longer be divided or broken down into smaller pieces of iron. This ultimate particle would be an atom of iron.

The ultimate particle of a compound substance is termed a *molecule.* For example, in the subdivision of a compound substance such as sugar, which is composed of the elements hydrogen, oxygen, and carbon, the molecule is the smallest particle into which it may be divided without losing its identity. If sugar were further divided into atoms, it would lose its properties, and its identity as sugar would be destroyed. Atoms and molecules will be studied in more detail in the next chapter.

SYMBOLS AND FORMULAS

The chemist finds it convenient to use abbreviations or *symbols* for the chemical elements. Instead of writing out *hydrogen,* for instance, the element is designated by the symbol H. The symbol of an element is usually derived from the first letter or letters of the English or Latin name of the element. In many cases only a single capitalized letter is used, as N for *nitrogen,* and P for *phosphorus;* in other cases two letters

from the name are used, only the first of which is capitalized; examples are He for *helium* and Ne for *neon*. The symbol for *sodium* is Na, which comes from the Latin, *natrium*. Many other symbols are derived from the Latin names of the elements; for example, *copper*, Cu; *iron*, Fe; *mercury*, Hg; and *silver*, Ag. A list of the chemical elements and their symbols will be found on the inside front cover of this book.

To the chemist the symbol is not only an abbreviation for an element; it also stands for one atom of the element in question. Thus S stands for one atom of sulfur; H, for one atom of hydrogen; and O, for one atom of oxygen. A number placed in front of the symbol indicates the number of atoms of that element; thus 3 H stands for three atoms of hydrogen, and 10 N stands for ten atoms of nitrogen.

A chemical compound is expressed in abbreviated form as a *formula*, which consists of the proper combination of symbols, representing elements which are present in the compound. Thus iron sulfide, which is composed of the elements iron and sulfur, is represented as FeS, in which Fe is the symbol for iron and S the symbol for sulfur. Sodium chloride, a compound of sodium and chlorine, has the formula NaCl, in which Na is the symbol for sodium and Cl the symbol for chlorine.

A formula, like a symbol, is more than an abbreviation, since it tells at once the relative number of atoms of the constituent elements in the compound. FeS stands for ferrous sulfide, which contains one atom of iron and one atom of sulfur. H_2O stands for two atoms of H (hydrogen) and one atom of O (oxygen), which compose water. A subscript 2 is placed after the hydrogen to indicate that two atoms of hydrogen are present in the molecule. A molecule of sulfuric acid, which contains two atoms of hydrogen, one atom of sulfur, and four atoms of oxygen, is represented as H_2SO_4; the subscript of the H is 2 to denote two atoms of hydrogen; the subscript of the O is 4 to indicate four atoms of oxygen present in each molecule of the compound. No subscript is necessary if only one atom of an element is present; thus in the formula H_2SO_4 no subscript is placed after S.

The compound sugar contains the elements carbon, hydrogen, and oxygen. Its formula is $C_{12}H_{22}O_{11}$, which tells us that each molecule of sugar contains twelve atoms of carbon, twenty-two atoms of hydrogen, and eleven atoms of oxygen.

EXERCISES

1 Express 12 in in centimeters, in millimeters, in decimeters, in meters

2 Add 5 25 g , 0 07000 kg., 0.25 g , 550 mg , 3 dg., 50 cg Ans. 76 85 g.

3 Add: 0.30 m., 250 cm., 2.4 m , 800 mm., 2 5 cm., 5 dm , 50 mm.

4 Add 2.5 l., 3500 ml, 0.25 l, 50 ml. Ans 6 3 l.

5 What is your weight in kilograms? What is your height in centimeters?

6 A box is 5 in wide, 10 in long, and 3 in deep Calculate the volume in cubic centimeters, in liters Ans. 2460 cc ; 2.46 l

7 Calculate the number of liters in a cubic meter Ans 1000

8 A container has the dimensions 3 m by 10 dm by 50 mm. Calculate its volume in liters Ans 150

9 One cubic millimeter of oil is spread out on the surface of water so that the oil film has an area of 1 square meter What is the thickness of the film in angstrom units? Ans. 10

10 Calculate the density of a block of wood, 25 cm × 100 mm × 0 05 m., the weight of which is 0 9 kg Ans. 72 g./cc.

11 Calculate the volume of a tank which has the dimensions 300 mm × 0 7 m. × 10 cm What would be the weight of gasoline, density 0.8 g per ml, which this tank could contain?

12 A piece of iron weighing 39 2 g displaces 5 ml of water when submerged Compute the density of the iron Ans 7 84 g /ml.

13 Make the following temperature conversions 200° C to F, 104° F to C, −150° C to A, 302° F to A, 0° A to F, 122° F to C., 50° C. to F.

14 Determine the temperature at which both a Fahrenheit thermometer and a centigrade thermometer would (*a*) have the same reading, (*b*) have the same numerical reading but be opposite in sign Ans (*a*) −40°

15 Calculate the quantity of heat required to raise the temperature of a quart of water (946 ml) from 20° C to 100° C Ans. 75.7 kc

16 When a gram of coal is burned, 7600 cal of heat are evolved Calculate the quantity of coal necessary to supply the heat required in the previous problem.

17 Classify the following as physical or chemical changes (*a*) rusting of iron, (*b*) molding of clay, (*c*) melting of iron, (*d*) digestion of food; (*e*) setting of mortar, (*f*) magnetization of iron, (*g*) souring of milk, (*h*) breaking of glass, (*i*) burning of coal

18 When coal burns, do the ashes weigh more or less than the coal? Reconcile this with the law of conservation of mass.

19 Trees grow taller and larger Is matter being created in the growing process? Explain

20 Analysis of compounds of *A* and *B*, *A* and *C*, *B* and *C* gives the following data

	GRAMS OF *A*	GRAMS OF *B*	GRAMS OF *C*
First compound	1	1 75	—
Second compound	2	—	4 30
Third compound	—	7 00	8.60

Which of the laws of chemical change is illustrated by this set of data?

21 Titanium combines with chlorine to form three compounds on the basis of the following experimental data

	COMBINING WEIGHTS IN GRAMS		WEIGHT OF COMPOUND FORMED
	Ti	Cl	
Compound *A*	48	71	119
Compound *B*	24	53.25	77.25
Compound *C*	6	17 75	23 75

Which laws of chemical change are illustrated by this data?

22 It is found experimentally that every pure sample of zinc white, as zinc oxide is called, contains 4.08625 g. of zinc per gram of oxygen. What is the equivalent weight of zinc?

23 Given the following data: 45 g. of Sc (Scandium) combines with 106.5 g. of chlorine; 35.5 g. of chlorine combines with 1 g. of hydrogen; 1 g. of hydrogen combines with 8 g. of oxygen. Determine the equivalent weight of Sc.

Ans. 15.

24 Three oxides of chromium on analysis gave the following data:

	CHROMIUM (per cent)	OXYGEN (per cent)
First compound	76.5	23.5
Second compound	68.4	31.6
Third compound	52.0	48.0

(*a*) What is the equivalent weight of chromium in each of the three compounds?
(*b*) Does the law of multiple proportions apply here? If so, explain.

Ans. (*a*) 26; 17.3; 8.7.

25 A compound of iron and oxygen is analyzed and found to contain 69.9 per cent iron and 30.1 per cent oxygen. What is the equivalent weight of iron in this compound? Ans. 18.6.

26 46 g. of sodium and 32 g. of sulfur combine to form the compound, sodium sulfide. 23 g. of sodium combines with 35.5 g. of chlorine to form the compound, sodium chloride. From a consideration of the law of equivalent weights, in what ratio by weight might sulfur and chlorine combine?

27 If 40 g. of calcium combines with 16 g. of oxygen to form calcium oxide, how much oxygen is required to form 14 g. of calcium oxide? Ans. 4 g.

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IN REALITY THERE IS NOTHING BUT ATOMS AND SPACE — SOLID AND INDIVISIBLE ATOMS IN AN INFINITE VOID

Democritus, 500 B.C.

three THE ATOM, ITS STRUCTURE AND BEHAVIOR

We learned from the laws of chemical change that (1) matter appears to be permanent, since no loss or gain of mass in chemical change has been detected (Law of Conservation of Mass), and (2) when elements combine to form a given compound, they do so in a fixed and invariable ratio by weight (Law of Definite Proportions).

These facts in themselves suggest that matter is made up of discrete particles which function as units during chemical change. The idea that matter is discontinuous—that it is made up of finite particles and is not all in one piece—was first conceived by the Greek philosophers. Democritus reasoned that matter consists of very small particles, which he termed *atoms*. He did not distinguish between "atoms" of compounds and elementary substances but believed that there were as many kinds of atoms as there were kinds of substances. It is surprising indeed that the Greek philosophers were able so nearly to guess the truth of the structure of matter, since their conclusions were based on pure deduction, without support of experimental data.

Dalton's atomic theory It was not until 1804, however, that the atomic theory was developed more fully and accepted by chemists and physicists. In that year John Dalton, an English schoolmaster, made the following assumptions about the structure of matter:

1 Substances are composed of tiny, indivisible particles called "atoms."
2 Atoms of any given substance are identical and have the same weight, size, form, etc.
3 The atom is the smallest part of an element which can enter into a chemical change.
4 Atoms of elements are permanent and cannot be decomposed.
5 Compounds are formed by the union of two or more atoms of elementary substances.

By means of these assumptions, Dalton was able to explain the laws of chemical change. Since, according to the theory, atoms are permanent and not decomposable, there would be no change in mass during chemical reaction. When chemical compounds react with one another, there is simply a rearrangement of the atoms within the compounds. This rearrangement or regrouping produces new substances which have entirely new properties. Since all the atoms present are simply regrouped during a chemical change, and the atoms retain their weights, there is no gain or loss of weight (the Law of Conservation of Mass). Furthermore, if the atoms possess characteristic weights, the union of two or more atoms would require that combination take place in a fixed ratio by weight (Law of Definite Proportions).

Dalton did not recognize differences between units of elements and units of compounds. Avogadro, an Italian physicist, was the first to differentiate clearly between the two. He defined an atom as the smallest particle of an element which can enter into chemical change; the term *molecule* was used to denote the smallest unit of a substance (element or compound) which can exist and retain all the properties of the substance. A molecule may be a combination of two or more like or unlike atoms (Figure 3–1).

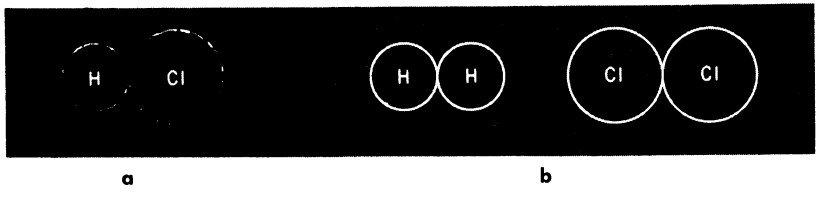


Figure 3–1 (a) A combination of unlike atoms is a compound. (b) A combination of like atoms results in an element whose smallest unit contains more than one atom.

The difference between molecules of compounds and elements is a bit confusing. Many elements will exist in the uncombined or free state as single atoms, and as such the atom and molecule are the same; others may exist in the free state only in pairs or some other number of atoms.

Atomic weights While atoms are much too small to be weighed individually, equal large numbers of atoms may be weighed and relative weights assigned to the elements by comparing their weights with some arbitrary standard. Because it is the most abundant of the chemical elements and because it combines chemically with most of the other elementary substances, oxygen has been chosen as the standard of atomic weights. Chemists have assigned the number 16 to one atom of oxygen. An atom of sulfur weighs twice as much as an atom of oxygen and on the basis chosen above has a relative weight of $2 \times 16 = 32$. An atom of iron weighs approximately $3\frac{1}{2}$ times as much as an atom of oxygen and therefore has a relative weight of about $3\frac{1}{2} \times 16 = 56$. In a similar manner relative weights have been assigned to the atoms of other elements. These numbers are relative weights and do not represent the actual weight or absolute weight of the atom of the element in question. Thus, when we say that the atomic weight of carbon is 12, we mean that one atom of carbon is $\frac{12}{16}$ or $\frac{3}{4}$ as heavy as one atom of oxygen, which is our standard. One atom of lead, atomic weight 207, weighs $\frac{207}{16}$ times as much as one atom of oxygen. (See the inside front cover of this text for atomic weights of the elements.)

The number 16 has been assigned to oxygen because on this basis the lightest known element, hydrogen, has a relative weight of about 1 (1.008). Of course a number larger than 16 might have been assigned to oxygen, but this would mean unnecessarily large numbers for the atomic weights of other elements. If, for example, the number 100 were assigned to oxygen, sulfur would have an atomic weight of 200, iron an atomic weight of 350, and so on.

Equivalent weights and atomic weights Equivalent weights constitute fundamental information from which atomic weights are derived. A simple relationship exists between the equivalent weight of an element and its atomic weight, as shown by the expression:

$$\text{Equivalent Weight} \times X = \text{Atomic Weight}$$

where X is a small integral number. The reason atomic weights are not always equal to equivalent weights is the fact that atoms of the different elements do not always unite one atom to one atom. It was stated in Chapter 2 that 1.008 parts by weight of hydrogen combine with 8 parts by weight of oxygen to form water, and it might appear at first sight that the atomic weight of oxygen should be 8 instead of 16. However, it may be shown experimentally that two atoms of hydrogen unite with one atom of oxygen in forming water; therefore, the combining capacity of the oxygen atom is twice that of the hydrogen atom. Some atoms, such as magnesium, have a combining capacity of 2; others,

such as aluminum, have a capacity of 3; and so on. This combining capacity of various elements, called *valence*, determines the magnitude of X. The determination of atomic weights will be studied in detail in Chapter 13.

The student must keep in mind that an atomic weight is a *number* which expresses *the relative weight of the atom* in comparison to one atom of the arbitrarily selected standard (oxygen as 16). Thus, an atomic weight may be given in any unit of measure—grams, ounces, pounds, tons, and so on. However, the chemist finds it most convenient to work with grams.

The atomic weight of an element expressed in grams is termed a *gram atomic weight* or a *gram atom*. For example, a gram atomic weight or gram atom of oxygen is 16 grams, and a gram atom of sulfur is 32 grams.

Molecular weights The smallest particle of a compound which can exist as such has been termed a *molecule*. A molecule of a compound is formed by the union of two or more atoms of the elements of which the compound is composed. The weight of a molecule will be the sum of the weights of the constituent atoms. For example, a molecule of water is composed of two atoms of hydrogen and one atom of oxygen, H_2O. The weight of a molecule of water, or the *molecular weight* of water, is then $(2 \times 1 = 2)$ plus $(1 \times 16 = 16) = 18$. Molecular weight, like atomic weight, is a *relative* weight. For a given compound, the molecular weight is the weight of a molecule of the compound compared to the weight of one atom of oxygen—that is, to 16. The molecular weight of 18 for water means that one molecule of water is $\frac{18}{16}$ as heavy as one atom of oxygen, the standard of comparison. Molecular weights may be given in any unit of measure. Usually, the chemist finds it most convenient to give a molecular weight in grams.

The molecular weight expressed in grams is termed a *gram molecular weight;* thus, a gram molecular weight of water is 18 grams. The term *gram molecular weight* is usually contracted to *gram mole,* or simply *mole.* These terms are synonymous.

Extensions of Dalton's theory Dalton's atomic theory has undergone considerable change in recent years, and we now perceive several errors in the original assumptions. We now know that all atoms of any given element are not identical. For example, two kinds of chlorine atoms are known; one has an atomic weight of 35, and the other an atomic weight of 37. Similarly, lead with atomic weights of 205, 206, and 207 has been shown to exist.

We know, too, that atoms may be disintegrated. Many elements, such as uranium and radium (radioactive elements), are spontaneously disintegrating, and their atoms are being transformed into atoms of

Subatomic particles of matter The idea that atoms are indivisible persisted for many years after the postulations of Dalton, and it has been only in the last fifty years or so that evidence has accumulated which indicates that atoms may actually be decomposed and resolved into subatomic particles much smaller than any known atom. Atoms of all of the elements are now regarded as composed of three subatomic particles of matter:

1 *Electrons:* units of matter carrying negative charges of electricity.
2 *Protons:* units of matter carrying positive charges.
3 *Neutrons:* neutral units of matter of about the same mass as the proton.

The electron The electron was the first of the subatomic particles to be discovered. Knowledge of the electron began with a study of the discharge of electricity through gases at reduced pressures. For this study, a so-called cathode ray tube (Figure 3–2) may be used. It consists of a tube of glass in which are sealed two metal discs, and a glass side arm through which the tube may be evacuated by means of a pump. The metal discs act as electrodes between which a discharge of electricity will take place when the electrodes are connected to a source of high potential such as an induction coil. The nature of the discharge, then, is studied as the pressure is reduced. At atmospheric pressure an irregular violet colored discharge takes place. As the pressure is reduced, the discharge becomes pink, and finally the whole tube glows. At very low pressures, streaks of white light seem to emerge at right angles from the negative pole or cathode and to cause the appearance of a greenish fluorescence on the glass walls where the rays strike. These rays were originally referred to as *cathode rays* and at first were thought to be light rays. An obstacle placed between the cathode and the glass wall casts a sharp shadow on the wall opposite the cathode, thus indicating that the rays travel in straight lines. A pinwheel placed in the path of the rays revolves, or if the rays are allowed to strike a piece of metal foil, the foil becomes hot. These observations suggested that the rays were material in nature. In 1879 Sir William Crookes showed that the rays were bent in an arc by an electromagnetic field. Subsequently, Sir J. J. Thomson showed that the rays were deflected toward

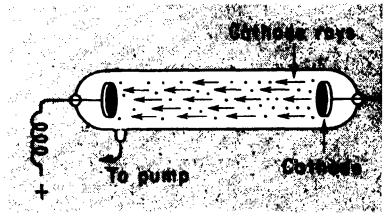


Figure 3–2 Cathode ray tube. Electrons are emitted from the cathode in straight lines.

a positively charged plate in an electric field and therefore must possess a negative charge. These negatively charged particles issuing from the cathode came to be called *electrons.* By observing the extent or magnitude of the electron's deflection in magnetic and electric fields, Thomson determined that the mass of a single electron is about $\frac{1}{1837}$ that of the hydrogen atom. Since electrons can be generated by using any cathode or any gas in the tube, it would seem that electrons are constituents of atoms of all elements.

The magnitude of the *charge* of an electron was determined by R. A. Millikan. A container was constructed with electrically chargeable plates at top and bottom. Electrons and positively charged particles were produced in the container by a beam of X rays. Fog droplets were introduced into the container and the rate of fall of a given fog droplet was viewed as the plates were electrically charged or discharged. A fog particle could be accelerated in its fall, suspended in midair, or actually made to rise, depending on the charge of the plates. The explanation is that the fog droplet attaches electrons and thus becoming negatively charged, it would tend to move to the positively charged plate. The number of electrons adsorbed per droplet would influence the rate of movement to the positive plate, but all changes in velocity as electrons were adsorbed could be compensated by appropriate changes in charge between plates. It was noted that all changes in velocity of the rise or fall of the fog droplets were related to multiples of a certain unit charge between the plates. This unit charge between the plates must equal the electron charge and was found to be 1.59×10^{-19} coulombs.

The actual *mass* of an electron has not been determined directly but may be calculated, as has already been mentioned, from data obtained by measuring the effect of magnetic and electrostatic fields upon a stream of cathode rays. From the deflection of the stream in a magnetic field and its counterbalancing by an electrostatic field, the ratio of charge to mass of the electron is obtained, and from this the mass has been calculated to be 9.107×10^{-28} g.

The proton After electrons were found to be generated in a cathode ray tube, it was natural to ask whether or not positively charged particles were emanating from the region of the positive pole or anode of the tube at the same time that electrons were being generated at the cathode. In 1886 Goldstein found that if the cathode is perforated with a cylindrical hole, a beam of rays passes through the cathode into a region behind the cathode and away from the anode. These rays were called *positive rays* or *canal rays.* When these rays in magnetic and electric fields were studied in much the same manner as the cathode rays were investigated, it was shown that they possess a unit positive charge or an integral multiple of this charge, and are composed of particles of the residual gas used in the tube. Particles of lowest mass were found when hydrogen was the residual gas. The particles consist of hydrogen atoms with a unit positive charge; in other words, each particle is a hydrogen atom which has lost one electron. Since a smaller

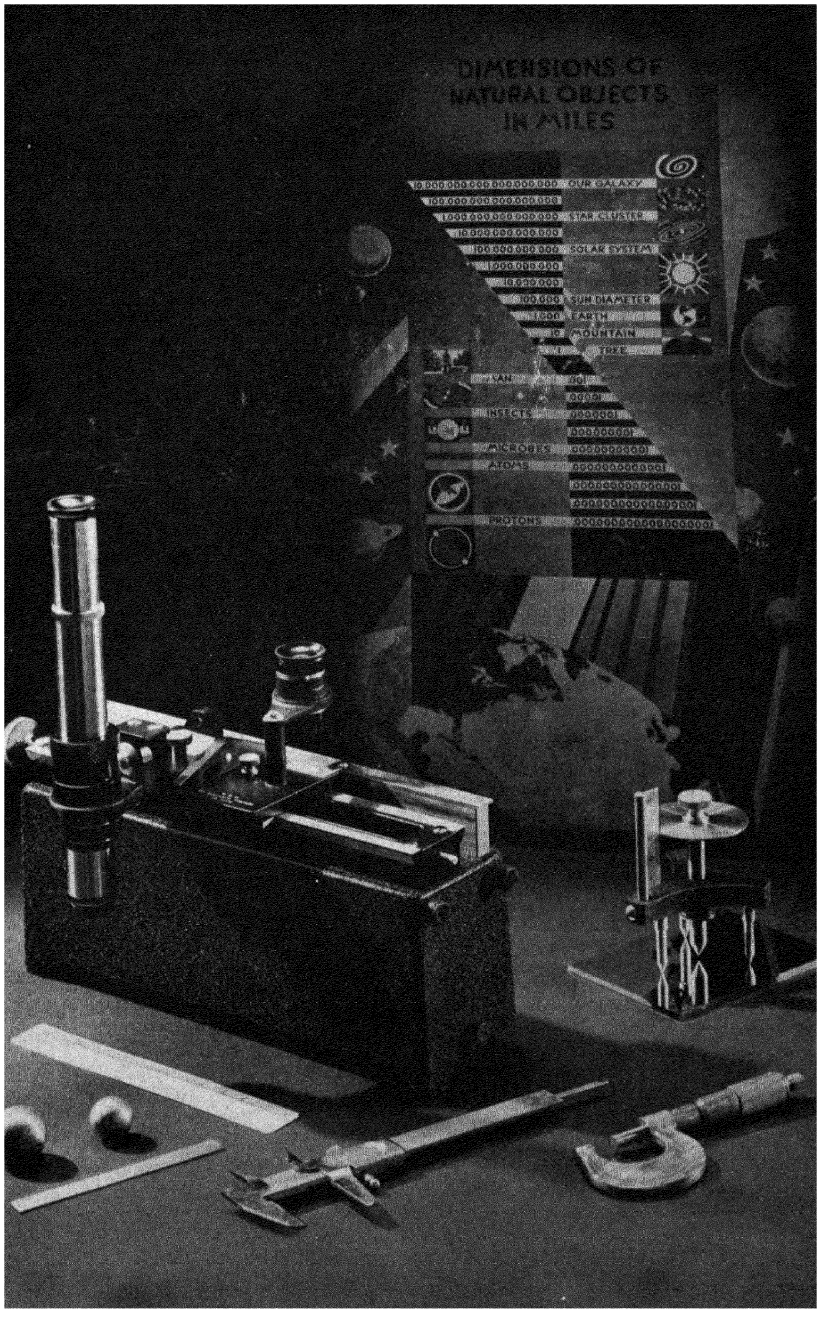


Figure 3–3 Precision instruments and relative sizes of natural objects.

positively charged particle than this has not been found, there is strong evidence that these particles are fundamental building units in the structure of atoms of all of the elements. These subatomic particles are called *protons.*

The neutron In 1932 Chadwick observed that neutral particles of a mass approximately that of the proton were produced when beryllium was exposed to the radiations from a radioactive substance (Chapter 31). It was at first thought that each particle consisted of one proton and one electron; however, these neutral units of matter, which are called *neutrons,* are now regarded as a new and fundamentally distinct kind of particle.

X rays In 1895, Roentgen discovered a new kind of radiation of very short wave length emanating from a cathode ray tube in which a metallic element was made a target of the cathode rays (Figure 3–4). For lack of a better name, the radiations were called *X rays.* The X rays are capable of penetrating wood, paper, and flesh but are stopped by bones and metallic substances. Modern medical practice calls for the use of X-ray photographs in diagnosis of disease and fractured limbs, and X rays have been a powerful tool in studies of the structure of matter.

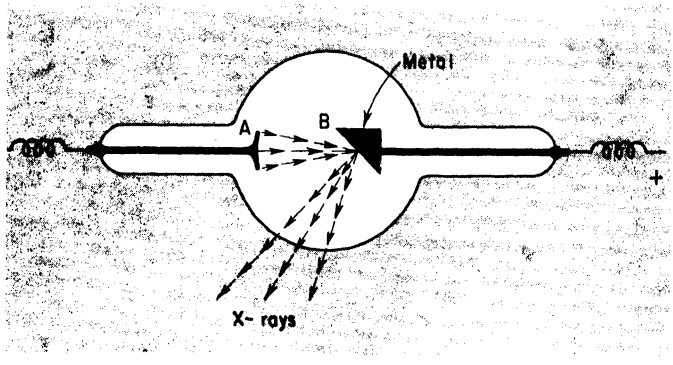


Figure 3–4 X-ray tube. Electrons are emitted and brought to a focus by the concave cathode A. The cathode rays, on striking a metal target B, produce X rays of a frequency characteristic of the metal.

The modern theory of atomic structure Although Dalton believed that atoms were solid, impenetrable particles, today scientists know that the atom is mainly free space. According to the modern picture, the atom consists of a comparatively compact center or nucleus, which is surrounded by an orbital structure. Except for the hydrogen atom, *the nucleus of an atom contains both protons and neutrons,* but no electrons, while *the outer structure of the atom consists of electrons only.* These electrons move

in orbits or energy levels about the nucleus. Since only neutrons and protons are contained in the nucleus, the nucleus of an atom must always bear a net positive charge.

Protons and neutrons have approximately the same mass as the hydrogen atom, while the electron has only about $\frac{1}{1837}$ the mass of the hydrogen atom. Since the protons and neutrons are responsible for most of the mass of the atom, most of this mass is concentrated in the nucleus.[1] The electrons, which are almost negligible in weight as compared to the protons and neutrons, are separated from the nucleus by relatively great distances, in much the same way that planets in the solar system are situated at great distances from the sun. Since all atoms are electrically neutral, the number of electrons (negatively charged particles) is equal to the number of protons (positively charged particles) in the atom.

The hydrogen atom The hydrogen atom is the simplest of all atoms, consisting of a single proton and a single electron. The proton makes up the nucleus of the atom around which the electron moves. The hydrogen atom is represented diagrammatically in Figure 3–5, in which the small circle represents the nucleus; + indicates a proton; the white dot, an electron; and the broken circle represents the orbit in which the electron moves.

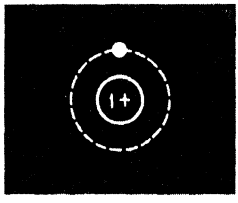


Figure 3–5 The hydrogen atom.

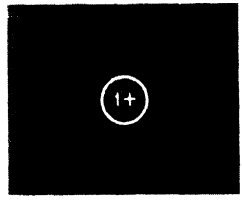


Figure 3–6 A hydrogen ion.

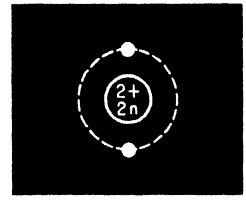


Figure 3–7 The helium atom.

Under certain conditions, the electron may be removed from the hydrogen atom, in which case only the nucleus which is a single proton remains. This particle may be represented as H^+ (Figure 3–6). A particle having an excess of either positive or negative charge is termed an *ion;* thus H^+ is a hydrogen ion. It becomes evident that a hydrogen ion and a proton are one and the same thing. The atomic weight of hy-

[1] The relative size of the nucleus and its density may be visualized from the following approximate figures. An average atom has a radius of about 1×10^{-8} cm., whereas the nucleus has a radius of about 1×10^{-12} cm.; in other words the radius of the nucleus is about $\frac{1}{10000}$ that of the atom. While the density of liquid or solid elements varies from less than 1 to 22.4 g./cc., the density of the nucleus is estimated at about 10^{14} g./cc., which would be 10^8 or 100 million tons per cubic centimeter.

drogen is approximately 1 (actually 1.008), and since the mass of the hydrogen atom is almost entirely contained in the nucleus, it follows that the mass of the nucleus of a hydrogen atom—and therefore of a proton—is very nearly equal to one. Neutrons have practically the same mass as protons and therefore must have a weight also very close to unity.

The structure of other atoms The element of simplest structure next to hydrogen is helium, which has an atomic weight of 4. The number 4 indicates that four units of weight are necessary in the nucleus of the atom. These four units of weight must be in protons or neutrons or both. As a matter of fact, the helium nucleus is composed of two protons and two neutrons. Two electrons must be present in the atom to balance the charge of the two protons, and these two electrons revolve in an orbit about the nucleus (Figure 3-7). The symbol *n* in Figure 3-7 represents a neutron.

The student must be cautioned not to take these diagrams of atoms literally. These are not intended to be pictures of atoms but are simply a means of showing the component parts and their approximate relative positions. Atoms are *three dimensional.* Electrons should be visualized as moving continuously in all directions on the surfaces of hollow concentric spheres, with the nucleus at the center. Nor do our diagrams give us a true picture of atomic dimensions. If a nucleus were pictured as about the size of a pea, the orbital structure should be shown at a distance of more than two hundred feet away. It is hard to visualize the immense spaciousness of the atom, and our simple diagrams are likely to give us false impressions of actual structures. We should point out that much about atomic structures is still obscure—the scientist is learning about them slowly but surely.

As we progress to the elements of higher atomic weight, the structures become more complex, with additional orbits in which additional electrons move (Figures 3-8, 9, 10 and 11).

The capacity of the first orbit (called the K energy level) about the

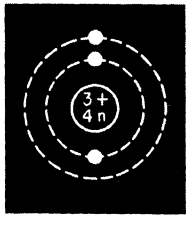


Figure 3-8 The lithium atom.

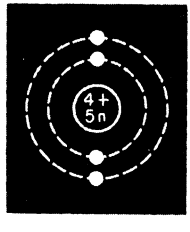


Figure 3-9 The beryllium atom.

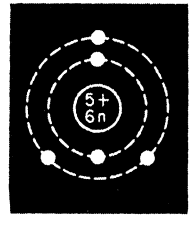


Figure 3-10 The boron atom.

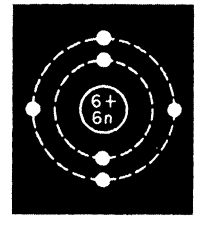


Figure 3-11 The carbon atom.

nucleus of an atom is two electrons; in no case is this number exceeded. We may say, then, that two electrons represent a stable or saturated condition for the first orbit of an atom. A total of eight electrons may be present in the second orbit of an atom (*L* energy level), eighteen electrons in the third orbit (*M* energy level), and thirty-two electrons in the fourth orbit[2] (*N* energy level) (Figure 3-12).

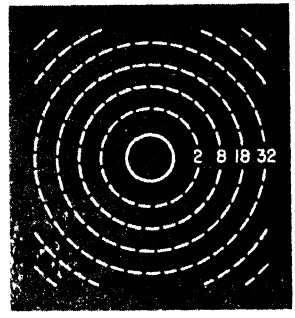


Figure 3-12 The maximum number of electrons in the various orbits of atoms is: first orbit, 2; second orbit, 8; third orbit, 18; fourth orbit 32.

We shall learn, however, that the *number of electrons in the outermost orbit of an atom may never exceed eight.* The third orbit of an atom may have as many as eighteen electrons, provided it is *not* the outer orbit, and the fourth orbit may have as many as thirty-two electrons, provided it is *not* the outermost orbit. The arrangement of electrons in the various orbits about the nucleus for the elements is shown in Table 3-1 (page 36).

Quantum numbers and subshells The electrons in an atom group themselves into successive shells (or energy levels) in which there are 2 electrons in the first shell, 8 in the second, 18 in the third, 32 in the fourth, and so on. However, spectral studies indicate that the electrons in a given shell do not move in exactly the same orbits or energy levels. The electrons in the different orbits are best described by sets of numbers known as *quantum numbers,* of which there are four:

1. The *principal quantum number,* designated by n, corresponds to the shell in which the electron moves. Instead of describing an electron by the numerical value of its principal quantum number—for example, 1, 2, 3, etc.—it is sometimes the practice to employ the capital letters *K, L, M.* Thus a *K* electron is an electron having a principal quantum number of unity; for an *L* electron the value of n is 2, and so on.

2. The *azimuthal quantum number,* designated by l, gives a measure of the angular momentum of an electron in its orbital motion about the nucleus. The introduction of this term indicates that the main shells of electrons may be considered as being made up of one or more *subshells.* These subshells of electrons possess *nearly* the same energy as one another, but not exactly so. The term l may have values of 0 to $(n - 1)$. Hence for the first main shell where $n = 1$, l can have only a value of 0. For the first shell, then, the subshells and main shell would coincide. When $n = 2$, l can have values of 0 and 1. This would correspond to two subshells within the second main shell. When $n = 3$, l may have the values 0, 1, 2, corresponding to 3 subshells.

3. *Magnetic quantum number,* designated by m, accounts for the behavior of the electrons in a magnetic field. m may have values from $-l$ to $+l$, including 0.

[2] The maximum number of electrons that may appear in an orbit may be determined from the equation

$$\text{Max. No. of Electrons} = 2n^2$$

where n is the number of the orbit.

TABLE 3–1 Distribution of Electrons of the Elements

[illegible]	[illegible]	[illegible]	NUMBER OF ELECTRONS IN VARIOUS ENERGY LEVELS						
			K	L	M	N	O	P	Q
Hydrogen	H	1	1						
Helium	He	2	2						
Lithium	Li	3	2	1					
Beryllium	Be	4	2	2					
Boron	B	5	2	3					
Carbon	C	6	2	4					
Nitrogen	N	7	2	5					
Oxygen	O	8	2	6					
Fluorine	F	9	2	7					
Neon	Ne	10	2	8					
Sodium	Na	11	2	8	1				
Magnesium	Mg	12	2	8	2				
Aluminum	Al	13	2	8	3				
Silicon	Si	14	2	8	4				
Phosphorus	P	15	2	8	5				
Sulfur	S	16	2	8	6				
Chlorine	Cl	17	2	8	7				
Argon	Ar	18	2	8	8				
Potassium	K	19	2	8	8	1			
Calcium	Ca	20	2	8	8	2			
Scandium	Sc	21	2	8	9	2			
Titanium	Ti	22	2	8	10	2			
Vanadium	V	23	2	8	11	2			
Chromium	Cr	24	2	8	13	1			
Manganese	Mn	25	2	8	13	2			
Iron	Fe	26	2	8	14	2			
Cobalt	Co	27	2	8	15	2			
Nickel	Ni	28	2	8	16	2			
Copper	Cu	29	2	8	18	1			
Zinc	Zn	30	2	8	18	2			
Gallium	Ga	31	2	8	18	3			
Germanium	Ge	32	2	8	18	4			
Arsenic	As	33	2	8	18	5			
Selenium	Se	34	2	8	18	6			
Bromine	Br	35	2	8	18	7			
Krypton	Kr	36	2	8	18	8			
Rubidium	Rb	37	2	8	18	8	1		
Strontium	Sr	38	2	8	18	8	2		
Yttrium	Y	39	2	8	18	9	2		
Zirconium	Zr	40	2	8	18	10	2		
Niobium	Nb	41	2	8	18	12	1		
Molybdenum	Mo	42	2	8	18	13	1		
Technetium	Tc	43	2	8	18	14	1		
Ruthenium	Ru	44	2	8	18	15	1		
Rhodium	Rh	45	2	8	18	16	1		
Palladium	Pd	46	2	8	18	18	0		
Silver	Ag	47	2	8	18	18	1		
Cadmium	Cd	48	2	8	18	18	2		
Indium	In	49	2	8	18	18	3		

TABLE 3-1 (Cont.)

ELEMENT	SYMBOL	ATOMIC NUMBER	NUMBER OF ELECTRONS IN VARIOUS ENERGY LEVELS						
			K	L	M	N	O	P	
Tin	Sn	50	2	8	18	18	4		
Antimony	Sb	51	2	8	18	18	5		
Tellurium	Te	52	2	8	18	18	6		
Iodine	I	53	2	8	18	18	7		
Xenon	Xe	54	2	8	18	18	8		
Cesium	Cs	55	2	8	18	18	8	1	
Barium	Ba	56	2	8	18	18	8	2	
Lanthanum	La	57	2	2	18	18	9	2	
Cerium	Ce	58	2	8	18	20	8	2	
Praseodymium	Pr	59	2	8	18	21	8	2	
Neodymium	Nd	60	2	8	18	22	8	2	
Promethium	Pm	61	2	8	18	23	8	2	
Samarium	Sm	62	2	8	18	24	8	2	
Europium	Eu	63	2	8	18	25	8	2	
Gadolinium	Gd	64	2	8	18	25	9	2	
Terbium	Tb	65	2	8	18	27	8	2	
Dysprosium	Dy	66	2	8	18	28	8	2	
Holmium	Ho	67	2	8	18	29	8	2	
Erbium	Er	68	2	8	18	30	8	2	
Thulium	Tm	69	2	8	18	31	8	2	
Ytterbium	Yb	70	2	8	18	32	8	2	
Lutetium	Lu	71	2	8	18	32	9	2	
Hafnium	Hf	72	2	8	18	32	10	2	
Tantalum	Ta	73	2	8	18	32	11	2	
Tungsten	W	74	2	8	18	32	12	2	
Rhenium	Re	75	2	8	18	32	13	2	
Osmium	Os	76	2	8	18	32	14	2	
Iridium	Ir	77	2	8	18	32	15	2	
Platinum	Pt	78	2	8	18	32	17	1	
Gold	Au	79	2	8	18	32	18	1	
Mercury	Hg	80	2	8	18	32	18	2	
Thallium	Tl	81	2	8	18	32	18	3	
Lead	Pb	82	2	8	18	32	18	4	
Bismuth	Bi	83	2	8	18	32	18	5	
Polonium	Po	84	2	8	18	32	18	6	
Astatine	At	85	2	8	18	32	18	7	
Radon	Rn	86	2	8	18	32	18	8	
Francium	Fr	87	2	8	18	32	18	8	1
Radium	Ra	88	2	8	18	32	18	8	2
Actinium	Ac	89	2	8	18	32	18	9	2
Thorium	Th	90	2	8	18	32	18	10	2
Protactinium	Pa	91	2	8	18	32	20	9	2
Uranium	U	92	2	8	18	32	21	9	2
Neptunium	Np	93	2	8	18	32	22	9	2
Plutonium	Pu	94	2	8	18	32	23	9	2
Americium	Am	95	2	8	18	32	24	9	2
Curium	Cm	96	2	8	18	32	25	9	2
Berkelium	Bk	97	2	8	18	32	26	9	2
Californium	Cf	98	2	8	18	32	27	9	2
Einsteinium	E	99	2	8	18	32	28	9	2
Fermium	Fm	100	2	8	18	32	29	9	2
Mendelevium	Mv	101	2	8	18	32	30	9	2
Nobelium	No	102	2	8	18	32	31	9	2

Hence for the first main shell, where $n = 1$, $l = 0$, and m can have only a value of 0. In the second main shell, where $n = 2$, l can have the values 0 and 1. When $l = 0$, $m = 0$, and when $l = 1$, m may be -1, 0, or $+1$.

4. *Spin quantum number*, designated by s, takes into account the spin of an electron about its own axis in a clockwise or counterclockwise direction. The direction of the spin is designated by $+$ or $-$.

If we follow the above set of rules for quantum numbers, we may easily calculate the number of electrons in the various subshells of the atoms.

For the first shell where $n = 1$, $l = 0$, and $m = 0$, $s = +$ or $-$. Since, according to Pauli's exclusion principle, no more than one electron can have the same values for the four quantum numbers, the first shell can have only two electrons.

$$\left\{\begin{array}{l} n = 1,\ l = 0,\ m = 0,\ s = + \\ n = 1,\ l = 0,\ m = 0,\ s = - \end{array}\right.$$

For the second main shell

$$\begin{array}{rl} n = 2,\ l = 0,\ m = 0, & s = + \\ & s = - \\ & \text{2 electrons} \end{array}$$

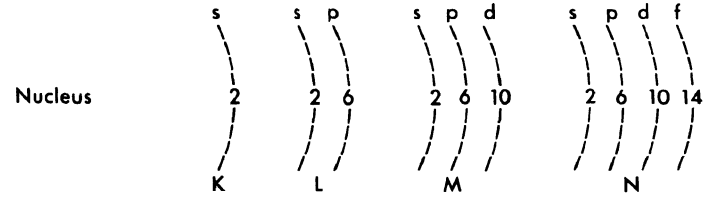
$$\begin{array}{rl} n = 2,\ l = 1,\ m = -1, & s = + \\ & s = - \\ m = 0, & s = + \\ & s = - \\ m = +1, & s = + \\ & s = - \\ & \text{6 electrons} \end{array}$$

The second shell, then, consists of two subshells, the first of which holds two electrons and the second six electrons, to make a total of eight. Following the same computation, it can be shown that the third main shell consists of three subshells, the first with 2 electrons, the second with 6 electrons, and the third with 10 electrons to make a total of 18. The fourth main shell would have 4 subshells holding 2, 6, 10, and 14 electrons respectively, to make a total of 32.

The various subshells are frequently designated by letters, s for the 2 electron subshell, p for the 6, d for the 10, and f for the 14. Thus the maximum electrons in the various subshells could be described as

2 s electrons
6 p electrons
10 d electrons
14 f electrons

The maximum number of electrons in the various subshells of the main energy levels may be shown in diagrammatic fashion.



may be shown from a consideration of the structures of several of the chemical elements. Let us first consider the elements lithium, sodium, and potassium (Figure 3–16).

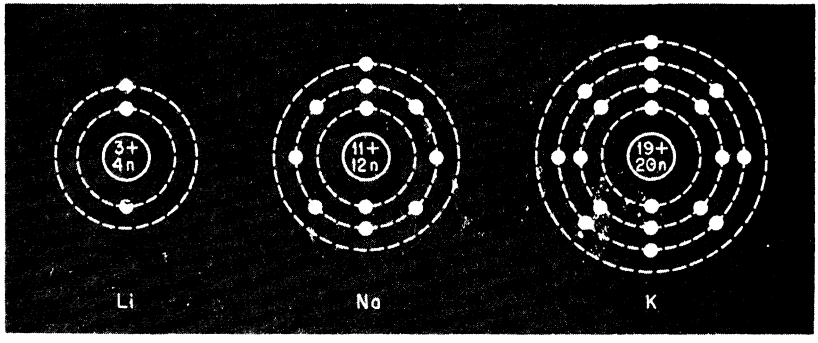


Figure 3–16 The outer structure of atoms of lithium, sodium, and potassium is similar; each atom has one outer or valence electron.

While there is little similarity in the inner structure of these atoms, we note that the outer orbit in each case contains one electron. Each of these atoms would tend to lose one electron, so that the valence of each would be +1. In a study of these elements later, we shall find that they are very similar in chemical properties. All are extremely active metals and this activity is related to the ease with which one electron can be removed from each of their atoms.

In a similar manner, consider the elements fluorine, chlorine, and bromine (Figure 3–17). Because of their similar structures—the outer structure of each atom contains seven electrons—we should expect fluo-

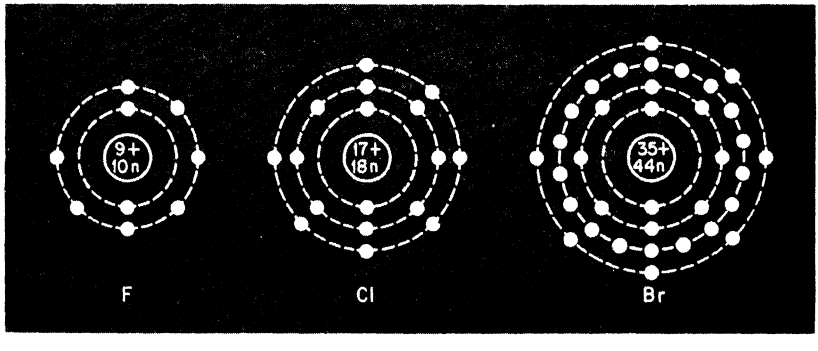


Figure 3–17 Atoms of fluorine, chlorine, and bromine each have seven electrons in the valence orbit.

rine, chlorine, and bromine to show similar chemical behavior. Each atom would tend to take on one electron to complete the quota of eight (in which case the valence of each would be -1). Since electrons are gained, we class these elements as nonmetals.

The elements helium, neon, and argon (Figure 3–18) have similar outer structures; the electrons in the outer orbit of each of their atoms

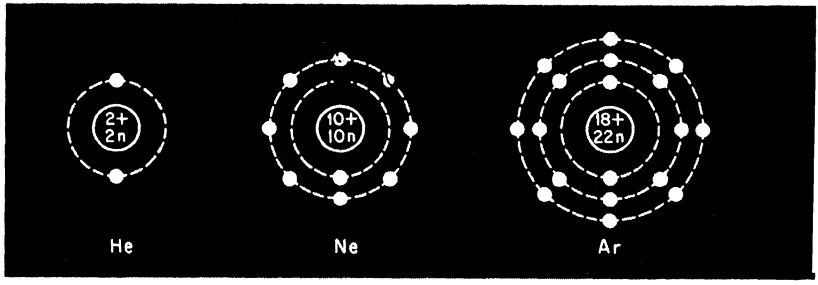


Figure 3–18 Structures of the inert gases, helium, neon, and argon.

represent a stable configuration. Helium has only two electrons in its outer orbit; however, we may recall that two electrons represent a stable configuration for the first orbit in the same way that eight electrons represent a stable configuration for the second orbit. Since these atoms have a completed outer orbit, we should expect these elements neither to gain nor lose electrons. Such is the case: these elements appear to be absolutely inert and show no tendency to combine with other elements. The fact that electrons are neither given up nor taken up means that there is no valence for these elements.

Isotopes We have pointed out that the mass of an atom is due almost entirely to the protons and neutrons present in the nucleus. Electrons have a negligible weight as compared to protons and neutrons. Since protons and neutrons have very nearly unit mass, it would seem that the weights of atoms (atomic weights) should be nearly whole numbers if we neglect the very small mass due to the electrons. However, an examination of the table of atomic weights (see inside of front cover of this book) shows that many of the elements have atomic weights which deviate considerably from whole numbers. For example, chlorine has an atomic weight of 35.46, and iron an atomic weight of 55.85.

Careful study has shown that most elements are really mixtures of two or more kinds of the element. Chlorine, for example, has been found to be made up of two kinds of chlorine, one of which has a mass number of 35 and the other of 37. In ordinary chlorine these two kinds are mixed in such a proportion as to give the average atomic weight of 35.46.

The two kinds of chlorine have the same chemical properties, but the masses of their atoms are different (Figure 3–19).

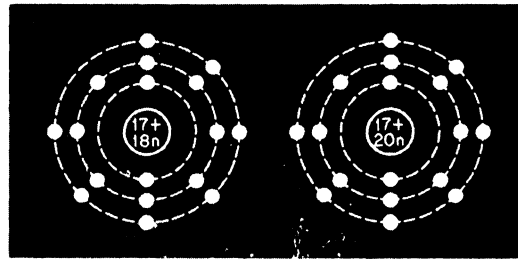


Figure 3–19 Isotopes of chlorine. Chlorine left has a mass number of 35; chlorine right has a mass number of 37.

We note that the outer structure of the two atoms is exactly the same; there are seven electrons in the outer shell of each, and so these atoms have the same chemical properties. The atomic number is the same for the two atoms; as a matter of fact, the only difference appears in the nucleus, which in the atom of mass number 35 has 18 neutrons and in the atom of mass number 37 has 20 neutrons. In reality we have the same element, chlorine, in both instances. Elements with the same atomic number but different mass numbers are termed *isotopes;* thus ordinary chlorine is a mixture of two isotopes.

Isotopes of most of the chemical elements are known at the present time. Table 3–2 (page 46) includes the stable isotopes of several of the elements. We may note that the number of isotopes of the elements varies from two isotopes in certain of the elements to ten isotopes in tin.

Measuring the mass of isotopes When gas molecules are bombarded with cathode rays, electrons are dislodged, leaving positively charged particles (ions). A beam of such ionized particles will be deflected on passage through magnetic and electrical fields. The magnitude of the deflection depends on various factors, such as the mass, charge and velocity of the positive ions and the dimensions of the apparatus. By keeping various factors constant, the mass of the positive particles may be determined. Such an arrangement is called a *mass spectrograph* (Figure 3–20).

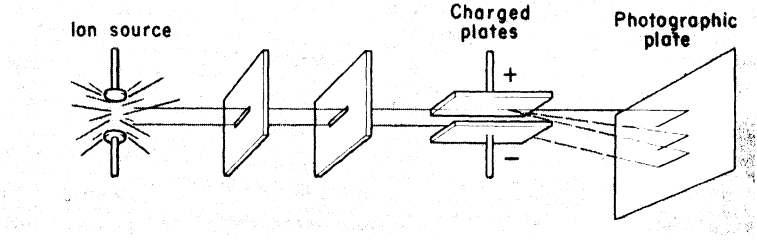


Figure 3–20 Mass spectrograph. Particles having a constant mass-to-charge ratio are focused at the same position on the photographic plate. By calibration of the apparatus, the isotopic masses may be ascertained.

TABLE 3–2 Isotopes of Selected Elements*

ELEMENT	ATOMIC NUMBER	ATOMIC WEIGHT	MASS OF ISOTOPES (MASS NUMBERS)
Hydrogen	1	1.008	1, 2, 3
Helium	2	4.003	4, 3
Lithium	3	6.940	7, 6
Beryllium	4	9.013	9, 8
Boron	5	10.82	11, 10
Carbon	6	12.011	12, 13
Nitrogen	7	14.008	14, 15
Oxygen	8	16.0000	16, 18, 17
Fluorine	9	19.00	19
Neon	10	20.183	20, 22, 21
Sodium	11	22.991	23
Magnesium	12	24.32	24, 25, 26
Aluminum	13	26.98	27
Silicon	14	28.09	28, 29, 30
Phosphorus	15	30.975	31
Sulfur	16	32.066	32, 34, 33
Chlorine	17	35.457	35, 37
Argon	18	39.944	40, 36, 38
Potassium	19	39.100	39, 41, 40
Calcium	20	40.08	40, 44, 42, 43
Chromium	24	52.01	52, 53, 50, 54
Manganese	25	54.94	55
Iron	26	55.85	56, 54, 57, 58
Cobalt	27	58.94	59, 57
Nickel	28	58.71	58, 60, 62, 61, 64
Copper	29	63.54	63, 65
Zinc	30	65.38	64, 66, 68, 67, 70
Arsenic	33	74.91	75
Bromine	35	79.916	79, 81
Silver	47	107.880	107, 109
Cadmium	48	112.41	114, 112, 110, 111, 113, 116, 106, 108
Tin	50	118.70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
Iodine	53	126.91	127
Barium	56	137.36	138, 137, 136, 135, 134, 130, 132
Platinum	78	195.09	195, 194, 196, 198, 192
Gold	79	197.0	197
Mercury	80	200.61	202, 200, 199, 201, 198, 204, 196
Lead	82	207.21	208, 206, 207, 204
Bismuth	83	209.00	209
Thorium	90	232.05	232
Uranium	92	238.07	238, 235

* Isotopes are listed according to decreasing abundance: the most abundant isotope is listed first. Their atomic masses are based on the most abundant oxygen isotope taken as 16. Atomic weights are based on the average oxygen atom taken as 16.

How atoms combine The theory of atomic structure gives us an explanation for the manner in which atoms combine. The valence electrons in the atom—that is, those electrons present in the outermost orbit—seem to be the determining factors in chemical combination. We learned that some atoms tend to give up electrons, while others tend to take up electrons; it would seem, then, that chemical combination

would be most likely to take place between atoms in which electrons could be given up by one atom and taken up by another. We would hardly expect combination to take place between atoms both of which tend to take up electrons, nor would we expect reaction to take place between atoms which tend to give up electrons. These suppositions based on the theory of atomic structure are borne out by actual fact. Metals, which tend to give up electrons, show little tendency to combine with one another, but they readily combine with elements (nonmetals) which will take up electrons. For example, since the sodium atom readily gives up an electron and a chlorine atom readily accepts an electron, we might expect sodium and chlorine to combine chemically. They actually do combine to form the compound sodium chloride. The change is represented diagrammatically in Figure 3–21. One electron

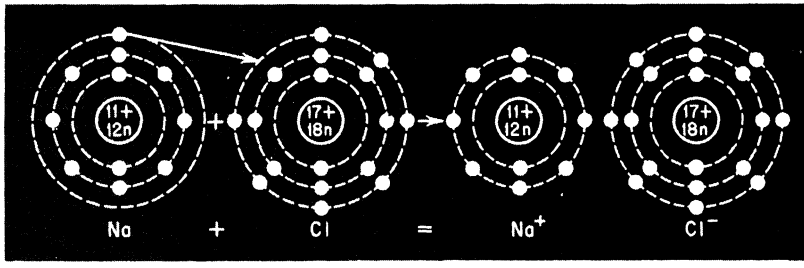


Figure 3–21 In the formation of the ionic compound, sodium chloride, an electron is transferred from the sodium atom to the chlorine atom.

is transferred from the sodium atom to the outer orbit of the chlorine atom, and in the compound sodium chloride thus formed, the two ions, Na^+ and Cl^-, are present. Such a compound as this in which ions exist is said to be *ionic* or *electrovalent;* and the transfer of electrons from one atom to another which results in the formation of ions is termed *electrovalence.*

The combination of one atom of magnesium with two atoms of chlorine to form the compound magnesium chloride, $MgCl_2$, is represented diagrammatically in Figure 3–22 (see page 48). In forming magnesium chloride, each of the chlorine atoms takes up one electron from the magnesium atom. The resulting compound is electrovalent or ionic and is composed of magnesium ions and chlorine ions in the ratio of one to two.

The structure of solid sodium chloride X-ray studies have shown that a crystal of sodium chloride is composed of sodium ions and chlorine

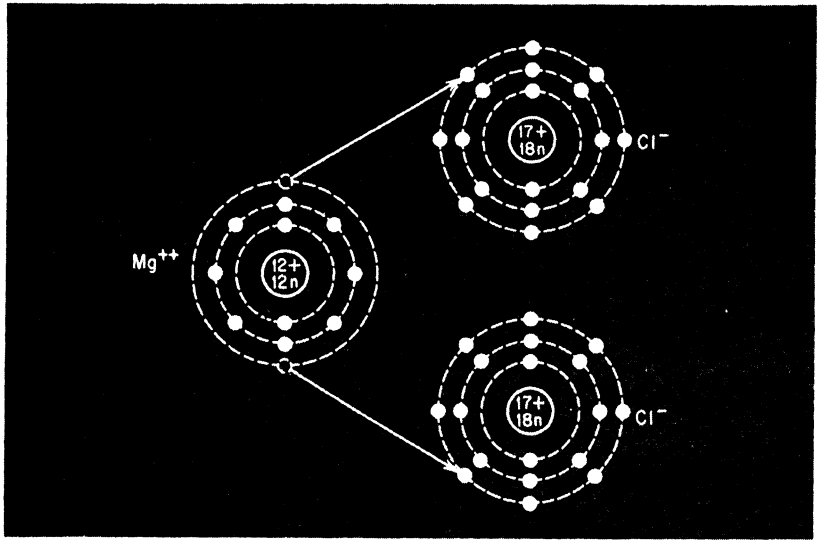


Figure 3–22 Magnesium chloride is an electrovalent compound; two electrons are transferred from a magnesium atom to two atoms of chlorine, resulting in the formation of magnesium and chlorine ions.

ions arranged in an orderly fashion, as shown in Figure 3–23, where the black dots represent chlorine ions and the light circles represent sodium ions. These ions are definitely oriented in relation to one another. If a sodium ion occupies the center of a cube, then a chlorine ion appears in the center of each of the six faces of the cube. All electrovalent compounds show an orientation of ions in the crystalline solid. When the solid is dissolved in water, the ions simply break away from the surface of the crystal and pass into the solution, where they are relatively widely separated and act as independent units.

It is incorrect to speak of a molecule of solid sodium chloride, since we cannot say that a sodium ion and a chlorine ion are paired to form a unit particle. Each of the ions in the crystal of sodium chloride is surrounded by six ions of opposite charge, and no one of the six ions is more closely associated with the central ion than any of the others. "NaCl" should be interpreted not as a molecule

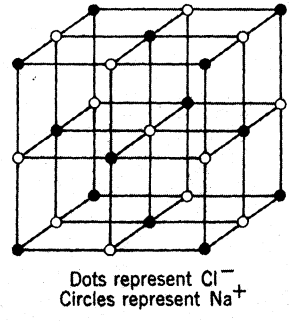


Figure 3–23 Structure of NaCl.

of sodium chloride, but rather as a formula which shows that this compound is composed of an equal number of sodium and chlorine ions. The formulas of all electrovalent compounds should be interpreted in this way.

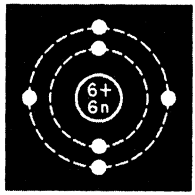


Figure 3–24 The carbon atom.

Sharing of electrons; covalence Chemical combination may take place without an actual transfer of electrons from one atom to another. For example, in the compound methane, CH_4, four atoms of hydrogen are combined with one atom of carbon. If we diagram the carbon atom, mass number 12 and atomic number 6 (Figure 3–24), we note that the outer orbit contains four electrons. We might assume that carbon would either take up or give up four electrons to reach a stable configuration, but actually the carbon atom does neither. Compounds of carbon are formed by a *sharing* of electrons. In the compound CH_4, each of the four hydrogen atoms shares its one electron with the carbon atom, while the carbon atom shares its four electrons with the four hydrogen atoms (Figure 3–25). No actual transfer of electrons takes place in this process, thus the compound is not ionic but molecular. Compounds formed by such a sharing process are termed *covalent* compounds.

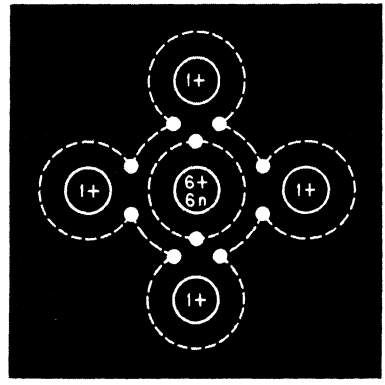
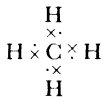


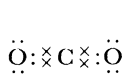
Figure 3–25 The methane, CH_4, molecule. Each of the four hydrogen atoms shares a pair of electrons with the carbon atom.

We may simplify Figure 3–25 by representing the compound CH_4 in the following manner:

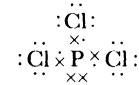


Only the outer structure of the atoms is shown; each of the dots represents one electron furnished by the carbon atom and each × represents an electron belonging to one of the four hydrogen atoms. A total of eight electrons surrounds the atom of carbon, which effectively fills its quota of eight electrons in the outer shell, and each hydrogen atom now has two electrons, which is a stable configuration for the first orbit. In this compound four *pairs* of electrons have been shared between the carbon and hydrogen atoms. The valence of the carbon is said to be four, since each pair of electrons represents one unit or bond of covalence.

Other typical examples of covalence are shown in the formulas below:



carbon dioxide



phosphorus trichloride

Note that each atom in these structures has a surrounding layer of eight electrons.

In some instances, electrons may be shared between two or more atoms of the same element. For example, two chlorine atoms combine to form a molecule of chlorine by a mutual sharing of electrons (Figure 3–26). Similar cases are O_2, H_2, N_2, F_2, and Br_2.

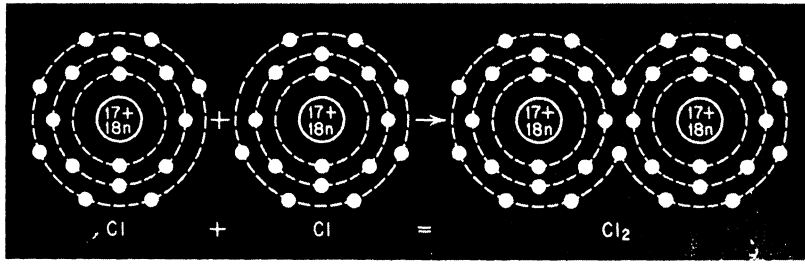


Figure 3–26 Two chlorine atoms share a pair of electrons to form a molecule of chlorine.

Molecular weights, formula weights, and moles The term *molecule* has a real significance when applied to covalent compounds, and we may properly refer to a molecular weight of the compound (weight of a molecule). The term has no significance when applied to electrovalent compounds, however; such compounds do not contain molecules. The parts of an ionic compound act as independent units, and molecular weight would lose its meaning if applied to compounds composed of ions. Hence we use the term *formula weight* in referring to electrovalent compounds. Thus, 2 NaCl indicates two formula weights of sodium chloride; 6 $Al_2(SO_4)_3$ indicates six formula weights of aluminum sulfate; and so on. The formula weight is obtained by adding up the atomic weights of the atoms indicated by the formula.

The term *formula weight* may actually be applied to all compounds whether electrovalent or covalent. When a formula weight stands for a molecule of a substance (covalent), the formula weight and molecular weight are the same. Thus, we may use the terms formula weight and molecular weight interchangeably for covalent substances. Like atomic weights and molecular weights, formula weights are *numbers* that express

relative weights. Formula weights may therefore be given in any unit of measure—grams, ounces, pounds, tons, and so on. Expressed in grams, the formula weight of a substance is called a *gram formula weight.* Chemists have extended the use of the terms *gram mole* and *mole* (see page 70) to include gram formula weights as well as gram molecular weights. Thus, a gram formula weight or mole of HCl is 36.5 grams; a gram formula weight or mole of NaCl is 58.5 grams; and so on.

EXERCISES

1 Define the terms: electron; proton; neutron; nucleus; nucleon; valence; electrovalence; covalence; ion; ionic compound; isotope; mass number.
2 Distinguish clearly between an atom and a molecule of an element.
3 Diagram the atoms of Be, Mg, and Ca. Would you expect these elements to exhibit similar chemical properties? Explain.
4 From our knowledge of modern atomic theory, would you expect the elements, neon and argon, to be active or inactive elements. Explain.
5 Show diagrammatically the formation of the ionic compounds: $CaCl_2$; MgO; AlF_3.
6 Carbon disulfide (CS_2) is a covalent compound. Show diagrammatically its formation. How many pairs of electrons are shared?
7 Explain the deviation of atomic weights of elements from whole numbers.
8 From a standpoint of atomic structure, how do metals differ from nonmetals?
9 How does an ion differ from an atom?
10 What is the relationship between the mass number of an element and the number of protons and neutrons in its atom?
11 Three isotopes of hydrogen are known, mass numbers 1, 2, 3. Diagram atoms of these three isotopes. How do they differ from one another?
12 Show by an electronic configuration (outer shell only) the arrangement of electrons in the following covalent compounds: PCl_3; CH_2Cl_2; H_2S; Al_2O_3; SiF_4.
13 Draw diagrammatic representations of Li^+, K^+, Ca^{++}, Al^{+++}, F^-, S^{--}.

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four

THE PERIODIC CLASSIFICATION OF THE ELEMENTS

Soon after Dalton's atomic theory had received wide recognition, many attempts were made to find a relationship between atomic weights and the chemical properties of the elements. It was well known that some elements were very similar to others in chemical properties—for example, chlorine, bromine, and iodine were very much alike in their chemical conduct, and sodium and potassium behaved similarly. It appeared possible that the elements could be grouped together in families on the basis of some common property. Accordingly, attempts were made to correlate atomic weights with the grouping of elements.

In 1829, Döbereiner arranged in groups of three (triads) several of the elements which were similar in chemical properties, and he showed that the atomic weight of one was approximately the mean of the other two. For example, chlorine (35), bromine (80), and iodine (127) constituted one such group. Br, with an atomic weight of 80, is approximately the mean of the atomic weights of Cl and I; that is, $\frac{35 + 127}{2} = \frac{162}{2} = 81$. Other "triads" of Döbereiner were:

Ca	40	S	32
Sr	87	Se	79
Ba	137	Te	127

In 1863, Newlands, an English scientist, pointed out that if the elements were arranged in order of increasing atomic weights, the eighth element was similar in chemical properties to the first, the ninth similar to the second, and so on, much like the octaves in music. New-

land's "law of octaves" did not hold for elements of higher atomic weights—with these, the interval between elements of similar properties seemed to be much greater than seven. Further, several elements, when placed according to Newland's arrangement, showed great dissimilarities to those elements with which a close similarity would be expected. There were so many discrepancies in the arrangement that Newland's idea was received with much ridicule, and it was many years before the significance of his discovery was appreciated.

In 1869, the Russian chemist Mendeleev extended Newland's ideas and was able to show a definite relationship between atomic weights and chemical properties. Mendeleev arranged the elements in order of increasing atomic weights and pointed out a recurrence of properties at very definite intervals or periods. These intervals were not always of the same length, but in each interval a gradual change in properties of the elements from the beginning to the end of the interval was apparent. On the basis of this arrangement, Mendeleev stated that *the properties of the elements are periodic functions of their atomic weights.* Since Mendeleev's time, the arrangement has remained basically unchanged, though it has undergone some modification. It is now known that the atomic number is a more fundamental property of an element than its atomic weight; hence, the modern periodic law is stated: *The properties of the elements are periodic functions of their atomic numbers.*

The periodic table Let us arrange the elements as Mendeleev did except that we shall use atomic numbers instead of atomic weights and shall include the inert elements, which were unknown when Mendeleev prepared his table. Omitting for the present the two lightest elements, hydrogen and helium, with atomic numbers of 1 and 2 respectively, we shall place in a horizontal row elements of atomic numbers 3 to 20 in order of increasing atomic numbers:

Element	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca
At. No.	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20

As we progress from lithium to fluorine, the properties of the elements change gradually from the very active metal lithium to the very active nonmetal fluorine. Neon, atomic number 10, which follows fluorine, is very inert or inactive and does not seem to fit logically in the arrangement next to the very active fluorine; however, we shall soon explain this seeming irregularity on the basis of modern atomic theory. Sodium, which follows neon, is a very active metal and similar to lithium; hence we may start a second horizontal row by placing sodium directly under lithium. Magnesium then comes next and is placed under beryllium; in chemical conduct, magnesium is very similar to beryllium. Contin-

uing this arrangement, aluminum falls below boron, silicon below carbon, and so on. When we reach potassium, we find an element very similar to lithium and sodium; hence we shall start a third horizontal row by placing K under Na. Our arrangement then assumes the form:

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca						

We find that elements falling in the same vertical column have very similar properties.

Hydrogen and helium may now be fitted into the scheme. Since He is an inert gas like neon and argon, it will be placed above these two elements. Hydrogen is more difficult to place, since it has few similarities to other elements. Although it does not have the properties of an active metal, it does exhibit a valence of 1 and may, therefore, be placed above sodium, which also exhibits a valence of 1. If we number the horizontal and vertical rows, our arrangement now becomes:

	I	II	III	IV	V	VI	VII	VIII
1.	H							He
2.	Li	Be	B	C	N	O	F	Ne
3.	Na	Mg	Al	Si	P	S	Cl	Ar
4.	K	Ca	..	..	.	.	..	..

The horizontal rows In the fourth horizontal row complications begin to appear, and it is necessary to modify our scheme somewhat. After potassium it is necessary to place eighteen elements in the arrangement before finding a recurrence of the properties of potassium. Some of the other elements following potassium show considerable differences in properties from the elements which appear just above them, and we are forced to observe dissimilarities as well as similarities in the vertical groups. Thus chromium differs considerably from sulfur, and manganese is very unlike chlorine. In the complete periodic arrangement shown in Figure 4–1, these elements are placed to one side of the row to indicate the dissimilarity. After manganese come the elements iron, cobalt, and nickel. Since these latter three elements are very similar to one another in properties but are unlike argon, they are placed together but set to the right of argon in Group VIII. Copper follows nickel, and since it is metallic and exhibits a valence of 1 like sodium and potassium, it is placed in Group I with these metals. It is set to the right, however, since it does differ considerably in many properties from both sodium and potassium. Similarly, the elements which follow copper are dis-

Figure 4–1 The periodic table, short form.

	I A	I B	II A	II B	III A	III B	IV A	IV B	V A	V B	VI A	VI B	VII A	VII B	VIII A	VIII B
1	1 H 1.0080														2 He 4.003	
2	3 Li 6.940		4 Be 9.02		5 B 10.82		6 C 12.011		7 N 14.008		8 O 16.000		9 F 19.00		10 Ne 20.183	
3	11 Na 22.991		12 Mg 24.32		13 Al 26.98		14 Si 28.09		15 P 30.975		16 S 32.066		17 Cl 35.457		18 Ar 39.944	
4	19 K 39.100		20 Ca 40.08		21 Sc 44.96		22 Ti 47.90		23 V 50.95		24 Cr 52.01		25 Mn 54.94		26 Fe 55.85	27 Co 58.94	28 Ni 58.71
		29 Cu 63.54		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 83.80	
5	37 Rb 85.48		38 Sr 87.63		39 Y 88.92		40 Zr 91.22		41 Nb 92.91		42 Mo 95.95		43 Tc 99		44 Ru 101.1	45 Rh 102.91	46 Pd 106.4
		47 Ag 107.880		48 Cd 112.41	49 In 114.82		50 Sn 118.70		51 Sb 121.76		52 Te 127.61		53 I 126.91		54 Xe 131.3	
6	55 Cs 132.91		56 Ba 137.36		57–71 *		72 Hf 178.50		73 Ta 180.95		74 W 183.86		75 Re 186.22		76 Os 190.2	77 Ir 192.2	78 Pt 195.09
		79 Au 197.0		80 Hg 200.61	81 Tl 204.39		82 Pb 207.21		83 Bi 209.00		84 Po 210		85 At 210		86 Rn 222	
7	87 Fr 223		88 Ra 226.05		89–102 **											

*Rare Earths

57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm 145	62 Sm 150.35	63 Eu 152.0	64 Gd 157.26	65 Tb 158.93	66 Dy 162.51	67 Ho 164.94	68 Er 167.27	69 Tm 168.94	70 Yb 173.04	71 Lu 174.99

**Radioactive Rare Earths

89 Ac 227	90 Th 232.05	91 Pa 231	92 U 238.07	93 Np 237	94 Pu 242	95 Am 243	96 Cm 245	97 Bk 249	98 Cf 249	99 E 253	100 Fm 254	101 Mv 256	102 No	

placed in each of the vertical columns. Each vertical column is now resolved into two columns and while there are similarities between the two columns in any vertical row of elements, there are also pronounced dissimilarities.

The horizontal rows are called *periods* and are numbered 1, 2, 3, and so on. The first three rows are termed *short periods*, since they contain only eight elements each (period 1 contains only the two elements hydrogen and helium). The fourth period is a *long period*, since it is made up of both the fourth and fifth horizontal rows, which contain a total of eighteen elements. These two rows are considered a single period because eighteen elements must be placed in the arrangement before coming to rubidium, which is the next element similar to lithium, sodium, and potassium. After leaving the fourth period, eighteen more elements, constituting another long period, must be placed before coming to cesium, which is similar to lithium, sodium, potassium, and rubidium. This period is followed by still another long period of thirty-two elements.

The periodic table is a continuous arrangement, and we should visualize it as placed on the surface of a cylinder rather than on a plane The elements then would assume positions as on a spiral, with elements of similar properties appearing in the same vertical line.

The vertical rows The vertical rows are called groups and are numbered from I to VIII. Each group is divided into two subgroups or families, one of which is called the *A* series and the other the *B* series. Thus in Group I, lithium, sodium, potassium, rubidium, and cesium constitute the *A* series; copper, silver, and gold constitute the *B* series. Similarly, in Group II, beryllium, magnesium, calcium, strontium, barium, and radium make up the *A* series; zinc, cadmium, and mercury make up the *B* series. The elements present in either the *A* or *B* series of one of the groups are often spoken of as a family of elements. Thus in Group I, the *A* series is referred to as the alkali family of metals; in Group II, the *A* series is known as the alkaline earth family; in Group VII, fluorine, chlorine, bromine, and iodine are known as the halogen family. The *A* series elements are referred to as *representative* or *main group* elements, and the *B* series as *transition* or *subgroup* elements.

The elements within either series of any one of the groups are very similar in chemical properties. Thus in series *A* of Group I, lithium, sodium, potassium, rubidium, and cesium exhibit marked similarities in properties: they are all very active metals, react vigorously with cold water, form strong bases, and have a characteristic valence of $+1$. The alkaline earth metals, including magnesium, calcium, strontium, and barium, likewise are similar chemically: they are distinctly metallic, are

very active, and exhibit a valence of +2. The halogens are a family of very active nonmetals, with a characteristic valence of −1.

The periodic table and modern atomic theory It is probably evident by this time that the periodic classification of the elements is intimately related to their atomic structures. The number of elements appearing in the short periods, 2 and 8, and the number in the long periods, 18 and 32, represent the maximum number of electrons in the various orbits of the atom.

The number of the group in the periodic table corresponds to the maximum number of electrons in the valence orbit of the atoms appearing in that group. Since eight is the maximum number of electrons in the valence orbit, eight is the maximum number of groups.

The rare gases of Group VIII*A* (except He, with a stable configuration of two) have a maximum of eight electrons in their outer orbits and therefore would be expected to be inert elements. The great activity of the nonmetals (Group VII*A*) on one side of the inert gases and the equally great activity of the alkali metals (Group I*A*) on the other side is readily explained by the ease with which these elements take up or give up an electron. The seeming irregularity of inert elements appearing between two active groups thus disappears.

Other seeming irregularities in the periodic arrangement may also be explained with the aid of modern atomic theory, though many of them are beyond the scope of this book. For example, the question might be asked: Why do the elements Fe, Co, Ni, which are much alike in properties, directly follow one another in the table? It will be recalled that elements of higher atomic weights may have incomplete inner shells of electrons (see Table 3–1, page 36). The inner shell of such an atom may add an electron while retaining the same number of electrons in the outer shell; this would mean another element with almost identical chemical properties. Thus the electronic configurations of Fe, Co, Ni are 2, 8, 14, 2; 2, 8, 15, 2; and 2, 8, 16, 2, respectively. While the outer shell in each case is the same, thereby accounting for similar properties, the third orbit differs by one electron in each instance and would account for slight differences in properties. The atomic numbers of Fe, Co, and Ni are 26, 27, 28, respectively; therefore these elements, although much alike chemically, should directly follow one another in the periodic arrangement. Many other examples could be cited in which incompleted inner orbits of atoms account for what appears to be an irregularity.

Long form periodic table Many modifications of the Mendeleev periodic chart have been proposed. One of the most useful arrangements is shown in Figure 4–2, in which each horizontal period begins with an

alkali metal (except the first period, which starts with hydrogen) and ends with an inert gas with a stable electronic structure, thus making a total of eighteen vertical groups instead of eight. This arrangement does away with subgroups, and each family of similar elements occupies a separate vertical column. The two short periods of eight elements each contain the representative or main group elements, and these groups are signified by the numbers I*A*, II*A*, etc. Elements which appeared as subgroups in the eight column chart of Mendeleev appear in separate groups designated by I*B*, II*B*, etc. Three of the groups, headed by Fe, Co, Ni, are included as VIII*B* elements. This arrangement is justified because of the close similarity in properties of these triads.

The *B* groups elements—that is, those which fit into the chart between Groups II*A* and III*A*—are termed *transition* elements. These elements have essentially the same outer configuration or valence shell (one or two electrons), but the next inner shell contains different numbers of electrons, and this incomplete shell gives rise to differences in properties of the transition elements. For example, after calcium in Group II*A*, electrons start to fill in the incomplete third orbit (capacity 18), while the fourth or outer orbit remains essentially unchanged. Thus Sc has 9 electrons in the third orbit, Ti has 10, V has 11, and so on. Added electrons continue to fill in this orbit until a stable configuration of 18 is reached. After Zn, electrons add to the outer shell—Ga with 3, Ge with 4, and so on.

After Ba in the arrangement, electrons start filling the fourth orbit from 18 to 32 electrons (capacity 32). These elements, atomic numbers 57–71, constitute a transition series within a transition series and are referred to as the *lanthanide* series or *rare earth* series. A second rare earth series, called the *actinide* series, starts after Ra. These series are placed below the main table.

From the chart it may be noted that four different classes of elements may be listed, as follows:

1. Elements in which all orbits have stable configurations[1] of electrons. These include the rare gases, He, Ne, Ar, and so on
2. Elements in which all orbits except the outermost have stable configurations. These are the main groups or *A* groups of elements. Electrons are filling the outer orbit.
3. Elements in which all orbits except the two outermost have stable configurations. These are the subgroups or *B* groups of elements. Electrons are filling from 8 to 18, into the next to outermost shell

[1] A stable configuration means 8, 18, or 32 electrons (except first orbit, which has 2 electrons)

last of which is the most active of the metals. The members of the group are very much like one another, however, in that all are quite active.

The fact that the members of a given family do not possess exactly the same chemical properties, even though the outermost orbits contain the same number of electrons, is explained by the fact that the internal configuration will have some effect, though usually slight, on the properties of the atom.

The halogens in Group VII*A* are very active nonmetals, but again we may observe a gradual change in activity from fluorine at the top of the group to iodine at the lower part. Fluorine is the most active and iodine is the least active; hence activity decreases as the atomic weights increase.

In Group V*A* we may also observe a gradual change in properties from top to bottom. Nitrogen at the top is a typical nonmetal, while bismuth at the bottom is usually classed as a metallic element. The elements in between exhibit more marked metallic than nonmetallic properties as the atomic weight increases.

It is interesting that modern atomic theory will explain the slight differences in properties of elements within a given family, as well as pronounced differences in properties of elements in different families. How this is done is in part explained in the next section.

Physical and chemical behavior of elements Although the student is not as yet familiar with the properties of specific elements, it is appropriate to make a few generalizations relating chemical and physical behavior of atoms to certain fundamental properties.

One of the most important properties of an atom which influences its behavior is its *size*. We would expect that as orbits or shells are added in the structure of atoms, the size would increase, and this is true. In the periodic classification we may note that the elements in a given period (horizontal row) have the same number of shells—for example one shell for period 1 elements H and He, two shells for period 2 elements, and so on. As a new period is started, a shell is added to the structure. It is apparent, then, that the vertical columns which represent families of elements will show a gradual increase in size in going from top to bottom as electron shells are added. Thus Fr is the largest atom of Group I*A*, Ra the largest of Group II*A*, and so on.

The change in size of atoms in a given period (horizontal row) is somwhat less obvious. In progressing from the left-hand side to the right-hand side in a given period, the atoms gradually decrease in size for example, the sodium atom in Group I*A* is larger than the magnesium atom in Group II*A*, and the latter atom in turn is larger than the aluminum atom in Group III*A*. The explanation of this decrease in

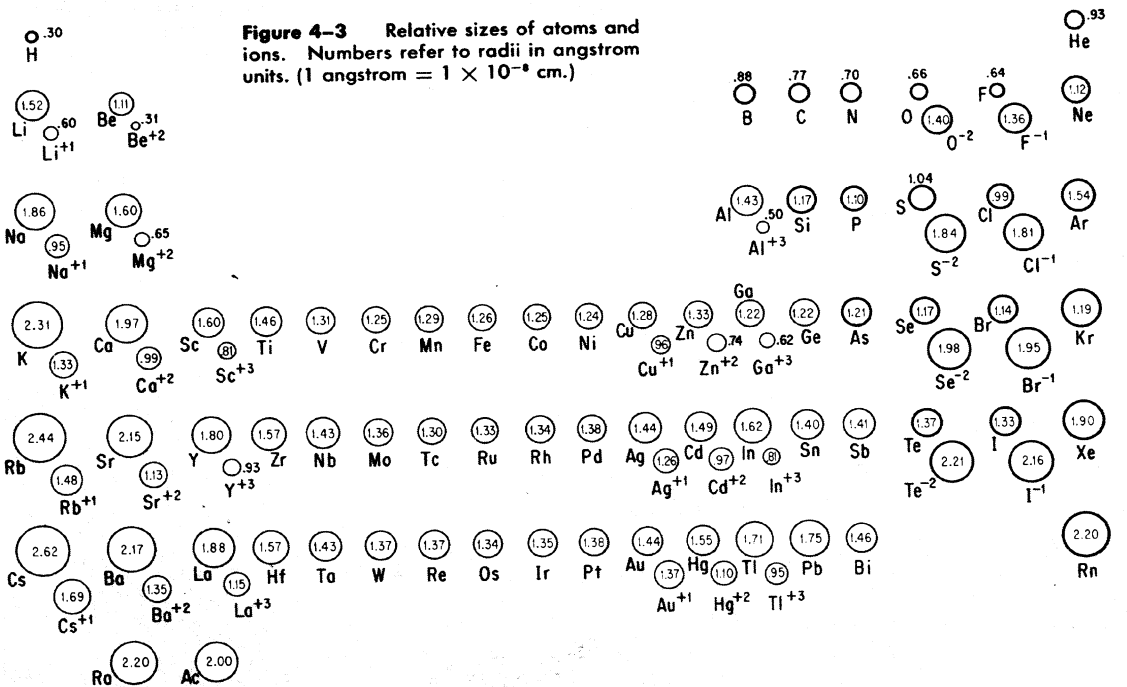


Figure 4–3 Relative sizes of atoms and ions. Numbers refer to radii in angstrom units. (1 angstrom = 1×10^{-8} cm.)

size is as follows: As the atomic number increases, the nuclear charge increases; this increased nuclear charge attracts the electrons in the shells more forcibly, pulling the shells in closer to the nucleus and thus shrinking the atom in size. Figure 4–3 shows diagrammatically the relative sizes of atoms and ions.

On the basis of these considerations, atoms of Group I*A* elements, the alkali metals, are the largest, and this would in part account for their lightness or low density. Group II*A* elements would possess a somewhat larger density because the atoms are somewhat smaller. In progressing from top to bottom in a given family the density increases since the atomic weight increases faster than atomic size Hence the heavier elements would appear toward the bottom of the table.

Ionization potential Another important property in determining chemical behavior of an atom is the ease with which it gives up electrons. Energy is required to pull away an electron, since the positively charged nucleus of an atom attracts all the electrons. The energy required to remove an electron completely is expressed as an *ionization potential,* which is the strength of an electric field measured in volts necessary to overcome the attraction of the nucleus and result in the formation of a positive ion. Elements in group I*A* have low ionization potentials, and since one electron is removed with little energy, these elements are very active. As the number of electrons in the outer orbit increases, the energy required for removal of electrons increases—that is, the ionization potential increases. See Figure 4–4. Group VIII*A* elements (inert gases) have the highest ionization potentials of all elements and are therefore the most stable.

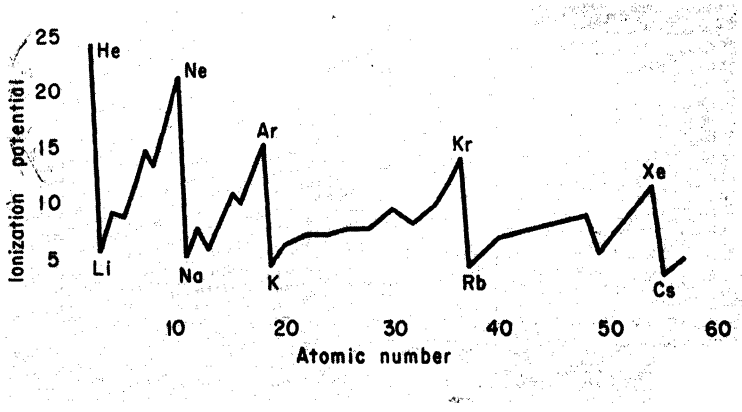


Figure 4–4 Ionization potentials (in electron volts) of the elements.

In the case of elements with nearly completed orbits, such as those in group VII*A* (the halogens), chemical behavior is determined largely by the tendency to take up electrons. This tendency, expressed as *electron affinity*, represents the energy given up by the atom in forming a negative ion. Elements of group VII*A* have high electron affinities and are therefore very active nonmetals.

As the tendency to give up electrons becomes less—that is, higher ionization potentials—in going from left to right in the table, the metals become less active: group II*A* metals are less active than group I*A*, and group III*A* metals are less active than those of group II*A*. When we reach a point toward the middle of the table, where electrons are more readily accepted and the element is more nonmetallic in properties, the activity increases up to the halogen family, group VII*A*. In a given period, the activity of metallic elements gradually decreases and the activity of nonmetallic elements gradually increases; thus, Mg is less active than Na but more active than Al; and S is more active than P but less active than Cl. We would reasonably expect less energy to be required in removing one electron from Na than in removing two electrons from Mg since, after one electron is taken away, it would be more difficult to remove a second one because of the increased attraction of the nucleus for the remaining electrons. Mg in turn should be able to give up two electrons more easily than Al to give up three, and so on. Similarly, it is reasonable to say that Cl can pick up one electron more readily than S can pick up two, or P three, since as electrons are picked up, the attraction of the nucleus for electrons lessens.

Now let us consider relative activity within a family of elements. Such elements have the same outer configuration; for example, members of Group I*A* all have a single electron in the outer shell. As shells are added and the outer electron is moved farther from the positively charged nucleus, the attraction between the nucleus and the outer electron becomes less and the latter is more easily removed. Hence the activity increases in going from top to bottom in a given group of metals; K, for example, is more active than Na and less active than Rb. In the case of nonmetals such as the halogen family, Group VII*A*, where the tendency is to acquire electrons, the smaller atoms will have a greater attraction for electrons since the distance between the nucleus and the outer shell is less: F is more active than Cl, which is more active than Br, and so on. In general, the activity of nonmetals decreases in going from top to bottom in the periodic table.

The change in chemical properties of the transitional elements—those in the *B* groups of the table—is much less pronounced than in the *A* series. That is because the added electrons are filling incompleted

inner shells rather than going into the outer shell, which is much more sensitive to releasing or acquiring electrons.

Stability of compounds We may think of a stable compound as one which is difficult to decompose. Although undoubtedly many factors contribute to the stability of a substance, two of the most important are the ones discussed above; namely, the size of the atoms or ions and the consequent closeness of approach to one another, and the ease of electron removal or electron affinity. The ease of electron removal or electron affinity is the more important criterion in predicting stability; thus the most stable compounds would be those composed from elements which most easily give up electrons and from elements with a high electron affinity. Compounds of the alkali metals with the halogens are very stable, since the former elements readily give up electrons and the latter readily acquire them. On the basis of position in the periodic table we might expect KCl to be more stable than NaCl; KCl more than KI; $BaCl_2$ more than $CaCl_2$; HF more than HCl; H_2O more than H_2S; BaF_2 more than MgI_2; and so on.

In ionic compounds (those formed by a transfer of electrons), the size of the ion is more important than size of the atom. The closeness of approach of an ion to a neighboring ion will determine the attractive forces between the ions and hence the tendency to remain in close association (stability). Obviously an ion formed by release of electrons would be smaller than the atom, since the outer shell is destroyed or removed; furthermore, on removal of an electron the nucleus exerts a stronger attraction for the remaining electrons and tends to pull them closer to the nucleus. As we progress in a given period from left to right in the periodic table, the ions become smaller as electrons are given up; thus, Mg^{++} is smaller than Na^{+}, and Al^{+++} is smaller than Mg^{++}, and so on. However, when electrons are taken up to form negative ions the size increases, since the attraction of the nucleus is distributed over a greater number of electrons than in the neutral atom and the ion tends to swell or expand. We would expect Cl^{-} to be smaller than S^{--} which in turn would be smaller than P^{---}. See Figure 4–3.

Division into metals and nonmetals While there is often no sharp line of division between metals and nonmetals, those elements which are classed as metallic always exhibit a positive valence, whereas nonmetals usually show a negative valence.

In the short form Mendeleev table, a diagonal line drawn from the upper left-hand corner to the lower right-hand corner divides the elements into two sections. Most of the elements falling below the line have metallic properties, while those above usually exhibit nonmetallic properties. Those elements falling on or near the diagonal usually

exhibit properties of both metals and nonmetals and are termed *metalloids.*

In the long form periodic table, the nonmetals appear to the far right and toward the top. The metallic elements are in far greater number, including Groups I*A*, II*A*, all of the *B* series or transition elements, and the heavier elements in Groups III*A* to V*A*. The transition elements (the *B* series), including the lanthanide and actinide series, would be expected to exhibit a positive valence and metallic characteristics, since none of these elements possesses more than two electrons in the outer orbit. The position of an element in the table is a good indication of its general physical properties; for example, the low melting metals such as Cd, Ga, Hg, Pb, and Sn appear just to the left and below the nonmetallic elements; the metals in the middle of the table, such as Fe, Co, Ni, Pd, Pt, and Au, are ductile and malleable; metals in Groups III*B* to VII*B* tend to be hard and brittle, with high melting points; and metals in Groups I*A* and II*A* are light and low melting.

Uses of the periodic table For the chemist, the periodic table is a very useful classification of the elements. Instead of learning the properties of more than 100 elements, the chemist may master the general properties of each of the groups. If an element is known to be in a certain group, then by association with other members of the same group, the properties of which are known, its properties may be predicted. As a matter of fact, before the discovery of many of the chemical elements, the properties of the unknown elements were predicted with a high degree of accuracy. Thus Mendeleev predicted the properties of eka-silicon, later named germanium, many years before it was discovered. How accurate his predictions were is evident from Table 4–1.

TABLE 4–1 Comparison of Predicted Properties of Eka-silicon with Known Properties of Germanium

PROPERTY	EKA-SILICON	GERMANIUM
Atomic weight	72	72.6
Characteristic valence	4	4
Density	5.5	5.47
Color	Gray	Grayish-white
Reaction with water	Will decompose steam with difficulty	No reaction with steam
Action of acids	Slight	No reaction with HCl, oxidized by HNO_3
Action of bases	Slight	No reaction
Properties of the chloride	Boiling point below 100°, density 1.9	Boiling point 86°, density 1.9
Properties of the oxide	White, refractory, density 4.7	White, refractory, density 4.703

Imperfections of the classification Despite its great usefulness, the periodic classification is not without its faults.

Hydrogen perhaps does not fit into the table entirely satisfactorily. It is usually placed in Group I*A*, since it does possess one valence electron (like the alkali metals) and combines with nonmetals such as the halogens and sulfur. However, the latter compounds are covalent in character and not like the electrovalent combination of alkali metals with the halogens. In some respects hydrogen resembles the members of Group VII*A*, since it appears to be nonmetallic in character and furthermore, like the halogens, may combine with the alkali metals to form ionic compounds. For example, sodium hydride (NaH) is ionic in character, like NaCl.

In the short form table, in which the *A* and *B* series fall within the same group, there is valid criticism that the two series are not similar in many respects. For example, Group I contains the most active metals—potassium, sodium, and so on—and also the very inactive metals—silver, copper, and gold. This objection is removed in the long form table, in which each series of elements is in a separate group.

In either table, a group of fifteen elements with very similar chemical and physical properties—the *rare earth* or *lanthanide* series, must be fitted into a single space. Of course, the long form table could be further elongated to take care of these elements, but this would make the table unwieldy without adding to its usefulness. In any event, these elements should perhaps be considered separately, since they constitute a unique group as far as structural characteristics are concerned. In these elements, as successive electrons are added, the electrons enter a deep inner orbit (the fourth) until the orbit has its capacity of thirty-two electrons, while the two outer orbits remain unchanged. Consequently, the chemical characteristics of these elements, which are governed mainly by the valence electrons in the two outer orbits, are very nearly the same for this entire group of fifteen elements. A second rare earth series, called the *actinide* series, starts with element number 89; its members, like those of the lanthanide series, are very similar in chemical behavior.

However, the advantages of making possible the study of the properties of a group of similar elements rather than the more tedious study of each element far outweigh any disadvantages of the periodic classification.

EXERCISES

1 From the standpoint of modern atomic theory, why would you expect the elements calcium, strontium, and barium to fall in the same group in the periodic table?

2 Point out two or three irregularities which would appear in the periodic table

if the elements were arranged in order of increasing atomic weights rather than increasing atomic numbers.

3 List four defects in the periodic table of Mendeleev.

4 On the basis of position in the periodic table, how would you expect the following atoms and ions to compare in size? Explain your answer in each case: (*a*) Li and Be, (*b*) Li^+ and Be^{++}, (*c*) Ca^{++} and Sc^{+++}, (*d*) S^{--} and Br^-, (*e*) Cu^{++} and Zn^{++}, (*f*) Cl^- and Ar, (*g*) Ra^{++} and Ba^{++}, (*h*) Al and Ga, (*i*) Si and S, (*j*) Zn^{++}, Cd^{++} and Hg^{++}, (*k*) O^{--} and F^-.

5 Which of the compounds in each of the following pairs would you expect to be more stable? Give reason for answer in each case: (*a*) LiBr and LiI, (*b*) CaS and $CaCl_2$, (*c*) HF and HCl, (*d*) CsBr and KCl, (*e*) HBr and HF, (*f*) H_2Se and H_2S, (*g*) H_2O and H_2S, (*h*) $AlCl_3$ and BF_3.

6 What is the fundamental difference in structure (electronic configuration) between the *A* and *B* divisions of elements in the periodic classification?

7 What changes in activity take place with increasing atomic weight of the

(*a*) metals in a given group?

(*b*) nonmetals in a given group?

(*c*) elements in a given horizontal series?

8 From the data recorded for the families of elements listed below, predict the properties of the last member of each family:

ELEMENT	DENSITY	MELTING POINT	BOILING POINT	COLOR
S	1.96	119	445	yellow
Se	4.5	217	680	gray
Te				
F		−223	−188	pale yellow
Cl		−102	− 35	greenish-yellow
Br	3.4	− 7	59	brown
I	4.93	113	183	black
At				
				SOL. OF SULFATE g./100g. H_2O
Mg	1.74	650	1107	27.
Ca	1.55	851	1487	.208
Sr	2.6	757	1384	.01
Ba	3.78	850	1640	.00024
Ra				

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five FORMULAS AND EQUATIONS

The meaning of a formula The chemist uses formulas to show the composition of compounds. Formulas are made up of the proper combination of symbols for the elements which are contained in the compound; at the same time the number of each kind of atom in the compound is indicated in the formula by placing subscripts after the symbols. Thus, the formula for sugar is $C_{12}H_{22}O_{11}$, since each molecule of sugar contains 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen. If only one atom of an element is present in a molecule of a compound, no subscript is necessary. A molecule of water, which is made up of two atoms of hydrogen and one atom of oxygen, is written as H_2O. *A subscript applies only to the element or radical of which it is the subscript.* A chemical formula, then, is considerably more than an abbreviation for a chemical compound; it indicates not only the compound in question but its composition as well.

A formula also permits us to calculate the molecular weight or the formula weight of the compound. Sulfuric acid has the formula H_2SO_4, which tells us that sulfuric acid is composed of 2 parts by weight of hydrogen (2×1, where 1 is the atomic weight of hydrogen), 32 parts by weight of sulfur (1×32, where 32 is the atomic weight of sulfur), and 64 parts by weight of oxygen (4×16, where 16 is the atomic weight of oxygen). Thus the weight of the molecule of sulfuric acid is the sum of the weights of the constituent atoms, $2 + 32 + 64 = 98$. Ninety-eight is the molecular weight or formula weight of the compound. Ninety-eight grams of sulfuric acid would be a gram molecular weight or mole of the compound; 98 grams of sulfuric acid contains 2 grams of hydrogen (2 gram atoms), 32 grams of sulfur (1 gram atom), and 64 grams of oxygen (4 gram atoms).

A coefficient placed before a formula multiplies every constituent of the formula which it precedes. For example, 3 $C_{12}H_{22}O_{11}$ denotes three molecules of sugar, which contain 36 atoms of carbon, 66 atoms of hydrogen, and 33 atoms of oxygen.

To illustrate further the information which may be derived from a formula, consider HNO_3, which represents one molecule of nitric acid. We derive the following from this formula:

1 One molecule of nitric acid contains 1 atom of hydrogen, 1 atom of nitrogen, and 3 atoms of oxygen.
2 Nitric acid is composed of 1 part by weight of hydrogen (see atomic weights), 14 parts by weight of nitrogen, and 48 parts by weight of oxygen.
3 The molecular weight of nitric acid is 63 (1 + 14 + 48 = 63).
4 One gram-molecular weight or formula weight—that is, one mole—of nitric acid, 63 grams, contains 1 gram of hydrogen (1 gram atom); 14 grams of nitrogen (1 gram atom); and 48 grams of oxygen (3 gram atoms).

Chemical equations When iron powder and sulfur powder are heated together, iron combines with sulfur to form the compound ferrous sulfide. This chemical change might be represented by the word statement:

Iron plus sulfur produces ferrous sulfide.

It is more convenient to represent the chemical change in the form of a *chemical equation* by using the symbols for the substances taking part in the chemical change to express the above relations as follows:

$$Fe + S = FeS$$

The symbols appearing to the left of the = sign are symbols for the *reactants*—that is, those things entering into the chemical change. The formulas to the right of the = sign represent the *products*, those things produced as a result of the chemical change. The chemist uses the word *reaction* synonymously with *chemical change.*

The above representation for the reaction between iron and sulfur is a true equation: the left side is equal to the right side in that one atom of iron and one atom of sulfur appear on each side. The equation is said to be balanced, since the same number of atoms of each kind appear on each side. The = sign is often replaced by an arrow, which indicates the direction in which the chemical change is taking place; thus

$$Fe + S \rightarrow FeS$$

The chemical equation, like the chemical formula, has a great deal more significance to the chemist than does a word statement. The equation representing the reaction of iron and sulfur gives us the following information:

1 One atom of iron combines with one atom of sulfur to produce one formula weight of ferrous sulfide, or one gram atom of iron combines with one gram atom of sulfur to produce one gram formula weight (one gram mole) of ferrous sulfide.
2 55.85 (see atomic weights) parts by weight of iron combine with 32.066 parts by weight of sulfur to form 87.916 parts by weight of ferrous sulfide.

The formula must always express the true composition of the substance. In the equation for the reaction of hydrogen and oxygen to form water, the formula for hydrogen must be written as H_2 and not as H, since in the free state two hydrogen atoms unite to form a unit particle (molecule) of free hydrogen; similarly, the formula for oxygen is O_2, since in the free state two atoms always unite to form a unit particle (molecule) of free oxygen. Therefore, in the equation for the reaction of hydrogen and oxygen the elements should be written as follows:

$$H_2 + O_2 \rightarrow H_2O \text{ (not balanced)}$$

It is evident that this equation is not *balanced,* since there are two atoms of oxygen on the left side of the equation and only one atom of oxygen on the right side. Since the formula of a compound is fixed and definite, we cannot write H_2O_2, or in any other way change the formula for water. We may, however, balance the equation as follows, since a number placed in front of a formula multiplies all the constituents in the formula which it precedes:

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

The coefficients (the numbers in front of the formulas) represent the number of molecules or formula weights undergoing chemical change. If a single molecule enters into a change, no number is placed in front of the formula. The above equation tells us that two molecules of hydrogen combine with one molecule of oxygen to form two molecules of water, or that two moles of hydrogen (4 grams) combine with one mole of oxygen (32 grams) to give two moles of water (36 grams).

Ordinary sugar, when heated, decomposes into carbon and water, and the change may be represented by the equation

$$C_{12}H_{22}O_{11} \rightarrow C + H_2O \text{ (not balanced)}$$

To balance the equation, 12 atoms of carbon are necessary; hence the number 12 is placed in front of the symbol for carbon. To balance the hydrogen and oxygen atoms, a coefficient of 11 is needed in front of the formula for water:

$$C_{12}H_{22}O_{11} \rightarrow 12\,C + 11\,H_2O$$ [1]

Balancing of equations is largely a matter of trial and error; small coefficients should be tried until a balance is obtained. A good general rule to follow is to balance elements other than hydrogen and oxygen first; then to balance hydrogen atoms, if present; and finally to balance oxygen atoms, if present. It will be found that the oxygen atoms are usually balanced when the others have been taken care of.

Radicals In many chemical changes certain groups of atoms may function as a unit, in which case the same group or combination of atoms will appear on both sides of an equation. For example, in the reaction

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

one atom of sulfur and four atoms of oxygen make up the sulfate group, SO_4, which remains intact in the change. Such groups are termed *radicals* and may be treated as units in the chemical equation. Other such groups or radicals are hydroxide, OH; nitrate, NO_3; carbonate, CO_3; ammonium, NH_4; and phosphate, PO_4.

In writing a chemical formula of a compound one formula weight of which contains more than one unit of a radical, it is customary to enclose the radical in parentheses and indicate the number of units of the radical in the formula weight by placing the proper subscript after the parentheses. For example, calcium hydroxide is written as $Ca(OH)_2$ rather than as CaO_2H_2, which would express the true composition of the compound equally well. Enclosing a radical in parentheses enables us to recognize immediately that such a group functions as a unit. The subscript outside the parentheses applies to everything within the parentheses: the subscript 2 in $Ca(OH)_2$ indicates two atoms of oxygen as well as two atoms of hydrogen present in each formula weight. A formula weight of aluminum sulfate, $Al_2(SO_4)_3$, contains 2 atoms of aluminum, 3 atoms of sulfur, and 12 atoms of oxygen. A coefficient placed in front of the formula necessarily multiplies everything in the formula; thus, 3 $Al_2(SO_4)_3$ would contain 6 atoms of aluminum, 9 atoms of sulfur, and 36 atoms of oxygen.

Some types of chemical change We are not prepared at this point to discuss the many types of chemical change which may occur, but we

[1] It would be incorrect to make the 12 a subscript of the carbon, thus C_{12}, since this would imply that twelve atoms of carbon remain together as a unit particle.

can indicate here the more important types and study them in detail later. Most chemical changes may be classified as one of the following four types:

(*a*) *Combination.* Many compounds are formed by direct *combination* of two or more elements or compounds. The following equations are examples:

$$\mathrm{Fe + S \rightarrow FeS}$$
$$\mathrm{CaO + CO_2 \rightarrow CaCO_3}$$
$$\mathrm{2\,Na + Cl_2 \rightarrow 2\,NaCl}$$

We note in the above that a *single* substance is formed by a combination of two substances. The combining substances may not in every case be elements; for example, in the second equation above, two compounds, calcium oxide and carbon dioxide, are the reactants. A *combination* reaction, then, is one in which a *single* substance is produced by the union of two or more substances.

(*b*) *Decomposition.* Water may be broken down into hydrogen and oxygen by means of an electric current according to the equation

$$\mathrm{2\,H_2O \rightarrow 2\,H_2 + O_2}$$

Sugar, when heated, decomposes to form a charred mass, which is essentially carbon, and water in the form of steam. The equation for the change is represented:

$$\mathrm{C_{12}H_{22}O_{11} \rightarrow 12\,C + 11\,H_2O}$$

These are *decomposition* chemical changes, reactions in which two or more substances are produced from a *single* substance. This type of change is the reverse of combination. A compound may not always decompose into its constituent elements; this is illustrated in the decomposition of sugar, where water, a compound substance, is one of the products.

(*c*) *Replacement or substitution.* In this type of chemical change one element replaces another from its compounds. For example, in

$$\underset{\text{hydrochloric acid}}{\mathrm{Zn + 2\,HCl}} \rightarrow \underset{\text{zinc chloride}}{\mathrm{ZnCl_2}} + \mathrm{H_2}$$

zinc replaces, or substitutes for, the hydrogen in the compound hydrochloric acid.

If chlorine is passed into a solution of sodium bromide, the chlorine replaces the bromine:

$$\underset{\text{sodium bromide}}{\mathrm{2\,NaBr}} + \underset{\text{chlorine}}{\mathrm{Cl_2}} \rightarrow \underset{\text{sodium chloride}}{\mathrm{2\,NaCl}} + \underset{\text{bromine}}{\mathrm{Br_2}}$$

(*d*) *Double decomposition.* A solution of silver nitrate reacts with a solution of sodium chloride according to the equation

$$\underset{\text{silver nitrate}}{AgNO_3} + \underset{\text{sodium chloride}}{NaCl} \rightarrow \underset{\text{silver chloride}}{AgCl}\downarrow + \underset{\text{sodium nitrate}}{NaNO_3}$$

There has been a double exchange, since silver and sodium have both exchanged position. Such a chemical change is termed *double decomposition.*

In the above reaction the silver chloride[2] is insoluble and *precipitates* from the solution, or, in other words, separates from the solution as a solid. The sodium nitrate, being soluble, remains in solution and may be separated from the insoluble AgCl by filtration (Figure 5–1).

Calculation of percentage composition from a formula Since the formula of a compound is fixed, we may calculate the per cent of each element present from a consideration of the parts by weight of each element in one formula weight of the compound. Consider the formula of water, H_2O. The atomic weights of hydrogen and oxygen are 1 and 16 respectively; hence the formula weight of H_2O is 18. One formula weight of water is made up of 18 parts by weight, 2 parts of which are hydrogen and 16 parts of which are oxygen. The fraction of hydrogen is $\frac{2}{18}$ and the fraction of oxygen is $\frac{16}{18}$. These fractions may, of course, be converted to percentage by multiplying by 100. Thus the per cent of hydrogen in water is $\frac{2}{18} \times 100 = 11.1$ per cent, and the per cent of oxygen is $\frac{16}{18} \times 100 = 88.9$ per cent.

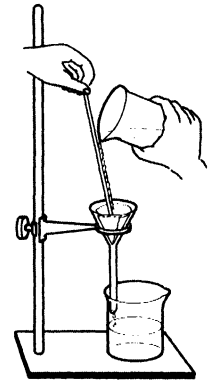


Figure 5–1 Filtration.

The calculation of percentage composition is further illustrated in the following examples:

PROBLEM 1: Calculate the percentage composition of aluminum sulfate, $Al_2(SO_4)_3$.

2 atoms of aluminum weigh	$2 \times 27 =$	54
3 atoms of sulfur weigh	$3 \times 32 =$	96
12 atoms of oxygen weigh	$12 \times 16 =$	192
	Formula weight	342

Per cent aluminum	$= \frac{54}{342} \times 100 =$	15.8
Per cent sulfur	$= \frac{96}{342} \times 100 =$	28.1
Per cent oxygen	$= \frac{192}{342} \times 100 =$	56.1
		100.00

[2] The downward arrow ↓ indicates the formation of a precipitate, in this case AgCl.

PROBLEM 2: Calculate the weight of iron in 350 pounds of Fe_2O_3. First, calculate the per cent of iron in the compound:

$$\begin{aligned} &2 \text{ atoms of Fe weigh} && 2 \times 55.8 = 111.6 \\ &3 \text{ atoms of oxygen weigh} && 3 \times 16 = 48 \\ &&\text{Formula weight} && 159.6 \end{aligned}$$

$$\text{Per cent iron} = 111/159.6 \times 100 = 69.9$$

$$\begin{aligned} \text{Weight of iron in 350 lb. of } Fe_2O_3 &= 350 \times 0.699 \\ &= 244.5 \text{ lb.} \end{aligned}$$

No matter what unit of weight is used in this type of problem—grams, kilograms, ounces, pounds, or tons—the manner of working the problem will be the same.

EXERCISES

1 List all the information derivable from the formulas: Al_2O_3; $C_{12}H_{22}O_{11}$.

2 Consider the compound sulfuric acid, H_2SO_4. At. wts. H = 1; S = 32; O = 16.

(*a*) How many atoms of each element are present in 1 molecule of H_2SO_4?

(*b*) What is the weight of a gram mole of H_2SO_4?

(*c*) How many gram atoms of each element are in 1 gram mole of H_2SO_4?

(*d*) How many gram moles in 392 grams of H_2SO_4?

(*e*) How many gram atoms of each element in 392 grams of H_2SO_4?

(*f*) How many gram moles in 1.96 grams of H_2SO_4?

3 Consider the balanced equation below. At. wts. N = 14; H = 1; O = 16.

$$\underset{\text{(ammonia)}}{4\,NH_3} + \underset{\text{(oxygen)}}{5\,O_2} \rightarrow \underset{\text{(nitric oxide)}}{4\,NO} + \underset{\text{(water)}}{6\,H_2O}$$

(*a*) How many moles of O_2 react with 4 moles of ammonia? How many moles of water would be formed?

(*b*) How many moles of ammonia react with one mole of oxygen? How many moles of NO and H_2O would be formed?

(*c*) How many gram moles of NO would be formed from 17 grams of NH_3?

(*d*) How many grams of H_2O would be formed from 4 gram moles of NH_3?

Ans. (*c*) 1; (*d*) 108.

4 (*a*) How many gram moles are present in 100 grams of each of the following substances: H_2SO_4; P_2O_5; H_2O; Cl_2; FeS? See atomic weight table inside front cover of this text.

(*b*) How many grams in 3 moles of each of the compounds in part (*a*)?

5 Balance the equations:

(*a*) $Ca + HCl \rightarrow CaCl_2 + H_2$

(*b*) $KClO_3 \rightarrow KCl + O_2$

(*c*) $NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$

(*d*) $Al + HCl \rightarrow AlCl_3 + H_2$

(*e*) $Na + H_2O \rightarrow NaOH + H_2$

6 Define the terms: symbol, formula, chemical equation, radical, percentage composition, formula weight, filtrate.

7 Balance the equations:

(*a*) $Ca(OH)_2 + HCl \rightarrow CaCl_2 + H_2O$
(*b*) $Al_2(SO_4)_3 + BaCl_2 \rightarrow BaSO_4 + AlCl_3$
(*c*) $Cu(NO_3)_2 + H_3PO_4 \rightarrow Cu_3(PO_4)_2 + HNO_3$
(*d*) $Bi_2(CO_3)_3 + HC_2H_3O_2 \rightarrow Bi(C_2H_3O_2)_3 + H_2CO_3$
(*e*) $(NH_4)_3PO_4 + KOH \rightarrow K_3PO_4 + NH_4OH$

8 Classify the following reactions as one of the four types given on pages 74–75.

(*a*) $Zn + 2\,AuCl \rightarrow ZnCl_2 + 2\,Au$
(*b*) $2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HCl$
(*c*) $2\,Na + 2\,HCl \rightarrow 2\,NaCl + H_2$
(*d*) $2\,BaO_2 \rightarrow 2\,BaO + O_2$
(*e*) $S + O_2 \rightarrow SO_2$
(*f*) $Na_2O + CO_2 \rightarrow Na_2CO_3$
(*g*) $Pb(NO_3)_2 + Na_2SO_4 \rightarrow PbSO_4 + 2\,NaNO_3$
(*h*) $Cl_2 + Hg \rightarrow HgCl_2$

9 Calculate the percentage of each element in the compounds:

(*a*) NaCl, (*b*) $CaCO_3$, (*c*) $K_2Cr_2O_7$.

10 Calculate the weight of zinc obtainable from one ton of the mineral ZnS.

11 A solution is 5 per cent $Cr_2(SO_4)_3$. From a ton of this solution one could obtain how many pounds of Cr?

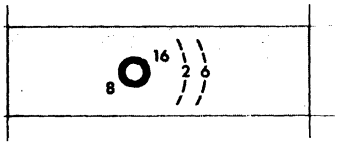
12 What is the per cent lead in the insecticide material lead arsenite, $Pb_3(AsO_3)_2$?

13 Calculate the percentage of aluminum in the clay mineral, $H_2Al_2(SiO_3)_4$.

14 What is the per cent of calcium in calcium chloride? What is the weight of calcium that might be obtained from 250 pounds of calcium chloride?

Ans. 90 lb.

15 When a piece of magnesium ribbon weighing 0.32 g. is burned in oxygen, the resultant oxide weighs 0.53 g. What is the percentage composition of the oxide?



six OXYGEN

Occurrence In beginning our study of the chemical elements, we shall select oxygen, the most abundant of all the elements and one which plays a very important role in our everyday life. In Figure 2–2, page 15, we note that oxygen makes up about one half of the earth's crust, which includes the atmosphere.

Oxygen occurs in both the free (uncombined) and combined states. In the free state it comprises approximately 20 per cent by volume of the air we breathe. Water is a compound of two elements, oxygen and hydrogen, both of which are colorless gases at ordinary temperatures; eight ninths of the weight of water is due to the oxygen present. Sugars, starches, fats, proteins, limestone, sand, clay, nearly all food products, cotton, and wool are some of the familiar oxygen-containing materials. Approximately 60 per cent by weight of the human body is oxygen.

The importance of oxygen When air is taken into the lungs, oxygen is taken up by the blood stream, which carries this vital substance to body tissues. The food we consume combines with oxygen, and this chemical change produces energy which maintains our body temperature and gives us strength for physical activity.

Oxygen has many other functions. Coal and wood must have oxygen to burn and produce heat. Oxygen in the air causes metals to corrode, wood to rot, paints to harden, gasoline to burn, iron to rust, and many other chemical processes to take place. Not only is oxygen the most abundant element, but also it is perhaps the most important element.

NOTE: In showing the atomic number and atomic weight of an element in conjunction with its symbol, the atomic number of the element is made a subscript just preceding the symbol while the atomic weight is placed as a superscript of the symbol. The numbers to the right of the symbol indicate the electronic configuration of the atom—in the figure for oxygen given at the head of this chapter, 2 electrons in the first energy level and 6 electrons in the second and outermost level.

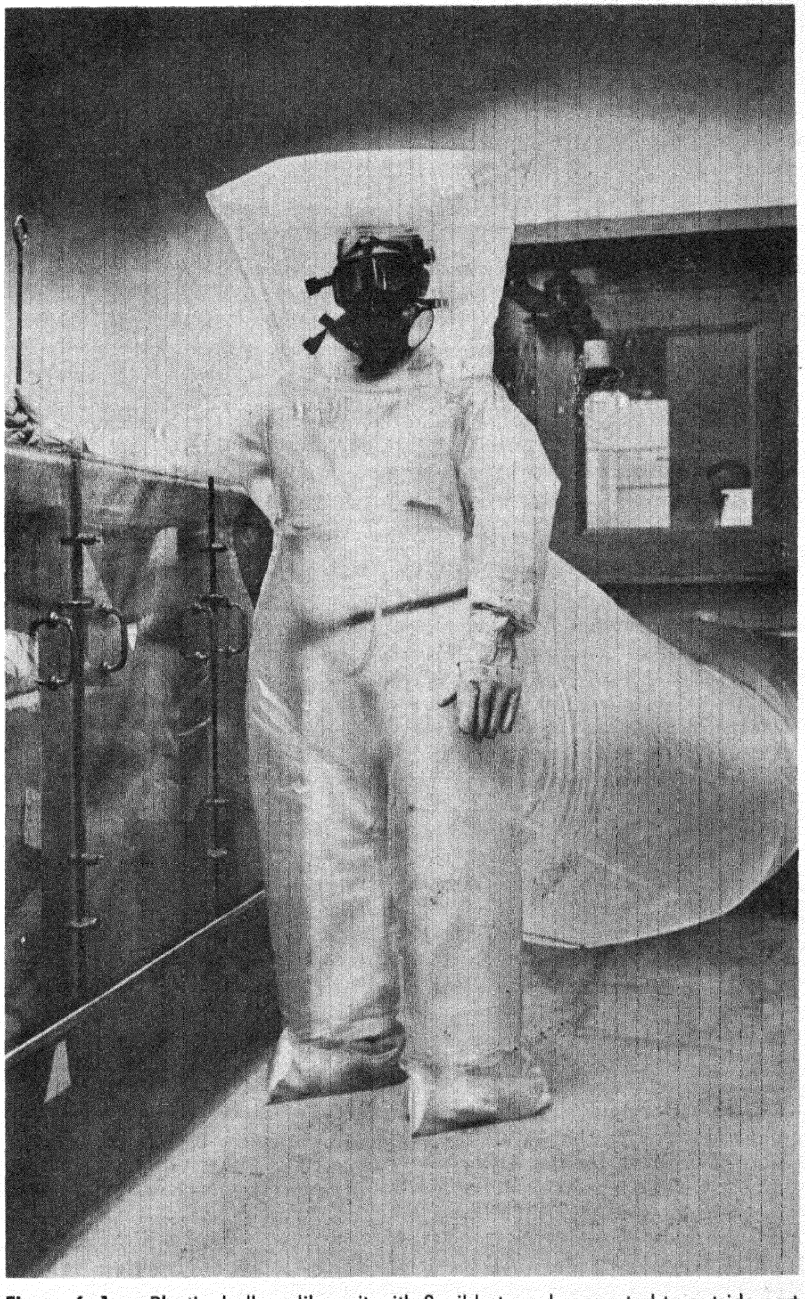


Figure 6–1 Plastic, balloon-like suit with flexible tunnel connected to outside port provides uncontaminated air for worker in atomic energy plant.

The discovery of oxygen Although oxygen is very abundant, it was not discovered until after many of the less common elements were well known. Joseph Priestley, an English clergyman, is credited with its discovery in 1774; it is, then, a relatively recent discovery.[1] Priestley was experimenting with many kinds of gases or "airs," which he obtained by heating various substances. The gases which Priestley prepared by heating various substances were not regarded by him as essentially different substances; rather, he thought of them as different kinds of air. In heating substances, Priestley made use of heat energy from the sun by focusing rays of light by means of a lens upon the object to be heated. When he heated mercuric oxide, he discovered that it yielded an "air" of unusual properties in which substances burned much more vigorously than in ordinary air. Although he found that combustion proceeded much more rapidly in this new "air," he did not associate it with the component of ordinary air in which combustion of many substances was known to take place. Following are portions of Priestley's own account of his experiments on oxygen:

On the 1st of August, 1774, I endeavoured to extract air from mercurious calcinatus per se (mercuric oxide); and I presently found that, by means of the lens, air was expelled from it very rapidly. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was, that a candle burned in this air with a remarkably vigorous flame. . . .

On the 8th of this month I procured a mouse, and put it into a glass vessel, containing two ounce-measures of the air from mercurious calcinatus. Had it been common air, a full-grown mouse, as this was, would have lived in it about a quarter of an hour. In this air, however, my mouse lived a full half hour; and though it was taken out seemingly dead, it appeared to have been only exceedingly chilled; for, upon being held to the fire, it presently revived, and appeared not to have received any harm from the experiment. . . .

From the greater strength and vivacity of the flame of a candle, in this pure air, it may be conjectured, that it might be peculiarly salutary to the lungs in certain morbid cases, when the common air would not be sufficient to carry off the phlogistic putrid effluvium fast enough. But perhaps, we may also infer from these experiments, that though pure dephlogisticated air might be very useful as a medicine, it might not be so proper for us in the usual healthy state of the body; for, as a candle burns out much faster in dephlogisticated air than in common air, so we might, as may be said, live out too fast, and the animal powers be too soon exhausted in this pure kind of air. A moralist, at least, may say, that the air which nature has provided for us is as good as we deserve.

My reader will not wonder, that, after having ascertained the superior goodness of dephlogisticated air by mice living in it, and the other tests above mentioned, I should have the curiosity to taste it myself. I have gratified that curiosity, by

[1] It is probable that oxygen was first discovered by the Swedish chemist Scheele in about 1771. His results were not made public until 1775, and Priestley's work had received considerable attention by this time.

breathing it, drawing it through a glass syphon, and by this means, I reduced a large jar of it to the standard of common air. The feeling to my lungs was not sensibly different from that of common air; but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that, in time this pure air may become a fashionable article in luxury. Hitherto only two mice and myself have had the privilege of breathing it. . . .[2]

The phlogiston theory The phenomenon of combustion was not very well understood until the nineteenth century. Combustion, or the production of fire, usually was associated with destruction of the material being burned. It was commonly known that most substances burned with a resulting loss in weight, since only a fraction of the original weight was left in the form of ash. It seemed natural to the alchemists that the combustible substance must contain something responsible for the burning which escaped during the process of combustion. This something supposedly present in combustible materials was called "phlogiston." However, it was known that when some substances burned, the residue after combustion weighed more than the original substance. This fact must have caused grave doubts in the minds of the chemists of that period about the correctness of the phlogiston theory. The phlogiston concept, however, was so firmly implanted in the minds of many of the alchemists that it was not soon discarded. Phlogiston with a negative weight was postulated; accordingly, as something burned with loss of negative phlogiston, the residue would possess a greater weight than the initial substance. It is difficult for us today to conceive of something with a negative weight.

It remained for Lavoisier to show that Priestley's "air" was the constituent in the air which caused substances to burn. Lavoisier recognized that since substances burned more vigorously in Priestley's "air" than in ordinary air, Priestley's "air" must be responsible for combustion in ordinary air, where it seemed to be less concentrated. Lavoisier proved this theory by heating mercury with air (see Figure 6–2). He found that a "red precipitate" (mercuric oxide) was formed on the surface of the mercury and the volume of air decreased by about one-fifth. On heating the "red precipitate" at a higher temperature, he found that a volume of gas was released exactly equal to the decrease in volume of the original air used. He concluded that air must be composed of two gases, one of which, in a concentration of approximately 20 per cent by volume, is responsible for combustion processes. Lavoisier said that burning was the combination of the burning substance with oxygen. The weight of the product would then be greater than the weight of the original substance by an amount equal to the weight of the substance in the air which united with the

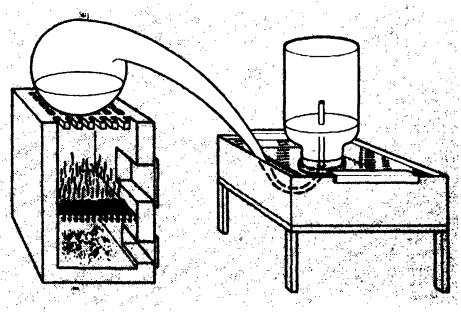


Figure 6–2 Lavoisier's apparatus for preparing mercuric oxide.

[2] *Alembic Club Reprints*, No. 1.

burning body. He called the inactive substance in the air "azote," a French word meaning lazy. We now know this substance as the element nitrogen. Lavoisier called the active ingredient "oxygen" which signifies acid former. He believed that all acids contain oxygen, but this latter view was erroneous, for we shall presently study several acids which contain no oxygen.

By overthrowing the phlogiston theory and giving us our modern concept of combustion, Lavoisier made an important contribution to chemistry.

Laboratory preparation (*a*) *By heating certain oxides.* Oxygen is conveniently prepared in the laboratory by repeating Priestley's experiment of heating certain substances. Mercuric oxide, a reddish powder, readily gives up its oxygen when heated, leaving metallic mercury as a residue (Figure 6–3):

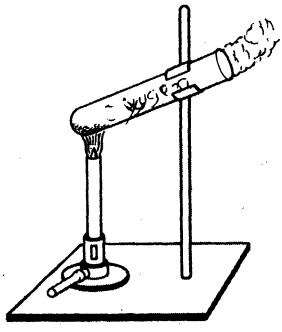


Figure 6–3 Heating mercuric oxide yields mercury and oxygen.

$$\underset{\text{mercuric oxide}}{2\,HgO} \rightarrow \underset{\text{mercury}}{2\,Hg} + \underset{\text{oxygen}}{O_2}$$

Silver oxide, gold oxide, and platinum oxide react similarly, yielding the metal and liberating oxygen when heated. These four metals, mercury, silver, gold and platinum are called the *noble* metals.

Certain dioxides are unstable toward heat, breaking down to give an oxide of the metal and free oxygen, for example,

$$\underset{\text{lead dioxide}}{2\,PbO_2} \rightarrow \underset{\text{lead oxide}}{2\,PbO} + O_2$$

$$\underset{\text{barium dioxide}}{2\,BaO_2} \rightarrow \underset{\text{barium oxide}}{2\,BaO} + O_2$$

We must not assume from the above reactions that all metallic oxides give up oxygen when heated. As a matter of fact, most of the oxides of metals are stable and undergo no change when heated.

(*b*) *By heating certain salts.* Potassium chlorate, a white crystalline substance composed of the elements potassium, chlorine, and oxygen, gives up all of its oxygen when heated above its melting point, 368°C., according to the equation

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

If we wish to collect some of the oxygen gas, in order to study some

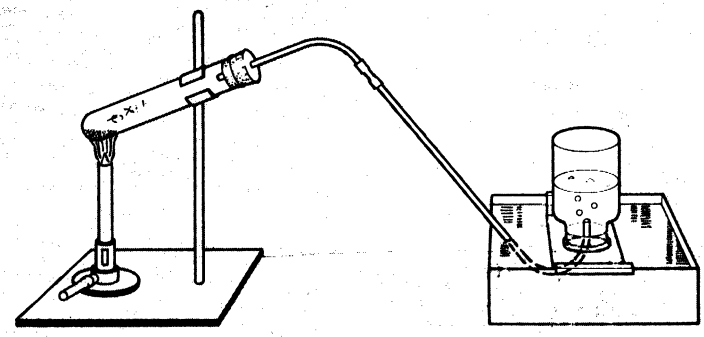


Figure 6–4 Collection of oxygen gas by displacement of water.

of its properties, we may use the apparatus shown in Figure 6–4. As oxygen gas is not very soluble in water, we may collect it by displacement of water as shown. As the gas is evolved, it displaces the water in the bottle, and we may collect the bottle full of the gas.

Potassium nitrate when heated yields oxygen, but the reaction differs from the decomposition of potassium chlorate in that only one-third of the oxygen in the potassium nitrate in released. This is evident from the equation

$$\underset{\text{potassium nitrate}}{2\,KNO_3} \rightarrow \underset{\text{potassium nitrite}}{2\,KNO_2} + O_2$$

Again it should be pointed out that not all oxygen-containing compounds give up their oxygen when heated; K_2SO_4 and SiO_2, for example, are stable toward heat.

(*c*) *The reaction of sodium peroxide with water.* Sodium peroxide, a white noncrystalline powder, reacts vigorously with water to give oxygen and sodium hydroxide:

$$\underset{\text{sodium peroxide}}{2\,Na_2O_2} + 2\,H_2O \rightarrow \underset{\text{sodium hydroxide}}{4\,NaOH} + O_2$$

Catalysts The speed of many chemical reactions may be increased or decreased by the addition of certain foreign substances. These substances do not appear to enter into the reaction; at least they are not permanently altered chemically. Such substances are called "catalysts" or "catalytic agents." When potassium chlorate is heated it melts to a clear liquid, and tiny bubbles of gas may be noticed escaping from the liquid. As indicated above, the gas is oxygen but its evolution is slow. The addition of a small amount of manganese dioxide to the potassium

chlorate greatly increases the speed at which the oxygen is evolved; furthermore, the oxygen gas is evolved at a much lower temperature. This added substance does not give up oxygen and remains unchanged in composition in the reaction, as may be seen by analysis of the reaction products. All of the catalyst added to the reaction mixture may be recovered and used over and over again. Since a catalyst does not appear to enter into the reaction, its formula is usually placed over the arrow in the equation; thus the catalytic decomposition of potassium chlorate would be represented:

$$2\,KClO_3 \xrightarrow{MnO_2} 2\,KCl + 3\,O_2$$

In some reactions the speed of reaction may be decreased by the presence of a catalyst; in most cases, however, catalysts are used to speed up chemical processes. A catalyst may be defined as *a substance which alters the speed of a chemical reaction but itself remains chemically unchanged.* Catalysts have important industrial applications because in many reactions speed is a decisive factor.

Commercial preparation of oxygen It would not be practical to make large quantities of oxygen by the methods employed in the laboratory, as the cost would be prohibitive. We might naturally expect to obtain large quantities of oxygen from those sources where it occurs most extensively. Since approximately 20 per cent of the atmosphere is composed of oxygen, air should be a potential source. Water is nearly 90 per cent oxygen. Since water is so readily available, we might expect to use it in preparing oxygen on an industrial scale. As a matter of fact, most of the oxygen for commercial purposes is obtained from air.

(*a*) *From the air.* Since air is essentially a mixture of oxygen and nitrogen gases, the problem is to separate these gases. When air is cooled to a temperature of approximately $-200°$, it becomes liquid. Air is actually liquefied by a combination of low temperature and high pressure. If compressed air is allowed to expand rapidly through a valve, heat is absorbed and the gas is cooled. (For explanation of this see Chapter 8.) The cooled gas may be compressed and again allowed to expand to further cool itself. By alternate compression, cooling, and expansion of air, the temperature is continuously lowered until the air becomes a liquid. During the cooling, water vapor and carbon dioxide in the air condense to liquids and are removed.

When a mixture of liquids is heated to the boiling point, the component with the lowest boiling point boils or distils off first; thus if an alcohol-water mixture is boiled, the first portion of the vapor will be richer in (have a higher percentage of) alcohol than the mixture from which it was distilled. (See Chapter 15 for a further discussion of this.)

examples of *oxidation*[4] reactions, and the substance which combines with the oxygen is said to be *oxidized.* Oxidation may take place at varying speeds. The formation of iron rust is normally a slow oxidation, but when iron is burned in pure oxygen, the reaction takes place much more rapidly, and heat and light are produced. An oxidation process in which heat and light are produced is called *combustion.* When most substances are oxidized, heat is evolved in the process. Thus when coal, gasoline, or wood are burned, the reactions produce heat. Whether the reaction takes place rapidly or slowly, the same quantity of heat is evolved, although a much higher temperature is reached in a rapid reaction because of the heat being generated during a brief period of time.

The amount of heat liberated per unit quantity of substance burned in called *heat of combustion.* For example, one gram of sulfur on burning to sulfur dioxide liberates 2200 calories, one gram of carbon burning to carbon dioxide yields 7900 calories. Heats of combustion of mixtures such as coal, fuel oil, or foods are called *calorific values.*

Reaction of oxides with water The oxides of the nonmetals, such as sulfur, carbon, and phosphorus, dissolve in water to form *acids,* a class of chemical compounds which have a sour taste and turn blue litmus paper red. (Litmus is a vegetable dye which is pink or red in acid solution.)

$$\underset{\text{sulfur dioxide}}{SO_2} + H_2O \rightarrow \underset{\text{sulfurous acid}}{H_2SO_3}$$

$$\underset{\text{carbon dioxide}}{CO_2} + H_2O \rightarrow \underset{\text{carbonic acid}}{H_2CO_3}$$

$$\underset{\text{phosphorus pentoxide}}{P_2O_5} + 3\,H_2O \rightarrow 2\,\underset{\text{phosphoric acid}}{H_3PO_4}$$

We may formulate the general rule: *If soluble, oxide of a nonmetal reacts with water to form an acid.*

The oxides of metals, if soluble in water, form *bases,* a class of chemical compounds which are bitter in taste, have a soapy feeling, turn red litmus paper blue, and in water solution contain the hydroxide, OH, radical:

$$\underset{\text{calcium oxide}}{CaO} + H_2O \rightarrow \underset{\text{calcium hydroxide}}{Ca(OH)_2}$$

[4] Oxidation reactions, however, are not confined to combinations with oxygen. The term "oxidation" has a much broader significance and will be discussed in more detail in Chapter 20.

The oxide of iron is insoluble in water, as are most of the metallic oxides. These insoluble oxides and water give no basic reaction to litmus paper.

Kindling temperature Chemical processes take place more rapidly when the temperature is raised. At ordinary temperatures iron rusts slowly, but at an elevated temperature the combination with oxygen takes place rapidly. If the temperature of a combustible substance is raised to a certain point in the presence of air or oxygen, the substance will burst into flame. The temperature at which this occurs is called the *kindling temperature* of the substance. The kindling temperature varies with the nature of the substance. This fact may be demonstrated by the following experiment. If small pieces of phosphorus, sulfur, and wood are placed in a shallow pan and the pan heated by means of a burner, it will be observed that the phosphorus takes fire when the pan is barely warm, the sulfur takes fire at a much higher temperature, and at a still higher temperature the wood bursts into flame. The kindling temperature of phosphorus is lower than that of sulfur, which in turn is lower than that of wood.

Spontaneous combustion We frequently hear of fires starting spontaneously. Spontaneous combustion will occur when the temperature of a substance has been raised to its kindling temperature; at this point oxidation is occurring so rapidly that the substance will burst into flame. A pile of oily rags or a pile of coal may take fire spontaneously. Spontaneous combustion is the result of a cumulative process which takes place rather slowly at first. (During the early stages the process is really not combustion, but a slow oxidation of the substance by the oxygen of the air.) If the combustible substance is a good heat insulator —that is, if it retains most of the heat given off in the oxidation process —the combustion stage may develop. The heat which is produced as a result of the oxidation process gradually accumulates, raising the temperature of the substance finally to the kindling temperature, at which point self-combustion takes place. Two conditions, then, are essential for spontaneous combustion: (1) an existing slow oxidation with the evolution of heat and (2) good heat insulation, or the ability of the substance to retain a large part of the heat generated in the oxidation process.

Uses of oxygen Oxygen has a number of important uses. In certain diseases such as pneumonia, tuberculosis, gas poisoning, and other respiratory impairments, pure oxygen may be administered in an "oxygen tent." Oxygen is often mixed with various anesthetic agents such as ethylene or nitrous oxide.

The largest amount of commercial oxygen is used in oxyacetylene

torches and the hydrogen-oxygen blowpipe for welding purposes. Since oxidation occurs so rapidly in an atmosphere of pure oxygen, high temperatures may be reached, sufficient for melting and cutting metals.

Airplanes carry tanks of oxygen which may be used when flying at high altitudes. Flights into the stratosphere where the concentration of oxygen is low necessitate the use of oxygen for the respiratory needs of the passengers. Oxygen is also used in pulmotors, basal metabolism machines, submarines, and diving bells.

Ozone If a high electrical discharge is allowed to pass through oxygen gas at low temperatures, a gas is formed with a peculiar, generator-room odor. The composition of the substance has been proved to be that represented by the formula O_3 and it has been given the name ozone, from the Greek "to smell." Since its boiling point is $-112°C.$, which is markedly higher than for oxygen ($-183°C.$), ozone may be condensed as a liquid from oxygen gas containing small percentages of ozone.

Ozone is quite unstable, breaking down to form oxygen

$$2\,O_3 \rightarrow 3\,O_2 + \text{energy}$$

with the liberation of a large amount of energy. Ozone is much more active than ordinary oxygen and reacts vigorously with most of the elements and many compounds. Organic matter is rapidly oxidized. Ozone is sometimes used to purify water by destruction of bacteria and micro-organisms, and to purify air which has become polluted. It finds limited use also as a bleaching agent.

An example of its chemical activity is the liberation of free iodine from iodides, such as potassium iodide; this property is the basis for testing for ozone.

EXERCISES

1 Why do substances burn better in pure oxygen than in ordinary air?
2 How may oxygen be collected during its laboratory preparation?
3 List four metals whose oxides are unstable toward heat.
4 Define: density, combustion, oxidation, kindling temperature, oxide, catalyst, exothermic.
5 What two conditions are necessary for spontaneous combustion?
6 List three important uses of oxygen.
7 What is the function of the carburetor in your car?
8 Compare the quantities of heat evolved during the rapid and slow oxidation of a given substance.
9 Can you suggest a method for demonstrating that MnO_2 is not changed chemically when it is employed as a catalyst in the decomposition of $KClO_3$?
10 Theoretically, what quantity of potassium chlorate could be catalytically decomposed with one gram of MnO_2? Ans. Any amount.

11 Lead dioxide gives up one half of its oxygen on being heated, potassium chlorate all of its oxygen and potassium nitrate only one third of its oxygen. Which of these compounds would be the cheapest source of oxygen in the laboratory if lead dioxide costs \$0.40 a pound, potassium chlorate \$1.25, and potassium nitrate \$0.90?

12 If all of the oxygen from the decomposition of 2.45 g. of potassium chlorate is used to burn carbon to carbon dioxide, what weight of carbon dioxide would be produced? Ans. 1.32 g.

13 Diagram the three isotopes of oxygen, mass numbers 16, 17, 18.

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seven HYDROGEN

Early history Hydrogen was prepared many times before it was identified as an elementary substance. Early investigators noted that acids acted with certain metals to produce a "colorless, odorless gas." Paracelsus (1493-1541) stated that when sulfuric acid is allowed to act on iron, "an air arises which bursts forth like the wind." Since the only named gas at this time was air, it was believed that this gas, later called hydrogen, was just another kind of "air." Henry Cavendish (1731–1810), who was given credit for the discovery of hydrogen in 1776, noted that "air" produced from the action of metals with acids was inflammable and that it burned in the air to produce water. Lavoisier gave this new "air" the name hydrogen, which signified "water former."

Occurrence Hydrogen is one of the more abundant of the chemical elements; by weight it makes up approximately 1 per cent of the earth's crust. Unlike oxygen, it is seldom found in the free state (uncombined with other elements); it is, however, found in the atmosphere in very small amounts (about .01 per cent) and in slightly larger amounts in gases issuing from volcanoes. Spectroscopic studies indicate that large amounts of free hydrogen are present in gases surrounding the sun and many stars.

In combination with other elements, hydrogen is widely distributed. Water is about one-ninth hydrogen by weight and eight ninths oxygen. Compounds of organic origin (those compounds associated with living organisms or their products), such as sugar, food products, fats, proteins, and oils, contain hydrogen. Combined with carbon, hydrogen is found in natural gas, kerosene, gasoline, and other petroleum products. It is also a constituent of all acids and hydroxides (bases), two classes of compounds which we shall presently discuss.

If we could count the atoms of the various elements present in the earth's crust, we would undoubtedly find that hydrogen atoms are ex-

ceeded in number only by atoms of oxygen; however, since hydrogen is the lightest of the elements, with an atomic weight of 1.008, the proportion of hydrogen by weight in the earth's crust is relatively small.

Action of hydrochloric acid on metals Certain metals have the property of displacing hydrogen from acids. When hydrochloric acid, HCl, is added to granulated zinc, hydrogen gas is evolved at a rapid rate:

$$\underset{\text{hydrochloric acid}}{2\,HCl} + Zn \rightarrow \underset{\text{zinc chloride}}{ZnCl_2} + H_2\uparrow$$

In this chemical change[1] the metal zinc has displaced or replaced the hydrogen in the acid. The hydrogen is set free, and the zinc combines with the chlorine to form zinc chloride. A compound formed by the replacement of the hydrogen of an acid with a metal is termed a *salt.* Thus zinc chloride is a salt of hydrochloric acid, since it is derived from that acid by replacement of hydrogen. It may be noted that zinc chloride is composed of the metal zinc and the nonmetal chlorine. A compound of a metal and a nonmetal may be called a salt (see page 17).

Aluminum reacts with hydrochloric acid to form aluminum chloride and hydrogen:

$$2\,Al + 6\,HCl \rightarrow \underset{\text{aluminum chloride}}{2\,AlCl_3} + 3\,H_2\uparrow$$

The action, once started, is more rapid than with zinc. Aluminum chloride is a salt of hydrochloric acid, since it is derived from the acid by replacement. (All salts of hydrochloric acid are chlorides.)

Iron and tin will replace hydrogen from hydrochloric acid, but less vigorously than zinc and aluminum:

$$Fe + 2\,HCl \rightarrow \underset{\text{ferrous chloride}}{FeCl_2} + H_2\uparrow$$

$$Sn + 2\,HCl \rightarrow \underset{\text{stannous chloride}}{SnCl_2} + H_2\uparrow$$

The activity series While many metals will displace hydrogen from acids, some will not; for example, copper, silver, mercury, gold. The displacement of hydrogen in an acid by a metal may be regarded as taking place because the metal is more active than hydrogen—thus zinc, aluminum, iron, and tin (see equations above) are more active than hydrogen. On the other hand, copper, silver, and so on, which will not displace hydrogen from acids would be regarded as less active than hydrogen.

We may determine the relative activity of metals by a series of further

[1] The upward arrow ↑ indicates the escape of a gas.

displacement reactions. For example, a strip of copper placed in a solution of a mercury or silver salt soon becomes coated with metallic mercury or silver:

$$\underset{\text{mercuric sulfate}}{Cu + HgSO_4} \rightarrow CuSO_4 + Hg$$

$$\underset{\text{silver sulfate}}{Cu + Ag_2SO_4} \rightarrow CuSO_4 + 2\,Ag$$

We may say that copper is more active than either mercury or silver, since the latter metals are displaced from their compounds. Similarly, zinc will displace iron from $FeCl_2$.

$$Zn + FeCl_2 \rightarrow ZnCl_2 + Fe$$

but will not displace Mg from $MgCl_2$

$$Zn + MgCl_2 \rightarrow ZnCl_2 + Mg \quad \text{(does not occur)}$$

Thus zinc is more active than iron, but less active than magnesium.



On the basis of such series of displacement reactions, metals may be arranged in an activity series as shown above and on the right side of this page (This series includes only the more common metals.) Hydrogen is placed in the list to divide those metals which displace hydrogen from acids from those which do not Those metals appearing above hydrogen in this series will displace hydrogen from an acid; those below hydrogen will not react with an acid to produce free hydrogen. The metals are arranged in order of decreasing activity with the most active metal at the top. Any metal will displace a metal below it (a less active metal) from its salt in water solution.

This activity series[2] is sometimes referred to as the "electromotive series of metals," since the position of the metals in the list may be determined from electromotive force measurements. See Chapter 32.

Action of other acids with metals The action of other acids on metals in most cases is similar to that of hydrochloric acid. For example, metals above hydrogen in the activity series displace the hydrogen from sulfuric acid to form a *sulfate* salt and free hydrogen:

[2] The position of elements will be altered to some extent by such factors as temperature, kind of solution in contact with metal, concentrations, and secondary action of metal ions with solvent Certain replacements which take place at one temperature and concentration may to some extent be reversed at other temperatures and concentrations, for example, hot hydrogen gas passed over iron oxide replaces iron, and sodium when placed in water acts much more vigorously than calcium

$$Zn + \underset{\text{sulfuric acid}}{H_2SO_4} \rightarrow \underset{\text{zinc sulfate}}{ZnSO_4} + H_2\uparrow$$

$$Fe + H_2SO_4 \rightarrow \underset{\text{ferrous sulfate}}{FeSO_4} + H_2\uparrow$$

Salts of sulfuric acid are called *sulfates;* $ZnSO_4$, then, is zinc sulfate and $FeSO_4$ is ferrous sulfate.

Phosphoric acid, H_3PO_4, acts similarly with metals above hydrogen to produce hydrogen and *phosphates:*

$$3\,Zn + 2\,H_3PO_4 \rightarrow \underset{\text{zinc phosphate}}{Zn_3(PO_4)_2} + 3\,H_2\uparrow$$

$$2\,Al + 2\,H_3PO_4 \rightarrow \underset{\text{aluminum phosphate}}{2\,AlPO_4} + 3\,H_2\uparrow$$

The action of nitric acid, HNO_3, on metals is somewhat different from that of most of the other acids. This is due to the fact that nitric acid possesses oxidizing properties in addition to acid properties (see Chapter 20). Nitric acid dissolves many of the metals appearing below hydrogen in the activity series, and its action on metals above hydrogen in the series produces substances other than free hydrogen. These reactions will be discussed at a later time.

In general, if the acid exhibits only acid characteristics, it will act on metals appearing above hydrogen in the activity series to liberate free hydrogen. We may formulate the general rule:

$$\text{Metal above hydrogen} + \text{Acid} \rightarrow \text{Salt} + \text{Hydrogen}$$

Laboratory preparation of hydrogen For the preparation of hydrogen in laboratory quantities, the action of sulfuric acid on zinc is frequently employed. The apparatus shown in Figure 7–1 may be used. Acid is added through the thistle tube and reacts with the zinc placed in the

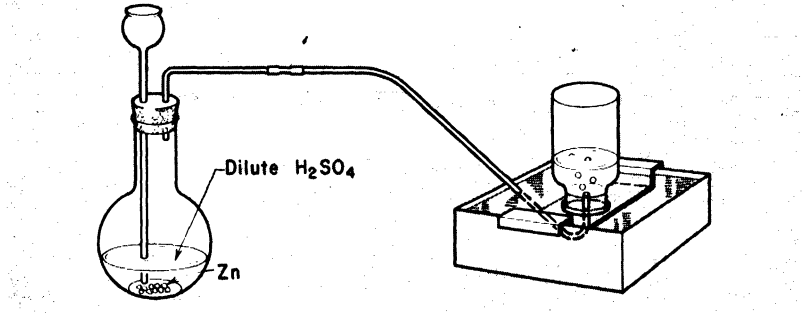


Figure 7–1 Apparatus for generating hydrogen.

flask. The hydrogen gas is collected by displacement of water in which it is relatively insoluble:

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

This reaction may be catalyzed by the addition of a few drops of copper sulfate solution. Zinc displaces the less active copper:

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

The finely divided copper deposits on the zinc and acts as a catalyst for the reaction.

Action of water on metals Those metals near the top of the activity series are sufficiently active to displace hydrogen from water. If a small piece of sodium metal is dropped into water, a very vigorous reaction ensues with the liberation of hydrogen gas. The experiment must be carried out with a great deal of caution, as the action may throw sodium or sodium hydroxide around.

Sodium displaces only one hydrogen atom in the water molecule, forming sodium hydroxide and hydrogen. Sodium hydroxide is a base and turns red litmus blue:

$$2\,Na + 2\,H_2O \rightarrow \underset{\text{sodium hydroxide}}{2\,NaOH} + H_2 \uparrow$$

Potassium, barium, and calcium displace hydrogen from water in a similar manner; in each case the metal hydroxide (base) and hydrogen are produced. These first metals in the activity series are sufficiently active to displace hydrogen from ice water:

$$\text{Metal (K, Ba, Ca, Na)} + H_2O \rightarrow \text{Metal Hydroxide} + H_2 \uparrow$$

The next nine metals in the activity series, magnesium, aluminum, manganese, zinc, chromium, cadmium, iron, cobalt, and nickel, while not active enough to displace hydrogen from cold water, will act with water in the form of steam. These metals displace all of the hydrogen in the water molecule and yield the oxide of the metal used and free hydrogen:

$$\text{Metal} + H_2O\,(\text{steam}) \rightarrow \text{Oxide of Metal} + H_2 \uparrow$$

Lead and tin, which follow in the series, are too inactive to act with water at any temperature to any noticeable degree.

Preparation of hydrogen from bases Certain metals will displace hydrogen from certain bases (metallic hydroxides) to yield hydrogen. For example, zinc or aluminum will act with either sodium or potassium hydroxide to liberate hydrogen:

$$Zn + 2\,KOH \rightarrow \underset{\text{potassium zincate}}{K_2ZnO_2} + H_2\uparrow$$

$$2\,Al + 6\,NaOH \rightarrow \underset{\text{sodium aluminate}}{2\,Na_3AlO_3} + 3\,H_2\uparrow$$

Commercial preparation of hydrogen (*a*) Electrolysis of water, described on page 85. (*b*) When steam is passed over carbon which has been heated to a high temperature, carbon monoxide and hydrogen gases are produced:

$$C + H_2O \rightarrow \underset{\text{carbon monoxide}}{CO} + H_2$$

Since both carbon monoxide and hydrogen are combustible, the mixture has fuel value and in many cases no attempt is made to separate the products. The mixture has been given the trade name "water gas."

Hydrogen may be separated from the mixture by cooling to a low temperature (about $-200°$) and liquefying the carbon monoxide. The hydrogen is left in the gaseous condition. The mixture of the two gases may be treated with steam in the presence of a catalyst to oxidize the carbon monoxide to carbon dioxide, and yield more hydrogen:

$$CO + H_2O \rightarrow \underset{\text{carbon dioxide}}{CO_2} + H_2$$

The carbon dioxide may be separated from the hydrogen by absorption in water or alkaline solution, leaving relatively pure hydrogen.

A reversible reaction If steam is passed over red hot iron filings in a tube (Figure 7-2, *a*), hydrogen gas is produced and may be removed from the opposite end of this tube:

$$3\,Fe + 4\,H_2O\,(\text{steam}) \rightarrow \underset{\text{iron oxide}}{Fe_3O_4} + 4\,H_2 \qquad (1)$$

This reaction is *reversible,* since it may be made to proceed in the opposite direction. For example, if hydrogen gas is passed over heated

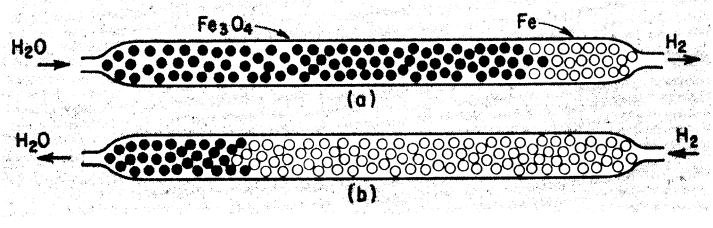


Figure 7–2 A reversible reaction.

iron oxide (Figure 7–2, b), metallic iron and steam are produced:

$$Fe_3O_4 + 4\,H_2 \rightarrow 3\,Fe + 4\,H_2O \qquad (2)$$

The latter is exactly the reverse of reaction (1). We shall find that many chemical reactions are reversible under certain conditions—that is, they may be made to proceed in *either* direction (see page 220).

Properties of hydrogen (*a*) *Physical.* Hydrogen is a colorless, odorless gas and is relatively insoluble in water, 100 ml. of water dissolves about 2 ml. of hydrogen gas under ordinary conditions of temperature and pressure. It is the lightest known substance; therefore it has the smallest density. Hydrogen gas can be liquefied and solidified only with considerable difficulty; the gas liquefies at temperatures below $-253°$, and solidifies at $-259°$.

Certain metals such as platinum and palladium have the property of adsorbing[3] large volumes of hydrogen, often adsorbing many hundred times their own volume of the gas. If the metal is finely divided, thus increasing its surface area, more gas will be adsorbed. This hydrogen appears to be more active than ordinary hydrogen in many reactions and is referred to as "activated hydrogen gas." This is the basis for the use of platinum as a catalyst for many reactions in which hydrogen is one of the reacting substances.

Hydrogen gas *diffuses* more rapidly than any other gas—by diffusion we mean that it mixes rapidly with other gases. All gases will diffuse or mix with one another, and the speed of diffusion is a function of the density of the gases—the lower the density, the more rapid the rate of diffusion. This property may be demonstrated by the following experiment. A beaker of hydrogen gas is placed over a porous clay pipe arranged as shown in Figure 7–3. The hydrogen gas passes into the pipe faster than the air can diffuse out, since hydrogen is the lighter gas and therefore diffuses more rapidly. As a result, the increased pressure inside the pipe and bottle forces liquid up through the jet.

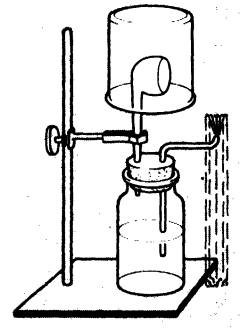


Figure 7–3 Apparatus to show relative rates of diffusion of air and hydrogen.

(*b*) *Chemical.* A mixture of hydrogen and oxygen gases may be heated moderately without any apparent action taking place; however, if the mixture is ignited by a spark, combination takes place with

[3] Adsorb means "adhere to a surface."

explosive violence to form water:

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

This action may be used as a basis for testing the purity of a sample of hydrogen. A small amount of the gas is ignited in a test tube; if a slight explosion occurs, the gas contains air or oxygen and is therefore impure. Pure hydrogen burns quietly with an almost colorless flame and does not support combustion.

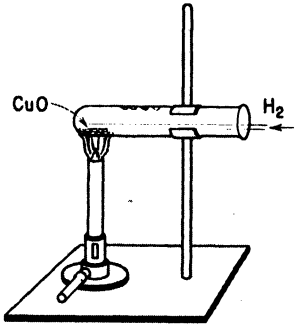


Figure 7–4 Reduction of cupric oxide by hydrogen gas.

When hydrogen gas is passed over heated copper oxide in a test tube, the copper oxide gradually changes from black to a copper-colored powder (Figure 7–4). Small drops of liquid condense on the sides of the test tube. The reddish deposit remaining in the test tube is metallic copper, and the liquid formed on the sides of the tube is water:

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

This reaction is another example of displacement, since the hydrogen has taken the place of the copper in the copper oxide. In such a chemical change, hydrogen is sometimes referred to as a *reducing* agent, since the compound has been reduced or changed to an element. Oxygen or those substances which give up oxygen in a chemical change are referred to as *oxidizing* agents; hence copper oxide in the above case is termed the oxidizing agent. The copper oxide may be said to be reduced and the hydrogen to be oxidized, and the entire process may be referred to as an oxidation-reduction reaction. Oxidation and reduction are simultaneous processes; one never takes place without the other. The terms oxidation and reduction have a much broader significance than indicated above, and the subject will be treated in more detail in Chapter 20.

Certain other metallic oxides may be reduced with hydrogen to form the free metal. Some of the less common metals—tungsten and molybdenum, for example—are prepared in a very pure condition in this manner. In general, the cost of production with hydrogen as a reducing agent is relatively high, and cheaper reducing agents are employed in the commercial preparation of most common metals.

Hydrogen combines directly with many nonmetals; for example,

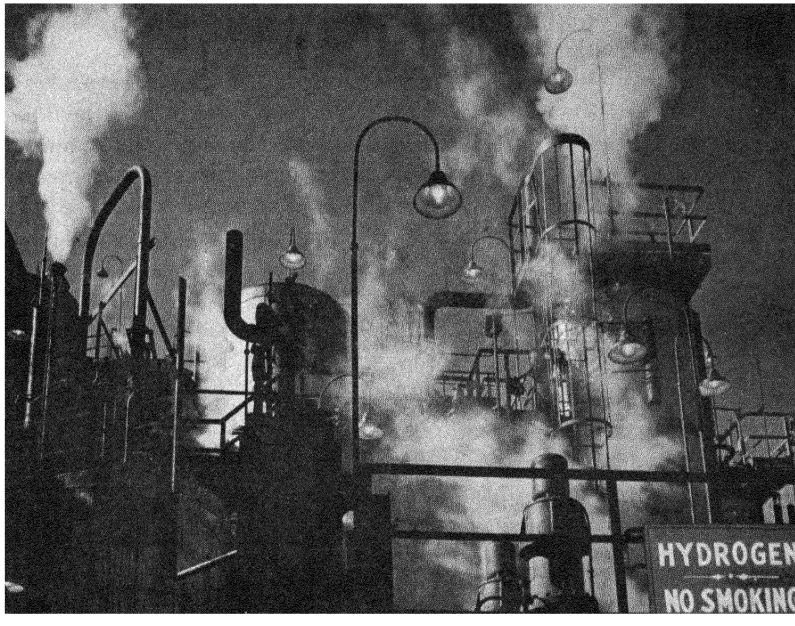


Figure 7–5 Note "No Smoking" sign near equipment in which hydrogen is used.

$$H_2 + S \rightarrow \underset{\text{hydrogen sulfide}}{H_2S}$$

$$H_2 + Cl_2 \rightarrow 2\,\underset{\text{hydrogen chloride}}{HCl}$$

Uses of hydrogen Since hydrogen is a very light gas, it has considerable lifting power in the air and is therefore used in lighter-than-air craft.[4] At one time, hydrogen gas was used exclusively in filling balloons and dirigibles; however, the gas is inflammable and therefore dangerous for this purpose. At the present time a mixture of hydrogen and noninflammable helium gases is used; the gases are mixed in such a proportion that the mixture is not inflammable.

Since 1925, large amounts of motor fuel and gasoline have been synthesized from coal. Coal contains carbon and compounds of carbon, hydrogen, and nitrogen. Gasoline is a mixture of several hydrocarbons (compounds of carbon and hydrogen), of which octane, C_8H_{18}, is an example. When finely powdered coal and hydrogen together are subjected to high temperatures and pressures, gasoline, lubricating oils,

[4] The lifting power of a substance in air is the difference in weight of a unit volume of air and a unit volume of the substance under the same conditions of temperature and pressure.

and other products are obtained. The process was first developed by Bergius in Germany.

Certain liquid fats combine with hydrogen at high temperatures in the presence of a nickel catalyst and in the process change from the liquid state to a solid or semisolid condition. Cottonseed and coconut oils are liquid fats which may be "hydrogenated" and used as substitutes for butter and lard, and for the production of soap.

Other uses of hydrogen include the catalytic preparation of ammonia and methyl alcohol.

EXERCISES

1 Point out several similarities and differences of hydrogen and oxygen.
2 What action, if any, takes place when iron (heated if necessary) is treated with (*a*) steam; (*b*) phosphoric acid; (*c*) oxygen; (*d*) hydrogen; (*e*) hydrochloric acid?
3 What are the advantages and disadvantages of using hydrogen in balloons?
4 Describe two procedures for the preparation of hydrogen from water.
5 What is the "activity series" and why is it of value to the chemist?
6 Balance the equations:

(*a*) $Fe + H_2O \rightarrow Fe_3O_4 + H_2$
(*b*) $Ca + H_2O \rightarrow Ca(OH)_2 + H_2$
(*c*) $CH_4 + H_2O \rightarrow CO + H_2$
(*d*) $C + H_2O \rightarrow CO_2 + H_2$

7 List five important uses of hydrogen.
8 In the electrolysis of water to which a small amount of sulfuric acid is added, how could you prove that the hydrogen and oxygen come from the water and not the acid?
9 Compare the relative efficiencies of hydrogen and methane (CH_4) for lifting a balloon.
10 With the aid of the activity series, predict which of the following reactions would take place:

(*a*) $Fe + Ag_2SO_4 \rightarrow FeSO_4 + 2\,Ag$
(*b*) $SnCl_2 + Mg \rightarrow MgCl_2 + Sn$
(*c*) $CaSO_4 + Cu \rightarrow CuSO_4 + Ca$
(*d*) $ZnCl_2 + 2\,Ag \rightarrow 2\,AgCl + Zn$
(*e*) $Hg_2SO_4 + 2\,Ag \rightarrow 2\,Hg + Ag_2SO_4$
(*f*) $Sn + 2\,HCl \rightarrow SnCl_2 + H_2$
(*g*) $Cu + H_2SO_4 \rightarrow CuSO_4 + H_2$

11 Which of the following metals would displace Cu from a solution of copper sulfate: Al, Sn, Ag, Au, Fe, Hg?
12 What change takes place in electronic positioning when Zn displaces Cu from $CuSO_4$?

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eight

THE GASEOUS STATE OF MATTER

Familiar properties of gases Matter in the gaseous state is characterized by its lack of any definite volume or shape. If a gas is placed in a closed container, it rapidly expands and very quickly becomes uniformly distributed throughout the entire space in the container. When a gas is cooled sufficiently, it becomes a liquid. Although all gases may be liquefied, some are changed to the liquid state only with a great deal of difficulty. Hydrogen and helium gases are the most difficult to liquefy, since temperatures near 0°A are necessary. On the other hand, such gases as chlorine and ammonia are liquefied quite easily.

If two gases are placed in a container, each gas acts independently of the other and diffuses uniformly throughout the volume of the container.

Gases may undergo expansion and compression. Air forced into an automobile tire is compressed; when the air is allowed to escape, it expands. Gases also exert pressure, and this pressure is exerted uniformly on all sides and top and bottom of the containing vessel. It is a remarkable fact that the physical behavior of gases is to a large degree independent of their nature or composition; for example, all gases respond in the same manner to changes in temperature and pressure. Several so-called gas laws describe this physical behavior, and in this chapter, these laws will be developed and utilized.

The measurement of air pressure The pressure of the atmosphere is measured with an instrument called a *barometer*. A simple barometer (Figure 8-1), can be prepared by inverting a piece of glass tubing about three feet long and closed at one end, filled with mercury, over a shallow pan containing mercury. The open end of the tube lies beneath

the surface of the mercury in the pan. The mercury will sink in the tube to such a level that the weight of the column of mercury is just equal to the weight of a column of air of equal cross section above the surface of the mercury in the pan. This column of air extends many miles high. The air exerts a pressure on the surface of the mercury in the container and supports the column of mercury in the tube. The exact pressure is determined by reading the difference between two mercury levels, the one in the tube and the other in the pan. The height of the mercury column is usually expressed in terms of millimeters. The average air pressure at sea level will support a column of mercury 760 mm. in height; this pressure is termed 1 atmosphere of pressure or *standard pressure*. A pressure of 50 atmospheres would be a pressure 50 times as great as that exerted by the atmosphere at sea level. In scientific work, pressures are usually referred to in terms of millimeters of mercury; thus a pressure of 700 mm. would be a pressure equal to that exerted by a column of mercury 700 mm. high. A column of water approximately 34 feet high would be supported by the atmosphere at sea level.

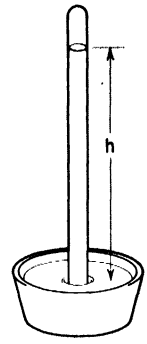


Figure 8–1 A mercury barometer.

The effect of pressure on the volume of a gas When the pressure on a gas is increased, the gas is compressed; an increase in pressure brings about a diminution of volume of the gas. Let us imagine a gas, such as air, enclosed in a cylinder fitted with a piston (Figure 8 2). We shall assume that the piston is weightless and frictionless. The pressure exerted on the gas will be adjusted by means of weights placed on the top side of the piston. Suppose we have 100 ml. of gas in the cylinder with a certain weight on the piston; if the weight on the piston is doubled, assuming that the temperature remains constant, the piston will move downward until the volume of gas is 50 ml. By doubling the pressure, the volume is halved; if the pressure is increased threefold, the volume becomes one-third of the original volume, and so on. The

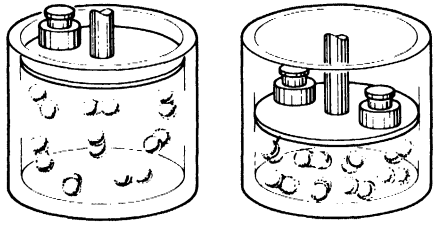


Figure 8–2 If the pressure upon a gas is doubled (at a constant temperature), the volume is halved (Boyle's Law).

relationship between the volume of a gas and the pressure was first stated by Robert Boyle in 1662 as follows: *The volume of a given mass of gas at constant temperature varies inversely as the pressure.* This relationship, which is virtually independent of the nature of the gas, is known as Boyle's Law.

By means of the law, we may calculate the volume of a gas at any pressure, provided we know the volume at a given pressure.

EXAMPLE 1. 100 ml. of gas are enclosed in the cylinder (Figure 8–2) under a pressure of 760 mm. What would the volume be at a pressure of 1520 mm.?

It is immediately evident that the corrected volume will be less than 100 ml., since the pressure has been increased from 760 to 1520 mm., and an increase in pressure results in a smaller volume. The volume will decrease in the same ratio that the pressure increases. The new volume then must be

$$100 \times \tfrac{760}{1520} = 50 \text{ ml.}$$

In the above calculation we have multiplied the volume by a fraction less than one, that is, $\frac{760}{1520}$. It is evident that had we multiplied by a fraction greater than one, the answer would have been greater than 100, which we know must be incorrect.

EXAMPLE 2. 100 ml. of gas at a pressure of 1000 mm. will occupy what volume at standard pressure (760 mm.)?

We reason that since the pressure is decreased (from 1000 mm. to 760 mm.), the volume must *increase.* Consequently the new volume will be greater than 100 ml., and we must multiply the original volume by a fraction greater than one. We have two possible ratios of pressures, $\frac{760}{1000}$ or $\frac{1000}{760}$. Since the ratio to be used must, in this case, be greater than one, we use the latter ratio, thus

$$\text{New Volume} = 100 \text{ ml.} \times \tfrac{1000}{760} = 131.6 \text{ ml.}$$

In computing a new volume, determine whether or not this new volume will be greater or less than the original volume. If the pressure is increased, the volume must be less; if the pressure decreases, the volume must be greater. Then multiply the original volume by a fraction (which is a ratio of the two pressures involved) so that the required condition will be satisfied.. If the volume is to increase, the fraction (ratic of pressures) must be greater than unity. If the volume is to decrease this fraction must be less than one.

Boyle's law may be written algebraically as follows:

$$v_2 = v_1 \times p_1/p_2 \quad \text{or} \quad p_1v_1 = p_2v_2$$

where v_1 is the volume at pressure p_1, and v_2 the volume at p_2.

The effect of temperature on the volume of a gas We are all familiar with the fact that a gas expands as the temperature rises. If the gas is placed in a closed container, expansion cannot take place, and the rise in temperature brings about an increase in pressure. If a gas is allowed to expand at a constant pressure, we may note a definite relationship between the volume change and temperature change.

Let us again make use of the cylinder and movable piston shown in Figure 8–2. Suppose the volume of a given mass of gas in the cylinder is 273 ml. at a given pressure and a temperature of 0°C. Now, keeping the pressure constant (by using a constant weight on the piston), let us heat the cylinder of gas. The piston will move upward and for every centigrade degree rise in temperature, the volume will increase 1 ml. At a temperature of 1°, then, the volume would be 274 ml.; at a temperature of 10°, the volume would be 283 ml.; at 273°, the volume would be 546 ml. or *double* that at 0°. If the temperature is decreased to 1° below 0°—that is, −1°—the volume decreases to 272 ml. A gas, then, at 0° contracts $\frac{1}{273}$ of its volume for every degree decrease in temperature, or it expands $\frac{1}{273}$ of its volume for every degree increase in temperature. Theoretically the volume of a gas would decrease to zero at −273°. This temperature is called absolute zero and is the basis of the absolute scale of temperature which was explained in Chapter 2. Actually this condition of zero temperature is never realized because all substances liquefy or solidify before the absolute zero temperature is reached. If the temperature is expressed as absolute temperature, it is evident that *at constant pressure the volume of a given mass of gas is directly proportional to the absolute temperature.* This is a statement of Charles' Law.

By means of Charles' law, we can calculate the volume of a gas at any temperature if we know its volume at any given temperature, assuming that the pressure remains constant.

EXAMPLE 1. A certain gas occupies a volume of 100 ml. at a temperature of 20°; what will its volume be at 10° if the pressure remains constant?

First, we must change these centigrade temperatures to absolute temperatures, since Charles' law states that the volume is directly proportional to the *absolute* temperature. We learned in Chapter 2 that centigrade temperature may be changed to absolute temperature by adding 273. Then

$$20° \text{ C.} = 20 + 273 = 293° \text{ A.}$$

and

$$10° \text{ C.} = 10 + 273 = 283° \text{ A.}$$

The temperature is being decreased (from 293 to 283), and since

decrease in temperature brings about a decrease in volume, the corrected volume will be less than 100 ml., and the correction factor must be less than unity The two possible ratios of temperature are $\frac{293}{283}$ and $\frac{283}{293}$. We must use the latter ratio, as this is the one which will give us a volume of less than 100 ml., thus

$$\text{New Volume} = 100 \times \tfrac{283}{293} = 96.6 \text{ ml}$$

EXAMPLE 2. The volume of a gas at 20° is 100 ml. What is the volume at 100°?

Again we first convert centigrade temperatures to absolute temperatures:

$$20^\circ \text{ C} = 20 + 273 = 293^\circ \text{ A}$$
$$100^\circ \text{ C} = 100 + 273 = 373^\circ \text{ A}$$

Since the temperature is increasing, the volume must increase. If the volume is to increase, we must multiply the original volume by a fraction greater than unity—that is, $\frac{373}{293}$. Hence

$$\text{New Volume} = 100 \times \tfrac{373}{293} = 127.3 \text{ ml}$$

In solving these problems, we always multiply the original volume by a fraction greater or less than unity. This fraction is a ratio of the absolute temperatures involved We reason that if the temperature is decreased, the volume likewise must decrease; consequently we must use the ratio less than one. If the temperature is increased, the volume must increase, so we use the fraction greater than unity

In accordance with Charles' law, we may write the general formula,

$$v_2 = v_1 \times T_2/T_1 \quad \text{or} \quad \frac{v_2}{v_1} = \frac{T_2}{T_1}$$

where v_2 is the volume at absolute temperature T_2, and v_1 is the volume at absolute temperature T_1.

The combined gas laws We have learned from Boyle's law that the volume of a gas at constant temperature is inversely proportional to the pressure, and from Charles' law that the volume at constant pressure is directly proportional to the absolute temperature. The two laws may be combined and stated as follows. *For a given mass of gas, the volume is inversely proportional to the pressure and directly proportional to the absolute temperature*

The general formula for the combined gas laws may be written,

$$v_2 = v_1 \times \frac{p_1}{p_2} \times \frac{T_2}{T_1}, \quad \text{or} \quad \frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

in which p_1 and T_1 are pressure and absolute temperature respectively

of the gas at volume v_1, and p_2 and T_2 are pressure and absolute temperature respectively at volume v_2.

It is obvious that if five of the six variables in the formulation $\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$ are fixed, then the sixth can be calculated.

It should be noted that if $v_1 = v_2$ (volume constant), it follows from the formula that *pressure is directly proportional to absolute temperature.*

Study the following problems carefully:

PROBLEM 1. A gas occupies a volume of 1 liter at a temperature of 27° and 500 mm. pressure. Calculate the volume of the gas if the temperature is changed to 60° and the pressure changed to 700 mm.

In solving this problem, first consider the volume change with change of pressure. The pressure is increased from 500 mm. to 700 mm. An increase in pressure decreases the volume, so we must multiply the original volume by a ratio less than one, $\frac{500}{700}$. Now consider the change in volume with change in temperature. The temperature is increased from 27° (300° A.) to 60° (333° A.). Since increase in temperature causes an increase in volume, the corrected volume must be greater than one liter. The original volume must then be multiplied by a ratio greater than unity, $\frac{333}{300}$. Correcting for changes in both temperature and pressure, we have

$$\text{New volume} = 1 \times \tfrac{500}{700} \times \tfrac{333}{300} = .79 \text{ liter}$$

PROBLEM 2. Calculate the pressure required to compress 2 liters of a gas at 700 mm. pressure and 20°C. into a container of 0.1 liter capacity at a temperature of −150°C.

We may reason this way: The final pressure must be the original pressure corrected for the volume change and the temperature change. Since a decrease in volume means an increase in pressure, the original pressure must be multiplied by the ratio of volumes greater than one, 2 liters/.1 liter. The temperature is decreasing from 293° A. (20° C.) to 123° A. (−150° C.) and since pressure decreases with decreasing temperature, the original pressure must be multiplied by a ratio of less than one, 123/293. Hence,

$$\text{New pressure} = 700 \text{ mm.} \times \frac{2}{.1} \times \frac{123}{293} = 5877 \text{ mm.}$$

Of course, we might substitute directly into the formula developed above to arrive at the same result:

$$\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$$

ORIGINAL CONDITIONS	FINAL CONDITIONS
$p_1 = 700$ mm.	$p_2 = ?$
$v_1 = 2$ liters	$v_2 = .1$ liter
$T_1 = 20° + 273° = 293°$	$T_2 = -150 + 273° = 123°$

Substituting:

$$\frac{(700 \text{ mm.})(2 \text{ liters})}{293°} = \frac{(p_2)(.1 \text{ liter})}{123°}$$

$$p_2 = \frac{(700 \text{ mm.})(2 \text{ liters})(123°)}{(.1 \text{ liter})(293°)} = 5877 \text{ mm.}$$

PROBLEM 3. 750 ml. of gas at 300 mm. pressure and 50° C. is heated until the volume of gas is 2000 ml. at a pressure of 700 mm. What was the final temperature of the gas?

In this case, since volume is directly proportional to absolute temperature, the original temperature must be multiplied by the larger ratio, 2000/750. Pressure is directly proportional to absolute temperature, so the original temperature must be multiplied by the ratio 700/300. Hence

$$\text{New temperature} = 323°\text{A.} \times \tfrac{2000}{750} \times \tfrac{700}{300} = 2010°\text{A.}$$
$$\text{Centigrade temperature} = 2010° - 273° = 1737°$$

Or, substituting directly into the formula:

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

ORIGINAL CONDITIONS	FINAL CONDITIONS
$p_1 = 300$ mm.	$p_2 = 700$ mm.
$v_1 = 750$ ml.	$v_2 = 2000$ ml.
$T_1 = 50° + 273° = 323°\text{A.}$	$T_2 = ?$

Substituting:

$$\frac{(300 \text{ mm.})(750 \text{ ml.})}{323°} = \frac{(700 \text{ mm.})(2000 \text{ ml.})}{T_2}$$

$$T_2 = \frac{(700 \text{ mm.})(2000 \text{ ml.})(323°)}{(300 \text{ mm.})(750 \text{ ml.})} = 2010°$$

$$\text{Centigrade temperature} = 2010° - 273° = 1737°$$

Sometimes it is convenient to use the general gas law formula

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

even though only two variables are involved. Suppose, for example, that one wishes to determine the change in volume of a gas caused by a given change of pressure, the temperature remaining constant. Instead of using the formula for Boyle's law (page 103), he could substitute directly in the general gas law formula, canceling out the two T terms, which are obviously identical. Or, if he wished, he could by algebraic manipulation derive the formula for Charles' law from the general gas law formula. Not the least of the advantages of the general formula is that it makes it unnecessary to memorize the three special formulas. Let us now use this method in the solution of an actual problem.

PROBLEM 4. A steel cylinder containing 10 liters of gas at a pressure of 4 atmospheres and a temperature of 40° C. is heated to 70° C. What is the pressure of the gas at the higher temperature?

ORIGINAL CONDITIONS	FINAL CONDITIONS
$p_1 = 4$ atm.	$p_2 = ?$
$v_2 = 10$ l.	$v_2 = 10$ l.
$T_1 = 40° + 273° = 313°$	$T_2 = 70° + 273° = 343°$

Since the volume is constant, the general formulation becomes

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Substituting:

$$\frac{4 \text{ atm.}}{313°} = \frac{p_2}{343°}$$

$$p_2 = \frac{(4 \text{ atm.})(343°)}{313°} = 4.383 \text{ atm.}$$

Standard temperature and pressure (STP) Since the volume of a given mass of gas changes with temperature and pressure, the volume is not defined unless the temperature and pressure of the gas are given. In order to get a comparison of the weights of equal volumes of gases, chemists have decided to refer all gas volumes to a standard set of conditions of temperature and pressure. We have already indicated (page 102) that the standard of pressure is the average pressure of the atmosphere at sea level, namely 760 mm. or 1 atmosphere. The standard temperature has been selected as the melting point of ice, namely, 0° C. or 273° A. Unless otherwise specified, when referring to gas volumes we shall assume standard conditions of temperature and pressure (abbreviated STP).

Deviations from the combined gas laws A gas which behaves exactly according to Boyle's and Charles' laws may be termed an *ideal* gas.

Actually, no gas is ideal; thus, deviations from ideal behavior are observed. This is so because (1) the molecules themselves occupy some space, thus restricting the space in which other molecules might move; and (2) a slight force of attraction exists between molecules so they do not move completely independently of one another. The first effect tends to make the volume larger, while the second effect tends to make the volume smaller than that calculated for ideal behavior. As the molecules of a gas get closer together, these effects are more pronounced, and greater deviations may be expected.

The proximity of molecules will depend upon both temperature and pressure—low pressures and high temperatures will keep the molecules farther apart, and closer conformity with the gas laws will follow under these conditions. Under usual laboratory working pressures and temperatures (about standard conditions), most gases conform fairly closely to ideal behavior (usually within 1 per cent), and the relationships between volume, pressure and temperature as expressed in Boyle's and Charles' laws are extremely useful in converting from one set of conditions to another.

Dalton's law of partial pressures *Each of the gases in a gaseous mixture behaves independently of the other gases and exerts its own pressure, the total pressure of the mixture being the sum of the partial pressures exerted by each gas present.* Since the atmosphere is composed of approximately 20 per cent oxygen and 80 per cent nitrogen, the oxygen exerts a partial pressure of about $\frac{1}{5} \times 760$ mm. $= 152$ mm., and the nitrogen a partial pressure of $\frac{4}{5} \times 760$ mm. $= 608$ mm.

Frequently gases in the laboratory are collected by displacement of water, as shown in Figure 8-3. The pressure of the gas inside the bottle is most conveniently measured by making it equal to the pressure of the atmosphere which can be determined with a barometer. If the level of water inside the bottle is adjusted to the same level as the water in the container outside the bottle, then the pressure inside the bottle must be equal to the pressure outside the bottle; that is, the pressure inside must be equal to the barometer reading. The pressure inside the bottle is equal to the sum of the pressures of *two* gases, the gas collected and *water vapor*. Above the liquid in the bottle, some of the water is in the form of vapor, the amount present depending upon the temperature and the

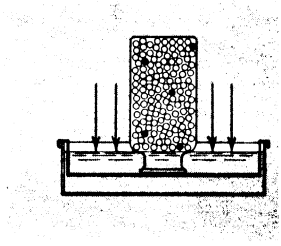


Figure 8-3 Collection of a gas over water. Molecules of the gas are shown by white circles; molecules of water vapor by black circles.

space above the liquid. At any given temperature, however, the pressure exerted by the water vapor is a constant

Since the pressure of the air as measured by the barometer is equal to the total pressure of the two gases inside the bottle, we may write:

$$P_{\text{air}} = P_{\text{gas}} + P_{\text{water vapor}}$$

Since we are interested in the actual pressure exerted by the gas, we may transpose the above equation

$$P_{\text{gas}} = P_{\text{air}} - P_{\text{water vapor}}$$

The pressure exerted by the water vapor at the temperature of the experiment may be obtained from a standard table of vapor pressures.

EXAMPLE Suppose 100 ml of oxygen were collected over water in the laboratory at a pressure of 700 mm and a temperature of 20°. What would the volume of the dry oxygen gas be at STP?

Vapor pressure of water at 20° (Table 11-3, page 148) is 17.5 mm. The actual pressure of the oxygen gas is then $700 - 17.5 = 682.5$ mm. Applying the combined gas laws, we obtain

$$\text{New Volume} = 100 \times \frac{682.5}{760} \times \frac{273}{293} = 83.67 \text{ ml}$$

Effusion and diffusion of gases If a gas is allowed to pass through a small opening, its rate of passage (effusion) depends upon the mass of the molecules, that is, upon the molecular weight. Heavy molecules move more slowly than light molecules. In experimenting with gases in 1832, Thomas Graham found that the comparative *rates or speeds of effusion of gases are inversely proportional to the square roots of their molecular weights.*

Examples. Oxygen gas (m.w. 32) is 32/2 = 16 times as heavy as hydrogen (m.w. 2). Therefore

$$\frac{\text{Speed of effusion of } H_2}{\text{Speed of effusion of } O} = \sqrt{\frac{32}{2}} = \sqrt{\frac{16}{1}} = \frac{4}{1}$$

The lighter gas, hydrogen, at a given temperature moves four times as fast as oxygen.

Consider the gases SO_2 (m.w. 64) and HBr (m.w. 81).

$$\frac{\text{Speed of effusion of } SO_2}{\text{Speed of effusion of HBr}} = \sqrt{\frac{81}{64}} = \frac{9}{8}$$

The lighter gas, SO_2, at a given temperature moves 1⅛ times as fast as HBr.

If a piece of sulfur is burned at one end of a closed room, the odor of sulfur dioxide is soon noticed throughout the room. SO_2 molecules have intermingled with molecules in the air. This property of two or more gases mixing and intermingling with one another is termed *diffusion*. While the rates at which molecules diffuse somewhat depend upon their masses, they do not conform closely to Graham's law of effusion.

The kinetic theory of gases We have learned in the preceding sections that all gases behave alike under the same set of conditions. Gases expand and may be compressed, the volume of any gas is affected in the same way by changes of temperature and pressure, regardless of the nature of the gas. All gases diffuse and mix with one another in all proportions. A mixture of gases exerts a total pressure which is the sum of the partial pressures of the constituent gases, regardless of their nature. The like behavior of gases is explained by the kinetic theory of gases.

Assumptions of the kinetic theory:

1 All gases are made up of tiny particles, called molecules.
2 The molecules are small in relation to the distances between them As molecules get closer together, attractive forces between molecules increase
3 Gas molecules are in a constant state of motion and move in straight lines in all directions until they collide with one another or with the walls of the container.
4 The molecules are perfectly elastic. When they collide, they rebound with perfect elasticity and without loss of energy
5 The velocity of the molecules changes with the temperature, increasing with increasing temperature and decreasing at lower temperatures.
6 The average energy possessed by the particles is the same, regardless of the mass. The kinetic energy (energy of motion) of the particles is proportional to the product of their mass and the square of their velocity The particles of high mass have a lower velocity than those of lower mass

How the theory explains the facts Since gases are supposedly made up of particles relatively far apart, they may readily be compressed, the molecules are simply crowded closer together. We know that solids and liquids can hardly be compressed at all, and we attribute this fact to the close proximity of the molecules in the solid and liquid states.

The diffusion of gases may be explained by the motion of the particles and the relatively large distances between the particles Since the particles of each gas are free to move about between the particles of one another, each gas is free to act relatively independently of other gases present in a mixture.

Pressure is due to the bombardment of the walls of the containing vessel with particles of the gas Since the particles are moving in all directions, and since, on the average, equal numbers of molecules are traveling in all directions, equal pressures are exerted on the bottom,

top, and sides of the containing vessel. The combined effect of all these collisions on a unit area gives the total pressure.

If the particles are enclosed in a smaller space (thus decreasing the volume), the collisions with the walls become more frequent, and the pressure is increased. Conversely, if the gas is expanded, fewer collisions take place, and the pressure is decreased. In other words, the volume of gas is inversely proportional to the pressure at constant temperature (Boyle's law).

If the temperature of a gas is increased, the energy of the particles is increased and they move faster. If the volume is maintained constant, the pressure must increase, since the number of collisions on the walls in a given time will now be increased. This explains the increase in pressure of a gas with increase in temperature at constant volume. Now if pressure is maintained constant when the temperature is raised, the gas must expand so that the number of collisions of the particles per unit area of the walls (pressure) will remain constant. An increase in volume with increase of temperature at constant pressure (Charles' law) is thus explained.

Since the particles in a gaseous mixture are free to move about in an independent fashion and each exerts a pressure of its own, then we would expect the total pressure of the gaseous mixture to be the sum of the pressures of all the molecular species present (Dalton's law of partial pressures).

The question might be asked, how can a light gas such as hydrogen exert as much pressure on the walls of a container as heavier oxygen gas? Since pressure is due to the sum of the magnitudes of blows of molecules on the confining walls, we are concerned with the kinetic energy of moving molecules. Energy of a moving particle is dependent upon both the mass and velocity as given by the formula

$$\text{Kinetic Energy} = \tfrac{1}{2} MV^2$$

where M is the mass of the particle and V its velocity. Recall from consideration of Graham's law of effusion that hydrogen gas effuses 4 times as fast as oxygen, whereas their comparative masses are 2 to 32.

$$\text{K. E. of Hydrogen} = \tfrac{1}{2} \cdot 2 \cdot 4^2 = 16$$
$$\text{K. E. of Oxygen} = \tfrac{1}{2} \cdot 32 \cdot 1^2 = 16$$

The kinetic energies of hydrogen and oxygen molecules are equal. It can likewise be further shown that at a given temperature the kinetic energy of all gas molecules is the same; the heavier gas molecules move more slowly than the lighter ones; insofar, as pressure on the wall of a con-

tainer is concerned, all gas molecules behave alike and hit with equal force.

Liquefaction of gases The kinetic molecular theory also explains the fact that gases may be liquefied. By slowing down molecular movement by decreased temperature, and forcing molecules nearer together by increased pressure, a state is reached where intermolecular attraction somewhat offsets the kinetic energy of particles and the conditions of the liquid state are obtained. At still lower temperatures the kinetic energy of molecules further decreases and the liquid changes to solid.

Both temperature and pressure, then, are factors in determining the condensation of a gas to liquid or, conversely, the vaporization of liquid to gas. Gaseous water at 100° C. and 760 mm. pressure will condense to liquid water as heat is removed. It similarly will condense to liquid if the pressure is increased. It should be emphasized that pressure must be defined to determine the condensation or boiling point. At a pressure of 3580 mm. in a pressure chamber, water will boil at 150° C. when heat is applied. Gaseous water will condense at 20° C. under 17.4 mm. pressure. This discussion will be expanded in Chapter 11.

Oxygen and hydrogen gases may be condensed to liquids at −183° C. and −252.5° C. respectively at 760 mm. pressure. At higher pressures they will condense at higher temperatures; at 50 atmospheres pressure, for example, O_2 will condense to liquid at −118° C.

Above a definite temperature for each gas, the kinetic energy of the molecules is of such magnitude that no increase in pressure however large can liquefy it. This temperature for each gas is its *critical temperature* and the concomitant pressure is the *critical pressure.* Oxygen cannot exist as a liquid above −118° C. even at pressures much higher than 50 atmospheres. Water cannot exist as a liquid above 374° C. no matter how high the pressure.

Gay-Lussac's law of combining volumes When water is electrolyzed (Figure 6–5, page 85), the compound is decomposed into its constituent elements, hydrogen and oxygen. Quantitative measurements show that the volume of hydrogen produced from a given weight of water is *twice* the volume of oxygen produced. When water is synthesized from its elements, this same relationship between the volume of oxygen and hydrogen holds—that is, twice as much hydrogen as oxygen *by volume* is required. The equation for the reaction is

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

We may note in the equation that the coefficients of the formulas are in exactly the ratio (2 to 1) in which hydrogen and oxygen combine by volume. These experiments illustrate an important law of chemistry,

first stated by Gay-Lussac: *Whenever gases appear or disappear in a chemical reaction, they do so in the ratio of small whole numbers by volume* It is assumed that all gases involved in such a reaction are at the same conditions of temperature and pressure. Ordinarily, in the change described above, the water formed as a product is allowed to condense to liquid water. However, if the water is allowed to remain in the form of gas (steam) and the volume measured, it is found that the volume of steam produced has the same volume as the hydrogen used, and twice the volume of the oxygen used, all gases being measured under the same conditions of temperature and pressure. We note again that the ratio by volume of the gases in the reaction is the same shown by the coefficients of the equation—that is, 2 to 1 to 2. The equation may be read as follows two volumes of hydrogen reacts with one volume of oxygen to produce two volumes of water vapor (gases at same conditions). Of course, any unit of volume might be used, for example, we may say that two liters of hydrogen reacts with one liter of oxygen to produce two liters of steam

Gay-Lussac's law applies to all substances in the gaseous state The equation

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

tells us that one volume of nitrogen combines with three volumes of hydrogen to form two volumes of ammonia The numbers in front of the formulas (coefficients) always give us the relationship between the gases *by volume*

The ratio in which substances combine by volume must not be confused with the ratio in which they combine by weight. Two parts by weight of hydrogen combines with 16 parts by weight of oxygen to form water Substances do not combine in the ratio of small whole numbers by weight.

Gram molecular volume Let us study further the equation for the electrolysis of water:

$$\underset{36\text{ g}}{2\,H_2O} \rightarrow \underset{\substack{4\text{ g}\\ 44.8\text{ l}}}{2\,H_2} + \underset{\substack{32\text{ g}\\ 22.4\text{ l}}}{O_2}$$

According to the equation 2×18 or 36 g. of water yields 2×2 or 4 g. of hydrogen and 2×16 or 32 g. of oxygen Experiment shows that 36 grams of water on being decomposed by the electric current produces 44.8 liters of hydrogen and 22.4 liters of oxygen, the gases being measured at standard conditions. Then, 44.8 liters of hydrogen at standard conditions must weigh 4 grams, and 22.4 liters of oxygen must have a weight of 32 grams. Four grams of hydrogen represent 2 gram molec-

ular weights, or 2 moles of hydrogen. If the volume of 2 moles is 44.8 liters, the volume of 1 mole of hydrogen must be 22.4 liters. Similarly 32 grams of oxygen represents 1 gram molecular weight of oxygen or 1 mole of oxygen, and the volume of 1 mole of oxygen is also 22.4 liters at standard conditions. If we should study the relationship between volume and weight of other gases, we should find that *one gram molecular weight (one mole) of any gas occupies a volume of 22.4 liters at standard conditions.* This volume, 22.4 liters, is called the *gram molecular volume* of a gas (Figure 8–4).

This relationship between volume and weight of a gas is used as a basis for the determination of molecular weights of substances in the gaseous state; it is simply a matter of determining the weight of 22.4 liters of the gas measured at standard conditions. This weight in grams is numerically equal to the molecular weight. Of course, this method is not applicable to those substances which are not readily converted into the gaseous condition.

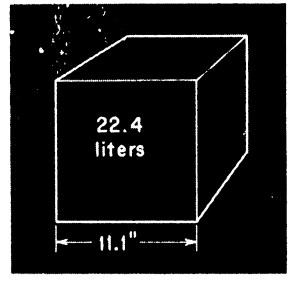


Figure 8–4 A gram molecular weight of any gas at standard conditions occupies a volume of 22.4 liters. This volume is contained in a cube 11.1 inches on an edge.

Avogadro's hypothesis. In the study of gases it was found that all gases behave alike under the same conditions. All gases expand and contract according to very definite physical laws. We now find that when gases combine, there is a simple ratio in which they react by volume. These facts suggest that the same physical structure is possessed by all gases. Avogadro, an Italian physicist, was the first to suggest that *equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.* This view was first held as a speculation, but evidence has accumulated until at present Avogadro's statement is regarded as a law. The number of molecules in one gram molecular weight (22.4 liters of the substance in the gaseous form at standard conditions) has been determined by several independent methods and been found to be 602,000,000,000,000,000,000,000 or 6.02×10^{23}. This number is inconceivably large. The following illustration may give the student some appreciation of its magnitude. Assume that the entire population of the world, about 2 billion, is engaged in counting the molecules in one gram molecular weight of a substance. Counting molecules at the rate of 2 per second and working 24 hours a day and 365 days a year, it would require about 5 million years to complete the job.

EXERCISES

1 Explain in terms of the kinetic molecular theory:

(*a*) the compressibility of gases
(*b*) diffusion of gases
(*c*) why gases do not settle
(*d*) Boyle's law
(*e*) Charles' law
(*f*) Dalton's law of partial pressures

2 A certain gas occupies a volume of 100 ml. at a temperature of 50° and a pressure of 700 mm. Calculate the volume of the gas if the temperature is raised to 100°, the pressure remaining constant. Ans. 115 ml.

3 Two liters of a gas at a pressure of 500 mm. will occupy what volume if the pressure is doubled, the temperature remaining constant?

4 Ten liters of a gas is collected at a temperature of 30° and a pressure of 700 mm. Calculate the volume of gas at standard conditions. Ans. 8.3 l.

5 500 ml. of gas at 20° and a pressure of 780 mm. will occupy what volume if the temperature is reduced to −150° and the pressure increased to 1560 mm.? Ans. 105 ml.

6 0.27 gram of dry gas occupies a volume of 354 ml. at a temperature of 18° and a pressure of 696 mm. Calculate the weight of 1 liter of the gas at standard conditions. Ans. 0.89 g.

7 When J. F. Piccard made a stratosphere flight in a balloon, the balloon seemed to be but half filled as it left the ground near Detroit; the gas temperature was about 27° C. and the pressure 700 mm. The volume of gas in the balloon was 80,000 cubic feet. What was the gas volume at high altitude (assuming no leakage) where the temperature was −3° C., and the pressure 400 mm.? Ans. 126,000 cu. ft.

8 If an industrial plant had a mixture of equal volumes of HCl and HBr gases in a porous container, what would be the comparative rates of effusion of these gases through the porous walls? The molecular weights of HCl and HBr are respectively about 36 and 81. Compare the kinetic energies of these two gases.

9 Given 600 ml. of a gas at standard conditions. If the pressure is trebled and the temperature is raised to 546° C., what volume will the gas then occupy? Ans. 600 ml.

10 60 liters of a gas was collected over water when the barometer read 741 mm. and the temperature 23° C. The vapor pressure of water at 23° C. = 21.1 mm. What volume would the dry gas occupy at standard conditions? Ans. 52.4 l.

11 Two gases, HCl (mol. wt. 36) and SO_2 (mol. wt. 64) are allowed to effuse through a small opening. Which gas effuses more quickly? How many times more quickly?

12 600 ml. of a gas at 27° C. and 1 atmosphere pressure is heated to 177° C. What pressure must be applied to the gas in order to maintain the same volume?

13 On a hot day the pressure in an automobile tire increases. If the air in a tire at 59° F. is under a pressure of 30 lb. per square inch and the pressure increases to 32 lb. per square inch on driving, (*a*) what is the temperature of the air in the tire, assuming no change in volume? (*b*) what would be the pressure in the tire if the temperature rises to 104° F.? Ans. (*a*) 93° F. (*b*) 32.6 lb./in.^{2}.

14 What is the molecular weight of a gas which effuses one third as fast as methane gas, CH_4 (mol. wt. 16)? Ans. 144.

15 If 50 ml. of gas at 27° C. is heated at constant pressure to a temperature of 327° C., what will the new volume be? Ans. 100 ml.

16 SO_2 and CH_4 are gases with molecular weights of 64 and 16 respectively. If SO_2 effuses through a certain opening at a rate of 3 ml. per second, at what rate will CH_4 effuse through the same opening? Ans. 6 ml./sec.

17 5.6 liters of phosgene gas, $COCl_2$, at standard conditions will weigh how many grams? Ans. 24.8.

18 11.2 liters of a gas at 0° C. and at 76 mm. pressure contains how many molecules? Ans. 3×10^{22}.

19 Determine the number of molecules in a drop of water which weighs 0.05 g.

20 Ten moles of hydrogen gas at 0° C. is forced into a steel cylinder with a volume of 100 ml. Compute the pressure of the gas in the cylinder.

21 A steel cylinder of 50 liters capacity contains helium at a pressure of 200 atmospheres at a temperature of 27° C. Assume that all of the gas can be used to fill a weather balloon, which is released in the air. At a height of 100,000 ft. the volume of the balloon is 200 cubic meters, and its temperature is −73° C. What is the pressure of the gas inside the balloon? Ans. 1/30 at.

22 If 40 liters of SO_2 (mol. wt. 64) effuses through a porous partition in 20 minutes, what volume of CH_4 (mol. wt. 16) will effuse through the same partition at the same temperature and pressure in 40 minutes?

23 600 ml. of hydrogen gas at 27° C. and one atmosphere is heated to 177° C. What pressure must be applied to the gas in order to maintain the same volume? Ans. 1.5 at.

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CHEMISTRY IS THAT SCIENCE WHICH DEALS WITH THE CAUSES AND EFFECTS OF THE DONATION, ACCEPTANCE, OR SHARING OF (ORBITAL) ELECTRONS BETWEEN ATOMIC OR MOLECULAR SPECIES, AND WITH THE ENERGY-POSITION RELATIONSHIPS OF THE ELECTRONS WITHIN THE SPECIES.

A. B. Simon

nine VALENCE AND OXIDATION NUMBER

Valence is a term used by the chemist to describe the nature of bonding forces between atoms and between ions. As knowledge of bonding forces has increased, the meaning of valence has undergone considerable revision.

In the beginning, valence was regarded simply as a measure of the combining capacities of atoms, and this concept has been most useful in writing formulas. But with the advent of modern atomic theory, usage of the term has changed, and we now describe more than one kind of valence or valency. Difficulties in expressing the valency of all elements in some compounds, particularly those compounds containing three or more elements, have led to the introduction of another term, "oxidation number." These various aspects of the general term "valence" will now be discussed in some detail.

Electrovalence and atomic structure In the study of atomic structure,

we learned that the outer orbit of an atom contains electrons called valence electrons. These valence electrons determine the way in which atoms combine with one another. We noted that all elements tend to complete the outer orbit of their atoms with electrons to form a stable configuration—one in which the outer orbit holds its capacity of electrons. The sodium atom has a single electron in its outer orbit and will give up this electron to other atoms. By giving up this single electron, the atom reverts to a more stable configuration. This type of valence resulting from transfer of electrons from one atom to another is called *electrovalence.*

Sodium is said to have an electrovalence of 1, since 1 electron is given up by the atom. Since the release of an electron leaves the sodium atom with an excess of 1 positive charge, we say the electrovalence is $+1$. The charged atom which remains after the release of an electron is a sodium ion, Na^+, and the charge on the ion is the electrovalence. Calcium, which gives up the 2 electrons in its outer orbit and becomes a calcium ion, Ca^{++}, has an electrovalence of $+2$; aluminum has an electrovalence of $+3$, since it gives up 3 electrons. In general, metals give electrons as they combine with other elements, and their electrovalence is the number of electrons given up and is positive.

Nonmetal atoms, in general, take up electrons and have a negative electrovalence. For example, an atom of chlorine takes up 1 electron to complete its outer shell of 8 electrons and thus becomes a chlorine ion, Cl^-. The electrovalence of chlorine is -1. Sulfur atoms accept 2 electrons from metal atoms, becoming S^{--}, and sulfur is said to have an electrovalence of -2.

Note that an element exhibits a valence *only when it is combined with some other element*—in other words, when it is a part of a compound. Electrovalence means a charge on the atom; an uncombined element is without charge and must therefore have 0 valence. Thus, Na by itself has 0 valence, but when combined it exhibits an electrovalence of $+1$.

Radicals—groups of atoms that remain together throughout a chemical change—also exhibit a valence. Since radicals are charged groups of atoms, they are in reality ions. In their formation one or more electrons are acquired (or lost) to give the group a net charge. Table 9-1 gives the common electrovalences of various elements and radicals.

The concept of valence is most easily explained by the theory that the outer orbit of metals gives up electrons and the outer orbit of nonmetals receives them. However, this theory of atomic structure is itself based largely on facts observed during the formation of compounds and on the weight relations between combined elements. Long before present day ideas of atomic structure were developed, chemists believed in the

TABLE 9–1 Electrovalences of Elements and Radicals*

+I	+II	+III	
H^+ or H_3O^+ (hydronium)	Ca^{++}	Al^{+++}	
Na^+	Mg^{++}	Fe^{+++} (ferric)	
K^+	Ba^{++}	Cr^{+++} (chromic)	
	Cd^{++}		
Ag^+	Zn^{++}	As^{+++}	
NH_4^+ (ammonium)	Pb^{++}	Sb^{+++}	
Cu^+ (cuprous)†	Ni^{++}	Bi^{+++}	
	Cr^{++} (chromous)		
Hg_2^{++} (mercurous)	Fe^{++} (ferrous)	La^{+++}	
	Cu^{++} (cupric)		
	Sn^{++} (stannous)		
	Mn^{++} (manganous)		
	Sr^{++}		
	Co^{++}		
	Hg^{++} (mercuric)		
−I	**−II**	**−III**	**−IV**
Cl^- (chloride)	O^{--} (oxide)	PO_4^{---} (phosphate)	SiO_4^{----} (silicate)
Br^- (bromide)	S^{--} (sulfide)	AsO_4^{---} (arsenate)	
I^- (iodide)	SO_3^{--} (sulfite)		
F^- (fluoride)	SO_4^{--} (sulfate)		
OH^- (hydroxide)	CO_3^{--} (carbonate)		
$C_2H_3O_2^-$ (acetate)	CrO_4^{--} (chromate)		
ClO_3^- (chlorate)	$C_2O_4^{--}$ (oxalate)		
NO_3^- (nitrate)	SiO_3^{--} (metasilicate)		
CN^- (cyanide)			

* SPECIAL NOTE: Table 9-1 constitutes one of the fundamental A, B, C's of chemistry. Much as one cannot spell without knowledge of the alphabet or do much arithmetic without multiplication tables, one cannot progress well in chemistry without knowing valence. ***Memorize Table 9-1.***

† The lower valence of a metal in a compound has long been designated with the suffix *-ous;* the higher valence with the suffix *-ic* for example, Cu^+ (cuprous) and Cu^{++} (cupric) ions. Salts containing these ions—for example, Cu_2SO_4 and $CuSO_4$—would be cuprous sulfate and cupric sulfate, respectively. A more recent method is to show the actual valence of the metal with Roman numerals; thus, Cu_2SO_4 is copper (I) sulfate; $CuSO_4$ is copper (II) sulfate. Similarly, $CrCl_2$ is chromium (II) chloride and $CrCl_3$ is chromium (III) chloride.

atomic theory and were writing formulas on the basis of that belief. Let us see how formulas and valences were determined.

Determination of formulas from analytical data Formulas may be derived from the results of analysis for each of the elements present in a pure chemical compound. These results are usually expressed in terms of percentage of each element present—that is, parts of each element present in 100 parts by weight of the compound. In order to arrive at the formula for the compound, it is necessary to have the relative number of *atoms* of each element present. By dividing the percentage of each element present by its atomic weight, we obtain quotients

which will be in the ratio of the number of atoms of each element. For example:

A compound on analysis is found to contain 1.59 per cent hydrogen, 22.2 per cent nitrogen, and 76.2 per cent oxygen. If we arbitrarily take 100 grams of the compound, then 1.59 grams will be hydrogen, 22.2 grams will be nitrogen, and 76.2 grams will be oxygen. The number of gram atoms of each of the three elements per 100 grams of compound will be: $\frac{1.59}{1} = 1.59$ gram atoms of hydrogen, $\frac{22.2}{14} = 1.59$ gram atoms of nitrogen, and $\frac{76.2}{16} = 4.77$ gram atoms of oxygen. The relative number of atoms will be in the same ratio as the number of gram atoms; namely

H	N	O
1.59	1.59	4.77

By dividing each number by the highest common divisor (1.59) of the three values, we obtain the ratio

H	N	O
1	1	3

Hence, the simplest formula for the compound is HNO_3.

A formula obtained thus from chemical analysis is an *empirical* formula. It tells us the ratios of the number of atoms of each element present in the compound, but it does not tell us the number of atoms in a molecule of the compound. The true molecular formula may be $H_2N_2O_6$ or $H_3N_3O_9$ or any other multiple of the simplest formula. To determine which is the correct molecular formula, we must know the molecular weight of the compound. (See Chapter 13 for methods of determining molecular weights experimentally.) If the molecular weight of the above compound were 126, the true molecular formula would be $H_2N_2O_6$. But since the molecular weight is known to be 63, the molecular formula must be HNO_3.

To derive a formula from percentage composition data:

1 Divide the percentage of each element by its atomic weight.
2 Divide the quotients obtained by the highest common divisor of all the quotients.
3 Write the simplest or empirical formula for the compound.
4 If the molecular weight or the approximate molecular weight is known, determine what multiple of the simplest formula most nearly gives the molecular weight; multiply the number of atoms of each element in the simplest formula by this multiple and write the true formula for the compound.

If the molecular weight cannot be determined or if the compound does not form molecules, the simplest empirical formula is used.

As a further example, consider aluminum fluoride, which analyzes 32.14 per cent aluminum and 67.86 per cent fluorine.

$$\frac{32.14}{27\ (\text{at. wt. Al})} = 1.19 \qquad \frac{67.86}{19\ (\text{at. wt. F})} = 3.57$$

This gives a 1.19–3.57 or 1–3 ratio; hence simplest formula is AlF_3.

Derivation of valence from formulas Valences may be derived from the formulas of a number of compounds that have been analyzed. If we choose hydrogen as a standard and assign it a valence of $+1$, we may deduce valences as follows:

Consider the formulas HCl, hydrogen chloride; H_2O, water; NH_3, ammonia; CH_4, methane. Each element has a different combining capacity for hydrogen: chlorine has the capacity to hold in combination 1 hydrogen atom; oxygen, 2 hydrogen atoms; and so on. Oxygen has a greater capacity for hydrogen atoms than does chlorine; nitrogen and carbon have still greater capacities for hydrogen. Since all molecules are electrically neutral, we may determine the combining capacity for each of these elements in terms of hydrogen atoms. If hydrogen has a valence of $+1$, then Cl must be -1 to balance the molecule electrically. The valence of oxygen in H_2O would be -2; of nitrogen in NH_3, -3; of carbon in CH_4, -4.

Now consider these formulas: NaCl, sodium chloride; $CaCl_2$, calcium chloride; $AlCl_3$, aluminum chloride. Since these compounds do not contain hydrogen, we cannot determine their valences in terms of hydrogen atoms directly from the formulas. But the compounds do contain chlorine, which is equivalent in valence to hydrogen, but of opposite charge. Since chlorine has a valence of -1, the valence of sodium, calcium, and aluminum must be $+1$, $+2$, and $+3$, respectively. Thus, we may derive the valence or combining capacities of elements from formulas of their compounds by a consideration of the hydrogen atoms in the molecule, or, in those cases where hydrogen is not present, an element whose valence is known in terms of hydrogen. Accordingly, the original concept was that *valence is a number, which for a given atom of an element is the number of hydrogen atoms this atom will combine with or replace.* This is still a useful idea of valence when applied to a great number of simple substances.

Radicals are treated as units in most chemical changes. In the formula H_2SO_4, it is obvious that the SO_4 (sulfate) radical must have a valence of -2, since one radical is combined with two hydrogen atoms.

The use of valence in writing formulas Since compounds are made

up of a combination of positive (+) and negative (−) units, in writing the formula for any given compound we must balance the combining capacities of the positive and negative units in such a way that the resulting combination is electrically neutral, in other words, the total charge of the positive part must balance the total charge of the negative part. For example, the compound aluminum chloride is composed of the elements aluminum and chlorine, so we may write down the symbol for Al and the symbol for the chloride unit thus:

$$\mathrm{Al} \qquad \mathrm{Cl}$$

Aluminum has a valence of +3, and chloride a valence of −1 (see Table 9–1). To balance electrically, 3 chlorine atoms must combine with 1 atom of aluminum; hence

$$\mathrm{AlCl_3}$$

must be the formula for aluminum chloride. Valence requires that the ratio of aluminum atoms to chlorine atoms in the compound be 1 to 3. Of course, we might write $\mathrm{Al_2Cl_6}$, which shows the composition of the compound correctly, but it is customary to use the smaller numbers 1 and 3. Consider the compound aluminum sulfate, which is composed of aluminum and the sulfate radical. We write down the symbols for each of these (it is customary to write the positive part first) thus

$$\begin{matrix} +3 & -2 \\ \mathrm{Al} & \mathrm{SO_4} \end{matrix}$$

We may for convenience write down the valence of the units above the formulas. In order to balance positive and negative charges in this compound, we must use a ratio of 2 aluminum atoms to 3 sulfate groups. Two aluminum atoms then will contribute a total of 6 positive charges which are balanced by a total of 6 negative charges contributed by the 3 sulfate groups. The formula for aluminum sulfate must then be

$$\mathrm{Al_2(SO_4)_3}$$

Experimental determination of valence The valence of a positive or negative group is really a measure of the combining capacity of that group in terms of hydrogen atoms or the equivalent of hydrogen atoms. Metals above hydrogen in the activity series displace hydrogen from acids; hence we may determine the relationship between the metal and hydrogen directly. If the metals sodium, magnesium, and aluminum are allowed to react with an acid, the following data are obtained:

1 gram atom (23 grams) of sodium displaces 1 gram atom (1 gram) of hydrogen.

1 gram atom (24.3 grams) of magnesium displaces 2 gram atoms (2 grams) of hydrogen.
1 gram atom (27 grams) of aluminum displaces 3 gram atoms (3 grams) of hydrogen.

Gram atomic weights (atomic weight in grams) of all elements contain the same number of atoms, namely 6.02×10^{23} (see Chapter 31). Thus, one atom of sodium is equivalent to one atom of hydrogen; therefore, the valence of sodium must be one. Similarly, one atom of magnesium displaces two atoms of hydrogen and therefore must have a valence of two. By similar reasoning, aluminum is shown to have a valence of three.

We may arrive at the valence of the metals sodium, magnesium, and aluminum in another way from the same data. The weight of an element which will combine with, or displace, 1 gram of hydrogen is termed the *equivalent* weight of the element. From the above data, it is evident that the equivalent weight of sodium is 23, since 23 grams of sodium displaces 1 gram of hydrogen. The equivalent weight of magnesium must be $\frac{24.3}{2}$ or 12.15, since 12.15 grams of magnesium would displace 1 gram of hydrogen. Twenty-seven grams of aluminum displaces 3 grams of hydrogen; hence 9 grams of aluminum would displace 1 gram of hydrogen. The equivalent weight of aluminum, then, is 9. *The valence of an element may be calculated by dividing the atomic weight of the element by its equivalent weight.* Thus, the valence of sodium is $\frac{23}{23} = 1$; the valence of magnesium is $\frac{24.3}{12.15} = 2$; the valence of aluminum is $\frac{27}{9} = 3$. The equivalent weight is always either equal to, or is some simple fraction of, the atomic weight.

Many of the elements do not displace hydrogen from an acid, nor do they combine directly with that element. In determining the valence of such an element, an element with which it does combine and whose valence is known may be used. For example, we know that chlorine has a valence of one, since one atom of chlorine combines with one atom of hydrogen in hydrogen chloride. If the element in question combines with chlorine, the weight of the element combining with 1 gram atom of chlorine (this would be an equivalent weight of the element) can be determined. The valence then is calculated by dividing the atomic weight of the element by its equivalent weight.

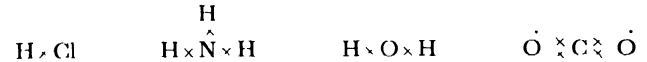
Covalence In the union of a chemically active metal with a nonmetal, there is a very decided transfer of electrons from the outer orbit of the metal atom to the nonmetallic atom, and the resulting compound is electrovalent. As pointed out in Chapter 3, electrons may also be shared between atoms, and the resulting compound is covalent. For

example, in the compound methane, CH_4, a pair of electrons is shared by each hydrogen atom with the carbon atom; in the compound carbon tetrachloride, CCl_4, each chlorine atom shares a pair of electrons with carbon:



Note the symmetrical ring of 8 electrons in the structure of each of these compounds. The question naturally arises: can a positive or negative character be assigned to the atoms in such compounds? There is some evidence that in compounds of this type the electron pairs are displaced toward certain atoms and away from others. For example, it is likely that in methane the electron pairs are closer to the carbon atom, whereas in carbon tetrachloride the electron pairs are probably closer to the chlorine atoms. On this basis we might assign a positive character to carbon in the first compound and a negative character to carbon in CCl_4. However, in the case of covalent compounds, ordinarily no attempt is made to assign positive and negative values; the valence as a number is stated without positive or negative charge. In the above examples, the covalence of carbon is simply the number 4

Other examples of covalent compounds are:



To eliminate the need for writing so many dots and x's, a dash is often employed to indicate a shared electron pair, two dashes to indicate two shared pairs, and so on. Thus:



In these compounds it is evident that hydrogen has a covalence of 1, oxygen 2, nitrogen 3, carbon 4. The *covalence* of an element is the *number of electron pairs shared* by the atom in question.

The atoms in covalent substances are held tightly together by shared electron pairs, and definite molecules are formed. This is in contrast to purely electrovalent compounds which as crystals are spatially placed ions, with no two ions forming an independent molecule. Electrovalent compounds when put in a solvent such as water indulge in a separation of the various positive and negative ions. If the covalent compound does not chemically react with a solvent—for example, with water—no

separation of the molecule takes place and no electrical current-conducting solution is formed. A covalent linkage between atoms—that is, an electron-pair sharing—seems to be a stronger bonding than an electrovalency. These different bondings in electrovalent and covalent compounds give rise to distinct differences in chemical behavior.

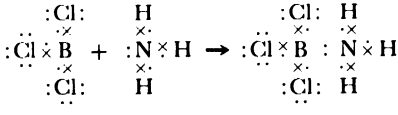
Polar and nonpolar bonds In our discussions so far we have described two principal types of bonds which hold atoms together; namely, the electrovalent or ionic bond, and the covalent bond. Although many substances appear to fall strictly into one or the other of these classifications, others seem to exhibit a bonding which is intermediate between the two. We may look at it this way: Elements vary in their affinity for electrons. Sodium and chlorine would represent two extremes. The sodium atom has little or no affinity for electrons; as a matter of fact, it readily gives up an electron. Chlorine, on the other hand, has a strong affinity for electrons. The compound NaCl is definitely electrovalent or ionic, and the ions are held together simply by attraction of the opposite charges.

Consider now a case in which two atoms with the same electron affinity combine. Such would be the situation in the chlorine molecule, Cl_2. Each chlorine atom has the same affinity for electrons, and the shared pair of electrons in the chlorine molecule would lie midway between the two atoms, giving rise to an electrically symmetrical molecule. Such a bonding of atoms may be described as *nonpolar.*

However, in a combination of unlike atoms such as HCl (a covalent compound), attraction for electrons would not be equal, and because of a displacement of the electron pair toward the chlorine atom, the molecule is not electrically symmetrical; the chlorine end of the molecule tends to be negative while the hydrogen end is positive. Such a molecule is described as *polar.* This situation approaches that present in ionic combinations, and such a polar molecule may be considered as having some electrovalent or ionic character. The degree of polarity of the molecule depends upon the relative attractions of the combining atoms for electrons. The combinations just cited (Cl_2, HCl, NaCl) represent the transition from a nonpolar to a polar and finally to an ionic substance.

Coordinate valence Many examples may be cited where molecules of one compound may combine with molecules of a second compound to form a more complex compound.

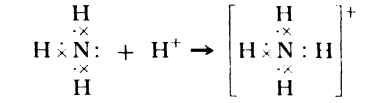
EXAMPLE. The compound BCl_3 will chemically unite with the gaseous compound NH_3 to give a new crystalline compound, $BCl_3 : NH_3$



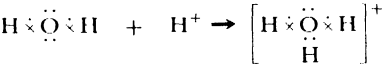
In this case the boron and the nitrogen atoms seem to share a pair of electrons, but the nitrogen atom contributes both of them. Sharing of an electron pair between atoms, where both of the electrons of the electron pair come from one of the atoms, constitutes a *coordinate* valence, a special kind of covalence. It is apparent from the diagram formula of $BCl_3{:}NH_3$ that valence bonds between boron and chlorine and between nitrogen and hydrogen are covalent, whereas the boron to nitrogen bond is coordinate valency. Actually, there is no difference once the bonds are formed, since each bond is a pair of electrons.

The formation of a coordinate valence linkage depends upon the existence of *a pair of unused electrons.* In the above example the nitrogen atom in the compound NH_3 has such an unused pair.

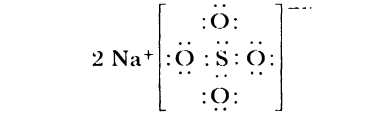
Ions as well as molecules may add to unused electron pairs; for example, ammonia may add H^+ to form ammonium ion, NH_4^+



A molecule of water contains 2 pairs of unused electrons and readily adds a proton to form hydronium ion, H_3O^+



Compounds with more than one kind of bonding Numerous compounds exist in which both electrovalence and covalence are exhibited; in general, salts which contain a radical exhibit both types of bonding. For example, consider the compound sodium sulfate. The salt is electrovalent and exists as sodium and sulfate ions in the crystalline form. However, within the SO_4^{--} ion the sulfur atom and oxygen atoms are held together by covalent linkages—electron pairs are shared mutually by sulfur and oxygen atoms. Na_2SO_4 may be represented diagrammatically:



To summarize: electrovalence involves actual transfer of an electron or electrons from one atom to another; covalence is a sharing of an electron pair between atoms, both atoms contributing an electron to the pair; and coordinate valence is a special case of covalence that exists between atoms when one of the atoms has furnished both of the electrons of the pair.

OXIDATION NUMBER

The positive and negative nature of electrovalence is quite easily understood. As covalence and coordinate valence as well as other possible interatomic bonds began to complicate the chemists' ideas, it became clear that a new designation had to be made to correlate the different kinds of valencies. Since all atomic linkages are believed to involve electrical attraction, although the electron sharing bonds cloud the simple picture, an *apparent charge* to each atom in combination may be assigned. It may be thought of as the charge on each atom of a compound if all the elements were electrovalent. Accordingly, chemists have agreed to use a term "oxidation number," which is determined from the set of rather arbitrary rules listed in Table 9-2.

TABLE 9-2 Rules for Determining Oxidation Numbers

OXIDATION NUMBER OF	MAGNITUDE OF, OR MANNER OF DETERMINING
Uncombined elements	Zero, 0
Hydrogen	+1
Oxygen	−2
Ions alone or in electrovalent compounds	+ or − according to their electrovalent charge
Elements in a binary covalent compound	The charge on each atom if the shared electrons are all assigned to the more electronegative of the atoms
The central element in a ternary compound	The apparent charge on the atom which will give the compound a neutral character when positive and negative oxidation numbers have been assigned to all other elements in the compound. The algebraic sum of the apparent charges in a compound is zero

Let us apply these rules to the determination of some oxidation numbers

Carbon in the free state has an oxidation number of 0. In CO, its oxidation state will be represented by the number +2 since oxygen is assigned a number −2. In CO_2, the oxidation number of carbon is +4. In CCl_4 the oxidation number of carbon is +4; in CH_4 each hydrogen is +1 in oxidation number, and carbon is −4.

In NaCl, an ionic compound, the oxidation number of sodium is +1, and of chlorine −1. In $AlBr_3$, the oxidation number of aluminum is +3, of each bromine −1. In the ionic compound $(NH_4)_2SO_4$, the oxidation number of each NH_4^+ is +1, of SO_4^{--}, −2. For an ion such as PO_4^{---}, the oxidation number of P must be +5, since the latter added to a total of −8 from the 4 oxygen atoms would leave a net charge of −3, which is the charge of the PO_4^{---} ion. Study these examples:

COMPOUND	OXIDATION NUMBER
H_2SO_4	sulfur, +6
$H_4P_2O_7$	phosphorus, +5
Al_2S_3	aluminum, +3; sulfur, −2
MgO	magnesium, +2
$NaMnO_4$	sodium, +1; manganese, +7
$Na_2Cr_2O_7$	sodium, +1; chromium, +6
$HBrO_3$	bromine, +5
SiO_4^{----}	silicon, +4
AsO_4^{---}	arsenic, +5

Oxidation and reduction[1] On page 87, it was stated that reactions with oxygen are *oxidation* processes. We may note that in all these cases the oxidation number of the element combining with oxygen has been increased from 0 to some more positive value. On the basis of the oxidation number concept, *oxidation is any process in which the oxidation number of an element is increased* and we are not restricted to the use of oxygen in bringing it about. For example, hydrogen will burn in chlorine to give hydrogen chloride:

$$H_2 + Cl_2 \rightarrow 2\,HCl$$

The oxidation number of hydrogen has been increased from 0 to +1; hence we may say that hydrogen has been oxidized. Looking again at this reaction of hydrogen and chlorine, we may note that the oxidation number of chlorine has *decreased* from 0 to −1. This latter process we shall call *reduction.* Oxidation and reduction, then, are mutually dependent processes; one cannot occur without the other.

Summarizing: Increase of oxidation number is *oxidation;* decrease of oxidation number is *reduction.*

Variable oxidation numbers Some elements exhibit more than one oxidation number; for example, the oxidation number of carbon in CO is +2 and in CO_2 is +4. As other examples, we may list the following:

COMPOUND	FORMULA	OXIDATION NUMBER	
Ferrous chloride	$FeCl_2$	of iron	+2
Ferric chloride	$FeCl_3$		+3
Nitrous oxide	N_2O	of nitrogen	+1
Nitric oxide	NO		+2
Nitrogen trioxide	N_2O_3		+3
Nitrogen dioxide	NO_2		+4
Nitrogen pentoxide	N_2O_5		+5
Manganese chloride	$MnCl_2$	of manganese	+2
Manganese dioxide	MnO_2		+4
Potassium manganate	K_2MnO_4		+6
Potassium permanganate	$KMnO_4$		+7

[1] The concept of oxidation-reduction will be treated in more detail in Chapter 20.

The concept of oxidation numbers is useful not only in describing the oxidation state of an element but also in the balancing of oxidation-reduction equations (Chapter 20).

EXERCISES

1 Prepare a form like the one below and fill in the blanks with formulas of compounds composed of the indicated positive and negative ions:

	Cl^-	SO_4^{--}	OH^-	PO_4^{---}	CO_3^{--}	SO_3^{--}	O^{--}	$C_2H_3O_2^-$	Br
Na^+									
Mg^{++}									
NH_4^+									
Ca^{++}									
Fe^{++} (ous)									
Fe^{+++} (ic)									
Zn^{++}									
Al^{+++}									
Cu^{++}									
K^+									

2 Determine the oxidation number of the underlined elements or radicals in each of the following compounds: $NaMnO_4$; $Ca(NO_2)_2$; $K_2Cr_2O_7$; MnO_2; H_2SO_4; $SnCl_4$; K_2MnO_4; KIO_3; $NaBrO_2$; $AgClO_4$; Na_2HPO_4; $NaCrO_2$; K_3AlO_3; $Al(NO_3)_3$; $H_2S_2O_7$; H_4SiO_4; H_2ScO_3; Na_2WO_4; $TiCl_4$; $Ca(ClO_2)_2$; $CaWO_4$; K_2PdCl_6; UO_2SO_4; $Pb_3(AsO_3)_2$; $Zn_3(VO_4)_2$.

3 Element Z forms the compound H_2Z. Element Z and element W form the compound WZ_3. What is the oxidation number of W and Z?

4 The atomic weight of the element X is 64. 8 grams of X displaces .25 grams of hydrogen from hydrochloric acid. What is the valence of element X?

Ans. 2.

5 1.2 grams of the element Y displaces 584 ml. of hydrogen (measured at S.T.P.) when treated with an acid. The atomic weight of the element Y is 23. What is the valence of Y? (22,400 ml. of H_2 weigh 2.016 grams.) Ans. 1.

6 From the following data, calculate the valence of the elements M and N.

ELEMENT	AT. WT.	WT. OF METAL USED	VOL. OF H_2 DISPLACED	ATMOSPHERIC PRESSURE	TEMP. °C.
M	36	1.2 g.	1762 ml.	700 mm.	17
N	65	0.822 g.	322 ml.	710.5 mm.	20

Ans. M–4; N–2.

7 A compound analyzes 32.38 per cent sodium, 22.57 per cent sulfur, and 45.05 per cent oxygen. What is its formula? What is the oxidation number of sulfur in the compound? Ans. Na_2SO_4.

8 A white solid is found to contain 15.656 per cent magnesium, 48.262 per cent arsenic, and 36.082 per cent oxygen. What is its formula? What is the oxidation number of arsenic in the compound?

9 A solid compound contains 45.1 per cent oxygen, 33.13 per cent chlorine and 21.6 per cent sodium. On heating 0.426 g. of this compound, 0.192 g. of oxygen is given off and a solid residue of a pure compound remains. Write a chemical equation for the reaction taking place. Ans. $2\ NaClO_3 \rightarrow 2\ NaCl + 3\ O_2$.

10 A compound contains 90.7 per cent Pb and 9.3 per cent oxygen. On being heated, oxygen is evolved and a compound remains which contains 92.8 per cent Pb and 7.2 per cent oxygen. Write a chemical equation for the reaction.

11 Given the following data, determine the empirical formula for each of the compounds listed:

COMPOUND	PER CENT COMPOSITION
A	Li, 12.6; S, 29.1; O, 58.2
B	C, 60; H, 13.3; O, 26.7
C	K, 30.7; S, 25.2; O, 44
D	Na, 17.5; Cr, 39.7; O, 42.8
E	C, 14.7; Cl, 65; H, 0.6; O, 19.6

12 The molecular weights of compounds B and D in exercise 11 are 180 and 327 respectively. Write true formulas for these compounds.

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ten CLASSIFICATION AND NAMING OF COMPOUNDS

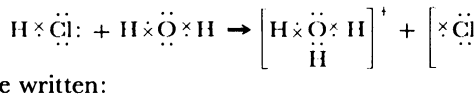
Chemistry would indeed be a tedious and monotonous subject if we were required to learn the properties and behavior of each of the many compounds which we are to use. Fortunately, most chemical compounds can be grouped together in a few classes. Then, if we can properly classify the compound, we are at once aware of the general properties of the compound from a knowledge of the properties of that class or group of compounds. For example, HCl is classed as an acid, and by becoming familiar with the behavior of acids as a distinct class, we are at once aware of the general properties of the compound. We shall learn that nearly all of the compounds which we are to study may be classified as acids, bases, salts, metallic oxides, or nonmetallic oxides. Of these five classes of compounds, the first three—namely, acids, bases, and salts—are by far the most important.

Acids We have used the term "acids" many times in our previous discussion. In the study of oxygen compounds we learned that the solution of a nonmetallic oxide in water produces an acid; for example,

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$P_2O_5 + 3\,H_2O \rightarrow 2\,H_3PO_4$$

All acids contain hydrogen which may be replaced by metals. The negative portion of the acid molecule is composed of a nonmetal or a radical (negative valence group). These negative valence groups (except oxide and hydroxide) are often referred to as acid radicals. All acids are covalent compounds in which the atoms are held together by a sharing of electrons. When an acid is dissolved in water, ions are formed

as a result of the transfer of a hydrogen ion (proton) from the acid molecule to the water molecule; for example,



which may be written:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

This is a case of coordinate valence as discussed on page 126, in which an unused pair of electrons from the water molecule combines with a hydrogen ion to form a hydronium ion. The hydronium ion is a hydrated hydrogen ion or proton, $H^+ \cdot H_2O$, and while the ionization of acids in aqueous solution depends upon its formation, we shall ordinarily use the simple H^+ in writing equations. Such equations are thereby simplified and easier to balance. (But see Chapter 18.)

The chief characteristic of an acid is its ability to furnish hydrogen ions (protons); therefore, an acid is usually defined as "a substance which may furnish protons."

While all acids contain hydrogen, not all compounds containing hydrogen can be classed as acids. For example, methane, CH_4, has no acid characteristics and does not furnish hydrogen ions in solution.

Properties of acids In general, aqueous solutions of acids are characterized by the following properties:

1. Have a sour taste. Lemons, oranges, and other citrus fruits owe their sour taste to the presence of citric acid; the taste of sour milk is due to the presence of lactic acid.
2. Turn blue litmus paper red. Litmus is a dye which has a red color in acid solution and a blue color in basic solution, and paper which has been soaked in litmus is referred to as litmus paper. Substances of this type, which enable us to determine whether a given solution is acid or basic, are called indicators. Methyl orange and phenolphthalein are other indicators frequently used by chemists.
3. React with certain metals to produce hydrogen. Reactions of this type were studied in connection with the preparation of hydrogen.
4. React with bases to produce salts and water.

Bases All metallic hydroxides are classed as bases. Of these, only NaOH, KOH, $Ca(OH)_2$, and $Ba(OH)_2$ are appreciably soluble in water. If these compounds are dissolved in water, the OH^- is common to all of their solutions:

$$NaOH \rightarrow Na^+ + OH^-$$
$$KOH \rightarrow K^+ + OH^-$$
$$Ca(OH)_2 \rightarrow Ca^{++} + 2\ OH^-$$
$$Ba(OH)_2 \rightarrow Ba^{++} + 2\ OH^-$$

An aqueous solution of NH_3, i.e. NH_4OH, is also classed as a base since OH^- ions are present in the solution.

In each of these compounds, we find a combination of a metal (or NH_4) with the hydroxide group. Just as the characteristic part of an acid is hydrogen ion, so the characteristic part of a base in water solution is the hydroxide ion, OH^-. Later, the concept of a base will be extended to include substances which do not furnish hydroxide ions in solution.

Properties of bases In general, water solutions of metallic hydroxides (bases) exhibit the following properties:

1 Bitter taste.
2 Soapy or slippery feeling.
3 Turn red litmus paper to blue color.
4 React with acids to form salts and water.
5 Most metallic hydroxides (bases) are insoluble in water. Of the common ones, only NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, and NH_4OH are soluble.

Salts An acid reacts with a base by double decomposition to produce a salt and water. Hydrogen from the acid combines with hydroxide from the base to form water molecules:

$$NaOH + HCl \rightarrow NaCl + HOH$$
$$Mg(OH)_2 + 2\,HNO_3 \rightarrow Mg(NO_3)_2 + 2\,HOH$$
$$2\,Al(OH)_3 + 3\,H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6\,HOH$$

The reaction of an acid with a base is called *neutralization.* If all the water is removed by evaporation from the solution after the reaction, the positive ions from the base combine with the negative ions from the acid to form a solid *salt.*

It was shown (Chapter 3) that the compound sodium chloride, a salt, is an electrovalent compound and is ionized in the solid or crystalline state, the crystal being made up of positive sodium ions and negative chloride ions oriented in a definite pattern. In general, most salts in the crystalline state are electrovalent and are composed of ions oriented in a definite way.

In general, then, salts are compounds between metallic ions and nonmetallic ions. They are the most numerous of chemical compounds, and many are industrially important. NaCl, for example is an essential food mineral; $Ca_3(PO_4)_2$ is used in making phosphate fertilizer; Na_2CO_3 is washing soda; $Cu_3(AsO_3)_2$ is an insecticide.

Writing equations in ionic form Since all acids, bases, and salts in aqueous solution give ions, the chemical equations in which these classes

of compounds are involved may show the ions present. An ionic equation is more instructive than a molecular equation since the actual chemical process is more clearly indicated. For example, if the first equation on page 134 is represented in ionic form, as follows

$$[Na^+ + OH^-] + [H^+ + Cl^-] \rightarrow [Na^+ + Cl^-] + H_2O$$

it is evident that the neutralization process involves only the combination of H^+ and OH^- to form water. Na^+ and Cl^- are incidental to the process. Of course, if the solution after neutralization is evaporated, Na^+ and Cl^- form crystals of NaCl, and the latter may be recovered as a solid. However, as long as the NaCl remains in solution, there is no tendency for Na^+ and Cl^- to combine.

In writing ionic equations, it is necessary to adopt certain rather arbitrary conventions. For example, if an insoluble substance like AgCl is produced in a reaction, that substance is shown in molecular form, even though the solid crystal is made up of ions. This convention is necessary to differentiate between a substance in which the ions are oriented in a definite pattern (the crystalline form) and one in which the ions are free to move about in a random manner.

The whole subject of ionic reactions will be considered in detail later (Chapters 18 and 19). However, to familiarize the student gradually with this method of writing equations, we shall henceforth represent a given reaction in both the molecular and ionic forms (if ions are involved in the reaction). A great deal more basic knowledge must be acquired by the student before he can be expected to handle ionic equations with facility.[1]

Type reactions of acids, bases, and salts Probably most of the chemical changes of inorganic chemistry involve the interaction of acids, bases, and salts. Just as we may classify hundreds of chemical compounds into a few groups or classes, so we may also classify hundreds of chemical changes into a few types of reactions. Once we recognize to which type a given chemical change belongs, we are able to predict the probable products of the reaction. The principal types of chemical changes involving acids, bases, or salts will now be shown. Examples are given for each type.[2]

A. Direct combination

1. Metal + Nonmetal → Salt

$$Cu + Br_2 \rightarrow CuBr_2$$
$$2\ Al + 3\ S \rightarrow Al_2S_3$$

[1] The instructor may emphasize the use of ionic equations here or defer serious consideration of them until the writing of ordinary molecular equations has been mastered. For pedagogical reasons, some may prefer to wait until ionization as a topic is being studied.

[2] See also the reaction of "oxides" on page 140.

Many of the metals and nonmetals combine directly to produce salts. In general, these combinations are limited to those in which either the metal or nonmetal is at least a moderately active element.

2. Hydrogen + Nonmetal → Acid

$$H_2 + Cl_2 \rightarrow 2\,HCl$$
$$H_2 + S \rightarrow H_2S$$

Hydrogen may react directly with the more active nonmetallic elements to form acids.

B. Decomposition

1. Salt $\xrightarrow{\text{heat}}$ Decomposition Products

$$2\,KClO_3 \rightarrow 2\,KCl + 3\,O_2$$
$$2\,Pb(NO_3)_2 \rightarrow 2\,PbO + 4\,NO_2 + O_2$$

Certain salts are unstable toward heat. No generalization can be made as to the decomposition products.

C. Simple replacement

1. Metal (above hydrogen) + Acid → Salt + $H_2\uparrow$

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$
$$Zn + [2\,H^+ + SO_4^{--}] \rightarrow [Zn^{++} + SO_4^{--}] + H_2\uparrow$$

$$2\,Al + 6\,HCl \rightarrow 2\,AlCl_3 + 3\,H_2\uparrow$$
$$2\,Al + 6[H^+ + Cl^-] \rightarrow 2[Al^{+++} + 3\,Cl^-] + 3\,H_2\uparrow$$

This displacement type of reaction was discussed in the preparation of hydrogen (Chapter 7).

2. Metal + Salt → Metal (less active) + Salt

$$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$$
$$Zn + [Cu^{++} + SO_4^{--}] \rightarrow Cu + [Zn^{++} + SO_4^{--}]$$

$$Fe + Ag_2SO_4 \rightarrow 2\,Ag + FeSO_4$$
$$Fe + [2\,Ag^+ + SO_4^{--}] \rightarrow 2\,Ag + [Fe^{++} + SO_4^{--}]$$

This type of reaction was discussed in connection with the activity series (Chapter 7). A metal will displace a less active metal from its salt in water solution.

3. Nonmetal + Salt → Nonmetal + Salt

$$Cl_2 + Na_2S \rightarrow S + 2\,NaCl$$

In this reaction, which is similar to the action of a metal with a salt, a nonmetal displaces a less active nonmetal from its salt.

4. Metal (only certain ones) + Base → Salt + $H_2\uparrow$

$$Zn + 2\,NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$$
$$Zn + 2[Na^+ + OH^-] \rightarrow [2\,Na^+ + ZnO_2^{--}] + H_2\uparrow$$

$$2\,Al + 6\,NaOH \rightarrow 2\,Na_3AlO_3 + 3\,H_2\uparrow$$
$$2\,Al + 6[Na^+ + OH^-] \rightarrow 2[3\,Na^+ + AlO_3^{---}] + 3\,H_2\uparrow$$

Certain metals, such as zinc and aluminum, react with the strong bases, sodium and potassium hydroxides, to yield a salt and hydrogen.

D. Double decomposition

1. Salt + Salt → New Salt + New Salt

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$
$$[Ag^+ + NO_3^-] + [Na^+ + Cl^-] \rightarrow AgCl\downarrow + [Na^+ + NO_3^-]$$

$$BaCl_2 + K_2SO_4 \rightarrow BaSO_4\downarrow + 2\,KCl$$
$$[Ba^{++} + 2\,Cl^-] + [2\,K^+ + SO_4^{--}] \rightarrow BaSO_4\downarrow + 2[K^+ + Cl^-]$$

This type of reaction takes place if one of the products (a salt) is insoluble and precipitates from solution. In the first reaction, silver chloride is insoluble, while in the second, barium sulfate is insoluble. The insoluble substance is denoted in an equation by a downward arrow.

2. Salt + Acid → New Salt + New Acid $\uparrow$

$$CaCl_2 + H_2SO_4 \rightarrow CaSO_4 + 2\,HCl\uparrow$$
$$3\,KNO_3 + H_3PO_4 \xrightarrow{\text{heat}} K_3PO_4 + 3\,HNO_3\uparrow$$

These reactions involve the formation of a volatile acid which is expelled from the reaction mixture. The volatile substance is indicated in these equations by the upward arrows. Reactions of this type are usually carried out in the absence of water, and since no ions are present in solution, the substances in the equation are represented only in molecular form.

3. Salt + Base → New Salt + New Base

$$AlCl_3 + 3\,KOH \rightarrow 3\,KCl + Al(OH)_3\downarrow$$
$$[Al^{+++} + 3\,Cl^-] + 3[K^+ + OH^-] \rightarrow 3[K^+ + Cl^-] + Al(OH)_3\downarrow$$

This type of reaction occurs if one of the products is insoluble or is expelled from the reaction mixture as a volatile substance.

4. Base + Acid → Salt + H_2O

$$Ca(OH)_2 + 2\,HNO_3 \rightarrow Ca(NO_3)_2 + 2\,H_2O$$
$$[Ca^{++} + 2\,OH^-] + 2[H^+ + NO_3^-] \rightarrow [Ca^{++} + 2\,NO_3^-] + 2\,H_2O$$
$$2\,KOH + H_2SO_4 \rightarrow K_2SO_4 + 2\,H_2O$$
$$2[K^+ + OH^-] + [2\,H^+ + SO_4^{--}] \rightarrow [2\,K^+ + SO_4^{--}] + 2\,H_2O$$

As pointed out previously, reactions of this type are termed neutralization reactions; the OH^- ions of the base combine with the H^+ ions from the acid to form water. On evaporation of the water, positive ions of the base combine with negative ions from the acid to form the solid salt.

The student should thoroughly familiarize himself with the types of reactions just listed, and it is suggested that he write equations for further examples of all of these types of reactions.

The types of reactions discussed above do not include all of the reactions which we are to study; a large share of the reactions of inorganic chemistry, however, fall into these types. With a knowledge of these types of chemical reactions, the student has a good preparation for the more complicated reactions to follow.

In order to write chemical equations successfully, the student must first be thoroughly familiar with the concept of valence; second, he must be able to classify compounds correctly; and third, he must know the more important general types of reactions and be able to classify the reaction in question under the proper type.

Nomenclature of acids, salts, and bases 1. *Naming of acids.* Because a number of nonmetallic elements exhibit several oxidation states, a series of acids in which a given nonmetal appears is possible. For example, chlorine forms the series: HCl; HClO; $HClO_2$; $HClO_3$; $HClO_4$. By replacing the hydrogen of these acids with a metal, a series of salts of these acids would be obtained: NaCl; NaClO; $NaClO_2$; $NaClO_3$; $NaClO_4$. Obviously to differentiate between the acids or the salts a system of naming is required. The system which has been adopted follows:

The suffix *ic* is used to denote the common oxygen-containing acid of an element; thus $HClO_3$ is chlor-*ic* acid.

The suffix *ous* denotes the acid in which the element exhibits its next lower oxidation state; $HClO_2$ is chlor-*ous* acid. Note the oxidation number of chlorine in $HClO_3$ is +5, whereas in $HClO_2$ its oxidation number is +3.

The prefix *hypo* and the suffix *ous* are used to denote the acid in which the nonmetal exhibits the next lower oxidation number below the

ous acid. Thus HClO is *hypo*-chlor-*ous* acid, in which chlorine has an oxidation number of +1.

The prefix *per* and the suffix *ic* denote the acid for the next higher oxidation state above the *ic* acid. Thus $HClO_4$ is *per*-chlor-*ic* acid, in which chlorine has an oxidation number of +7.

The prefix *hydro* and a suffix *ic* denotes an acid with no oxygen, thus HCl is *hydro*-chlor-*ic* acid.

Most of the *ic* acids contain 3 or 4 oxygen atoms per molecule. For example:

$HBrO_3$	bromic acid	H_2SO_4	sulfuric acid
HIO_3	iodic acid	H_3PO_4	phosphoric acid
HNO_3	nitric acid	H_3AsO_4	arsenic acid
H_2CO_3	carbonic acid	H_2CrO_4	chromic acid

2. *Naming of salts.* Salts are derived from acids and are named by using the suffix *ate* for a salt of an *ic* acid; the suffix *ite* for a salt of an *ous* acid; and the suffix *ide* for a salt containing no oxygen (salt of a hydro . . . ic acid).

We may summarize the above system as follows:

	ACID	SALT
Highest oxidation state	per . . . ic	per . . . ate
Common oxygen-containing acid	. . . ic	. . . ate
Next lower oxidation state	. . . ous	. . . ite
Next lower oxidation state	hypo . . . ous	hypo . . . ite
No oxygen	hydro . . . ic	. . . ide

EXAMPLES

ACID		SALT	
Formula	*Name*	*Formula*	*Name*
$HBrO_4$	perbromic acid[3]	$NaBrO_4$	sodium perbromate[3]
$HBrO_3$	bromic acid	$NaBrO_3$	sodium bromate
$HBrO_2$	bromous acid	$NaBrO_2$	sodium bromite
HBrO	hypobromous acid	NaBrO	sodium hypobromite
HBr	hydrobromic acid	NaBr	sodium bromide

3. *Naming of bases.* The nomenclature of bases is much simpler than that of acids, since metals usually form no more than two hydroxides. The name of the base in which the element has the higher oxidation state is based on a shortened form of the name of the element and the suffix *ic;* thus, $Fe(OH)_3$ is ferr*ic* hydroxide. In naming the hydroxide in which the metal has the lower oxidation state, the suffix *ous* is used;

[3] Actually, this compound does not exist, but the analogous iodine compound does.

thus, $Fe(OH)_2$ is ferr*ous* hydroxide. Other examples of bases in which the metal exhibits two oxidation states are:

$Ni(OH)_2$ nickelous hydroxide	$Sn(OH)_2$ stannous hydroxide
$Ni(OH)_3$ nickelic hydroxide	$Sn(OH)_4$ stannic hydroxide

Another method of naming frequently employed is to indicate the oxidation number of the metal with a Roman numeral. Thus, $Ni(OH)_2$ may be written as nickel (II) hydroxide; $Ni(OH)_3$ as nickel (III) hydroxide; $Sn(OH)_2$ as tin (II) hydroxide; $Sn(OH)_4$ as tin (IV) hydroxide, and so on. This method may be applied to any compounds in which the metal has a variable oxidation number.

Oxides The oxides of elements differ greatly in their physical and chemical properties. On the basis of their reactions with water, oxides may be conveniently divided into two groups, (1) nonmetallic oxides, and (2) metallic oxides.

1. *Nonmetallic oxides.* We learned in the study of oxygen that oxides of nonmetals react with water to form acids:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$P_2O_5 + 3\,H_2O \rightarrow 2\,H_3PO_4$$

A nonmetallic oxide which reacts with water to produce an acid and no other product is called an *acid anhydride.* Thus SO_2 is the anhydride of sulfurous acid, CO_2 is the anhydride of carbonic acid, and so on.

An acid anhydride reacts with a base to form a salt and water in the same way that the corresponding acid acts. For example:

$$\underset{\text{base}}{Ca(OH)_2} + \underset{\text{acid}}{H_2SO_4} \rightarrow CaSO_4 + 2\,H_2O$$

$$Ca(OH)_2 + \underset{\substack{\text{anhydride}\\ \text{of } H_2SO_4}}{SO_3} \rightarrow CaSO_4 + H_2O$$

In writing equations of this type, the salt formed will be derived from the acid of which the oxide is the anhydride; in the above example SO_3 is the anhydride of H_2SO_4, therefore the salt must be a sulfate. If the acid anhydride were P_2O_5, what salt would be formed?

2. *Metallic oxides.* Certain metallic oxides act with water to form metallic hydroxides (bases):

$$Na_2O + H_2O \rightarrow 2\,NaOH$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$

Oxides of metals are called *basic anhydrides.* Their formulas may be derived by subtracting water from the metallic hydroxides.

Basic anhydrides act like bases in their reactions with acids. For example:

$$\underset{\text{base}}{Ca(OH)_2} + \underset{\text{acid}}{H_2SO_4} \rightarrow CaSO_4 + 2\,H_2O$$

$$\underset{\substack{\text{anhydride}\\ \text{of } Ca(OH)_2}}{CaO} + H_2SO_4 \rightarrow CaSO_4 + H_2O$$

The oxides of sodium, potassium, calcium, and barium are readily soluble in water, reacting to form hydroxides. Oxides of other metals react slowly or not at all with water

3. *Reactions between metal oxides and nonmetal oxides.*

$$\text{Metal Oxide} + \text{Nonmetal Oxide} \rightarrow \text{Salt (combination)}$$

$$CaO + CO_2 \rightarrow CaCO_3$$
$$Al_2O_3 + 3\,SO_3 \rightarrow Al_2(SO_4)_3$$

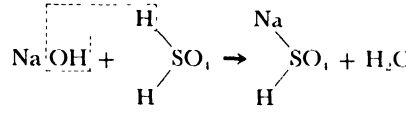
A gaseous nonmetal oxide such as CO_2 or SO_3, if passed over a metallic oxide which has been ground to a powder, may combine with it to form a salt. Two solid oxides when heated together may give the same type of reaction. For example:

$$PbO + SiO_2 \rightarrow PbSiO_3$$

Naming of oxides The nomenclature of metallic oxides is similar to that of bases. The oxide in which the metal exhibits the higher oxidation state is an *ic* oxide; thus, CuO is cupr*ic* oxide or copper (II) oxide. The oxide in which the metal has the lower oxidation state is an *ous* oxide; Cu_2O is cupr*ous* oxide or copper (I) oxide; FeO is ferr*ous* oxide or iron (II) oxide, and Fe_2O_3 is ferr*ic* oxide or iron (III) oxide.

In naming the oxides of nonmetals, a prefix is usually used to indicate the number of oxygen atoms in the molecule. Thus SO_2 is sulfur dioxide, CO_2 is carbon dioxide, SO_3 is sulfur trioxide, As_2O_3 is arsenic trioxide, P_2O_5 is phosphorus pentoxide, etc.

Acid and basic salts It is conceivable that in the neutralization of an acid by a base, only a part of the hydrogen might be neutralized, thus

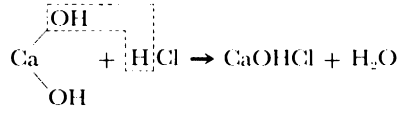


The compound $NaHSO_4$ has acid properties, since it contains hydrogen, and is also a salt, since it contains both a metal and an acid radical. Such a salt containing acidic hydrogen is termed an *acid salt.* Phosphoric acid, H_3PO_4, might be progressively neutralized to form the salts,

NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. The first two are acid salts, since they contain replaceable hydrogen. A way of naming these salts is to call Na_2HPO_4 di-sodium hydrogen phosphate and NaH_2PO_4 sodium di-hydrogen phosphate. These acid phosphates are important in the blood and have much to do in control of the alkalinity of the blood. The third compound, Na_3PO_4, which contains no replaceable hydrogen, is often referred to as *normal* sodium phosphate to differentiate it from the two acid salts.

Historically, the prefix "bi" has been used in naming some acid salts; in industry, for example, $NaHCO_3$ is called sodium bicarbonate and $Ca(HSO_3)_2$, calcium bisulfite. Since the "bi" is somewhat misleading, the system of naming discussed above is preferable.

If the hydroxyl radicals of a base are progressively neutralized by an acid, *basic salts* may be formed:



Basic salts have properties of a base and will react with acids to form a normal salt and water, thus

$$CaOHCl + HCl \rightarrow CaCl_2 + H_2O$$

Further examples of basic salts are $BiOH(NO_3)_2$, $Bi(OH)_2NO_3$, and $Pb(OH)C_2H_3O_2$.

Mixed salts If the hydrogen atoms in an acid be replaced by two or more different metals, a *mixed salt* results. Thus the two hydrogen atoms in H_2SO_4 might be replaced with sodium and potassium to yield the mixed salt, $NaKSO_4$. $NaNH_4HPO_4$ is a mixed acid salt that may be crystallized from urine.

Amphoterism Some hydroxides have the property of acting as acids under certain conditions and as bases under other conditions. For example, $Sn(OH)_2$ may react with an acid to form a salt and water:

$$\underset{\text{base}}{Sn(OH)_2} + 2\,\underset{\text{acid}}{HCl} \rightarrow \underset{\text{salt}}{SnCl_2} + 2\,H_2O$$

In this reaction, the $Sn(OH)_2$ is functioning as a base; but $Sn(OH)_2$ (this may be written as H_2SnO_2) functions as an acid in the reaction:

$$2\,\underset{\text{base}}{NaOH} + \underset{\text{acid}}{H_2SnO_2} \rightarrow \underset{\text{salt}}{Na_2SnO_2} + 2\,H_2O$$

Such compounds are termed *amphoteric.* We have said that a base contains a metallic element while an acid contains a nonmetal. In the

first reaction the element tin is acting as a metal, while in the second reaction it is acting as a nonmetal. While some of the elements are distinctly metallic and others nonmetallic, there are some which under certain conditions act as metals and under other conditions act as nonmetals. Other elements whose hydroxides are amphoteric are aluminum, zinc, chromium, and lead. Amphoterism will be discussed in greater detail in Chapter 28.

EXERCISES

1 (*a*) Name: $HClO_2$; $NaClO$; H_3AsO_4; $Cu_3(AsO_4)_2$; HI; Mg_3N_2; $Ni(OH)_2$; $Bi(OH)_2Cl$.
(*b*) Give formulas for aluminum sulfite, nitrous acid, calcium perchlorate.

2 Write balanced equations for: potassium oxide plus water; aluminum bromide plus sulfuric acid; zinc plus silver nitrate; $H_4SiO_4 + CuCl_2$.

3 (*a*) Name: Zn_3P_2; $KClO$; HNO_2; H_2CO_3; $Cr(OH)_3$; $CaSO_3$.
(*b*) Give formulas for sodium iodate, arsenious acid, potassium dihydrogen arsenate, bismuth dihydroxy nitrate.

4 Write equations for: arsenic oxide plus water; sodium oxide plus water; potassium sulfate plus barium iodide; aluminum plus bromine.

5 Write balanced chemical equations for five different ways of preparing $AlCl_3$. They need not be economically practicable.

6 Classify each of the following compounds as (1) acid, (2) base, (3) normal salt, (4) acid salt, (5) basic salt, (6) acid anhydride, (7) basic anhydride, (8) mixed salt:
(*a*) P_2O_5, (*b*) $NaNO_3$, (*c*) H_2SO_3, (*d*) NH_4Cl, (*e*) $CaOHCl$, (*f*) Na_2SO_4, (*g*) CuO, (*h*) HNO_3, (*i*) $MgNaPO_4$, (*j*) $KHSO_4$, (*k*) $NaHCO_3$, (*l*) $Mg(OH)_2$, (*m*) $NaNH_4HAsO_4$, (*n*) NH_4OH, (*o*) $Bi(OH)_2NO_3$, (*p*) $Ca(H_2PO_4)_2$, (*q*) $HClO$, (*r*) Fe_2O_3, (*s*) NaH_2PO_4, (*t*) CO_2, (*u*) H_2S.

7 $HBrO_3$ is bromic acid. Write formulas for (*a*) sodium perbromate, (*b*) hypobromous acid, (*c*) calcium bromite, (*d*) ferric bromate, (*e*) perbromic acid.

8 Write formulas of the anhydrides of the following acids and bases:
(*a*) H_2CrO_4, (*b*) KOH, (*c*) $Fe(OH)_3$, (*d*) $HAsO_2$, (*e*) $Mg(OH)_2$, (*f*) $HBrO$, (*g*) H_3AsO_4, (*h*) H_4SiO_4.

9 Complete and balance the equations:

(*a*) $Al + HCl \rightarrow$
(*b*) $CuCO_3 + H_3PO_4 \rightarrow$
(*c*) $BaCl_2 + MnSO_4 \rightarrow$
(*d*) $K_2O + HNO_3 \rightarrow$
(*e*) $MgOHCl + HCl \rightarrow$
(*f*) $SO_2 + H_2O \rightarrow$
(*g*) $MgF_2 + H_2SO_4 \rightarrow$
(*h*) $CO_2 + Ba(OH)_2 \rightarrow$
(*i*) $HClO + Ca(OH)_2 \rightarrow$
(*j*) $Fe(NO_3)_3 + NH_4OH \rightarrow$

10 Complete and balance:
(*a*) hypochlorous acid + calcium hydroxide
(*b*) cupric oxide + arsenious acid
(*c*) hydrosulfuric acid + ferric acetate
(*d*) cobalt nitrite + magnesium
(*e*) sodium di-hydrogen phosphate + di-hydroxy bismuth nitrate

eleven

WATER AND THE LIQUID STATE

In the study of water, the most familiar of liquids, we shall discuss characteristics of the liquid state in general. In oceans, lakes, and rivers water covers nearly three-fourths of the earth's surface, and it is a constituent of the soil and the atmosphere. The human body is more than 65 per cent water, and many of our foods contain an even larger percentage. Table 11–1 shows the approximate percentage of water in various familiar substances.

TABLE 11–1 Water in Familiar Substances

SUBSTANCE	PER CENT	SUBSTANCE	PER CENT
Beef	65–70	Plant tissue	50–75
Eggs	74	Tomatoes	85
Milk	87	Bacon	19
Apples	86	Butter	17
Vegetables (green)	90–95	Peanuts	9
Potatoes	78	Bread	35
Bone	50	Wheat	11
Muscle	75	Lard	0

Physical properties of water Pure water has a flat taste and is odorless and practically colorless in thin layers. If a deep section of it is viewed, it appears blue in color. Water has a maximum density at 4°, at which temperature 1 ml. weighs 1 gram. Above or below this temperature, 1 ml weighs less than 1 gram (Table 11–2). On the centigrade temperature scale, water freezes at 0° and boils at 100°.

Water has a specific heat of 1. *Specific heat* is defined as the number

TABLE 11-2 Density of Water from 0° to 100°

TEMP. ° C.	DENSITY g./ml.	TEMP. ° C.	DENSITY g./ml.
0	0.99987	50	0.9881
2	0.99997	60	0.9832
4	1.0000	70	0.9778
10	0.9997	80	0.9718
20	0.9982	90	0.9653
30	0.9957	100	0.9584
40	0.9922		

of calories of heat necessary to raise the temperature of 1 gram of a substance 1° C.; thus one calorie is necessary to raise the temperature of 1 gram of water 1°. The specific heat of water is one of the highest specific heats of substances.

When ice melts (changes from a solid to a liquid), heat is absorbed. About 80 calories of heat are required to melt 1 gram of ice. When water is frozen, an equivalent amount of heat is evolved. The heat absorbed when 1 gram of solid melts is called the *heat of fusion,* and the heat evolved when 1 gram of liquid freezes is called the *heat of solidification.*

The quantity of heat necessary to convert 1 gram of a liquid into a vapor is termed the *heat of vaporization.* For water, 539 calories of heat are necessary to change 1 gram of liquid water at 100° C. into vapor (steam) at 100° C. When water is condensed (changed from vapor to liquid), an equivalent amount of heat, called the *heat of condensation,* is given off. The heat of condensation is an important factor in the use of steam for heating purposes. Steam is introduced into radiators, where it is condensed to the liquid state. In this condensation process, 539 calories of heat are given up to the radiator for every gram of water condensed.

Water is a particularly good solvent. Practically all substances are more or less soluble in water, and a study of aqueous solutions is of primary importance to the chemist.

Properties of the liquid state A liquid has no definite shape but unlike a gas does occupy a more or less definite volume. Whereas a gas completely fills any container in which it is placed, a liquid does not. Molecules in the liquid state appear to be very much closer together than in a gas; that is, the free volume surrounding each molecule is much less. Evidence for this is the relatively small compressibility of liquids as compared to gases. High pressures are required to compress a liquid even a small fraction of its original volume; for example, a pressure of 3000 atmospheres (about 45,000 lb. per square inch) is nec-

essary to compress 1 liter of water at 0° C to 900 ml. For additional evidence we may consider the relative volumes of 1 mole of water in the liquid and gaseous states. One mole of water (18 g.) as a liquid at 100° C occupies a volume of about 18 ml, but when vaporized as steam, it occupies a volume of about 30,000 ml.

Like a gas, molecules in the liquid state are in a constant state of motion, but the movement is more restricted because of close proximity of molecules. This motion explains the diffusion of one liquid into another, however, the rate of diffusion of liquids is much lower than that of gases because of the restricted movement.

Molecules in a liquid are held together presumably by a large force of mutual attraction which is a function of the distance between molecules—the smaller the distance, the greater the force. When a liquid is vaporized, distance between molecules must be greatly increased, and energy must be expended in overcoming the attractive forces. Thus, a liquid has less energy than a gas.

Evaporation of a liquid Evaporation of a liquid means the conversion of the liquid to vapor, condensation, the conversion of vapor to liquid. If a liquid is placed in an open container, the molecules of the liquid gradually escape into the space above the liquid—the liquid evaporates. From an open container the molecules of vapor are dispersed into the atmosphere, and more molecules change into vapor to take their place. If this process is allowed to continue, all of the liquid will eventually be converted into the vapor state; in other words, evaporation continues until the liquid has disappeared.

If a liquid is contained in a closed vessel, the situation is somewhat different; evaporation does not seem to continue indefinitely. Some of the liquid will be converted into vapor, but after the atmosphere above the liquid becomes saturated with molecules, further evaporation of the liquid appears to cease. This vapor exerts a pressure which assumes a constant value at a given temperature. As the temperature of a liquid is increased, the vapor pressure increases. Let us study carefully the causes of these phenomena.

We shall try to imagine the state of affairs existing in a liquid which is contained in a closed vessel (Figure 11–1). If we could see the individual molecules, we undoubtedly would observe that a number of molecules of the substance are present in the space above the liquid. These molecules are moving about in a random fashion and are in a constant state of motion. Collision of these molecules with the walls of the vessel and the surface of the liquid gives rise to the pressure exerted by the vapor (vapor pressure). Probably a somewhat similar state of affairs exists in the body of the liquid, but the molecules of the liquid

are very close together, and movement of the molecules through the body of the liquid is more restricted. However, these molecules possess kinetic energy and move about through the liquid constantly. The molecules are probably held together by mutual attraction. Each molecule in the body of the liquid is attracted and held by the multitude of molecules about it. Occasionally, however, a molecule near the surface of the liquid may possess sufficient energy to break through the surface and thus pass into the space above the liquid. This molecule is thus converted from the liquid state to the vapor state. We may note, too, that some of the molecules which are in the atmosphere above the liquid are passing back into the liquid state. A molecule strikes the surface and passes into the body of the liquid. These molecules are thus condensed from the vapor state to the liquid state. Two continuous processes are occurring simultaneously, the conversion of liquid to vapor (evaporation) and the conversion of vapor to liquid (condensation). Eventually these two processes will be taking place with exactly the same speed, and the number of molecules at any given time in the form of vapor will be a constant, hence the vapor pressure of the liquid attains a constant value at a given temperature. When the rate of evaporation is exactly equal to the rate of condensation, a condition of equilibrium has been established. Equilibrium, though apparently a state of rest, actually is a state in which *two opposing processes are taking place with exactly the same speed.*

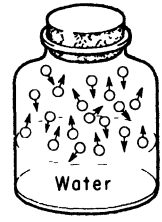


Figure 11-1 A liquid in a closed container soon comes to equilibrium with its vapor—the rate of evaporation is equal to the rate of condensation.

When the temperature of the liquid is increased, the kinetic energy of the molecules in the liquid increases, and relatively more of them escape into the vapor state than return to the liquid state. Since the number of molecules per unit volume determines the pressure of the vapor, the pressure must increase as the temperature is increased. Vapor pressures of liquids at various temperatures have been carefully determined; the vapor pressures of water between 0° and 100° will be found in Table 11-3. When the data in Table 11-3 are plotted with vapor pressure on the vertical axis and temperature on the horizontal axis, the vaporization curve for water is obtained (Figure 11-2).

All points on this curve represent an equilibrium between liquid water and gaseous water. The vapor pressure at any temperature can be obtained from the curve by extending a horizontal line from the point of intersection of a perpendicular corresponding to the temperature. At 70° the horizontal extension cuts the vertical axis at about

TABLE 11–3 **Pressure of Water Vapor, or Aqueous Tension (in millimeters of mercury)**

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
0° C.	4.6	65° C.	187.5
5°	6.5	70°	233.7
10°	9.2	75°	289.1
15°	12.8	80°	355.1
20°	17.5	85°	433.6
25°	23.7	90°	525.8
30°	31.7	94°	610.0
50°	92.3	97°	680.0
55°	118.0	100°	760.0
60°	149.4		

230 mm., consequently the vapor pressure of water at 70° is approximately 230 mm. (See Table 11–3, which gives 233.7 mm.)

The boiling point of a liquid When a liquid is heated in an open container, the escape of molecules from the liquid into the vapor is opposed by atmospheric pressure. As the temperature of the liquid is increased, the vapor pressure of the liquid increases and approaches the atmospheric pressure. The *temperature at which the vapor pressure of the liquid is equal to the external pressure is the boiling point of the liquid.* Thus water which boils at a temperature of 100° at a pressure of 760 mm. will boil at a temperature of 25° if the external pressure is 23.7 mm. Water boils on a mountain top at a temperature below 100°, since the pressure there is less than 760 mm. It is evident from the vaporization curve for water (Figure 11–2) that if the pressure above water is greater than 760 mm., the water will boil at a temperature above 100° C.

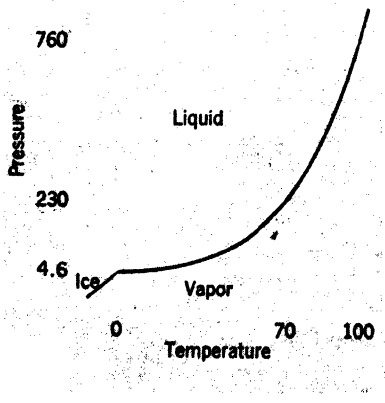


Figure 11–2 Vaporization curve for water.

Further application of heat at the boiling point of a liquid tends only to vaporize the liquid; the liquid absorbs heat in changing from the liquid to the vapor state. The temperature of the boiling liquid remains constant during conversion to vapor, and application of more heat only increases the speed of evaporation.

Refrigeration The evaporation of a liquid is an endothermic process and may be utilized to withdraw heat from a system, as in refrigeration. Heat is transferred from within the refrigerator to the outside, where it is dissipated by circulating air. This transfer of heat is accomplished by alternate condensation and evaporation of a nontoxic substance such as dichlorodifluoromethane, CCl_2F_2. Large commercial refrigerating systems frequently use NH_3. The essential parts of a household refrigerator are shown in Figure 11–3.

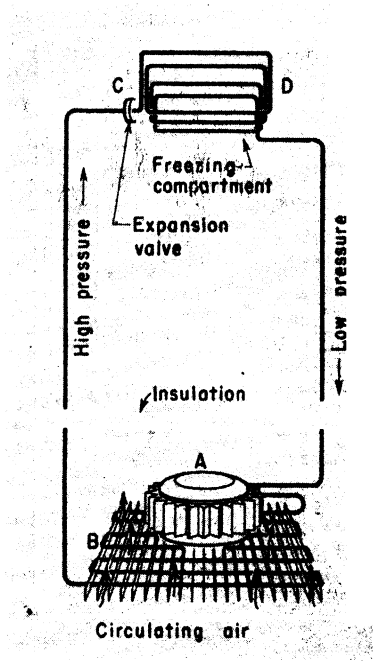


Figure 11–3 A household refrigerator. The gas used in the system enters compressor *A*, where it is liquefied. The resulting warmed liquid is passed through coils *B* where heat is removed by circulating air. The liquid is then passed through an expansion valve *C*. The liquid vaporizes and expands into cooling coils *D*, absorbing heat in the process. The gas then returns to the compressor to start the cycle again.

Surface tension A molecule in the center of a liquid is subject to gravitational pull in all directions by attraction of the molecules all around it. A molecule at the surface, however, is subject to attractional pull by the molecules of liquid at all sides and below it, but not by attraction upward (Figure 11–4). This lateral attraction and downward force on surface molecules without any upward force tends to make the surface of a liquid contract, much as a sheet of rubber stretched laterally in all directions tends to contract. This helps account for a small quantity of a liquid tending to form a spherical or drop shape as there is less surface area to a sphere than to any other shape for a given weight of a liquid. With care, a container can be slightly more than filled with water before it runs over because of the attractional tension between surface molecules. The surface membrane or skinlike layer of molecules is so tough that a small needle may be horizontally floated on it, and various insects walk or skate on this surface film.

Viscosity Liquids differ in their resistance to flow, or *viscosity*. Viscosity may be interpreted as the ease with which the molecules of a liquid

slide over and by one another. By comparing the times necessary for equal volumes of two liquids to flow through a given orifice, the *relative* viscosities may be determined. See Figure 11–5.

Volatile liquids Liquids are often spoken of as being volatile or nonvolatile. Volatile means easily vaporized—easily converted from a liquid to a vapor. Volatile liquids exert relatively high vapor pressures and have relatively low boiling points. Ether (b.p. 34.5°) and alcohol (b.p. 78°) are classed as volatile liquids, since conversion of liquid to vapor (evaporation) takes place rapidly at relatively low temperatures. Perfumes owe their use to their volatile nature. Liquids of high boiling point—for example, sulfuric acid (b.p. 330°) and mercury—(b.p. 357°) are classed as nonvolatile liquids.

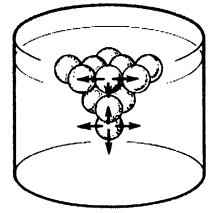


Figure 11–4 Molecules in the surface layer of a liquid have no upward attraction.

Purification of water Natural waters usually contain dissolved minerals or gases. This dissolved material gives water its taste (pure water has a flat taste). So-called "hard" waters precipitate soap or form a curd with soap because of mineral content.

Small amounts of mineral matter are desirable in drinking water, but suspended insoluble matter must be removed and bacteria must be killed. Filtration is the simplest process for removing suspended particles, and filtering water through prepared sand and gravel beds constitutes one of the main methods of treatment for drinking water supplies. Charcoal filter beds sometimes augment sand filters. Prior to passage of water through a filter bed, it may be allowed to stand in a reservoir or container to allow some suspended material to settle by gravity. Chemicals such as aluminum sulfate may be added to form a gelatinous aluminum hydroxide which aids in the coagulation, settling out, or filtering out of suspended matter. Since some harmful bacteria may not be retained in the filter beds, it is necessary to kill them by use of chemicals. Ozone is bubbled into water in some European cities; chlorine in the amount of about 1 part Cl_2 per million parts of water is the principal chemical used in the United States. At times bleaching powder, $CaOCl_2$, is substituted for Cl_2 because of its convenience in handling. A little

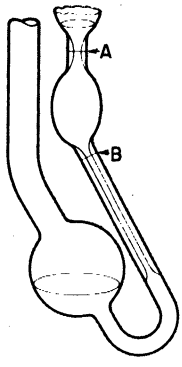


Figure 11–5 A viscosimeter. The time required for a liquid to flow from A to B is a measure of its viscosity.

$CuSO_4$ to kill algae growth in settling basin or reservoir water is also used.

Small quantities of water may be treated to kill bacteria by boiling or by adding one drop of household iodine per quart of water and allowing to stand a half hour.

Water is often purified by distillation, a process in which water is boiled and the vapor subsequently condensed. The process is conveniently carried out in the apparatus shown in Figure 11–6. The condenser, through which cold water is circulated, changes the vapor (steam) to a liquid which is collected in a receiver. Mineral matter, being nonvolatile, stays behind in the distilling flask. Gases contained in the water pass over with the first portion of the distillate, which may be discarded. Water purified in this way is called "distilled water."

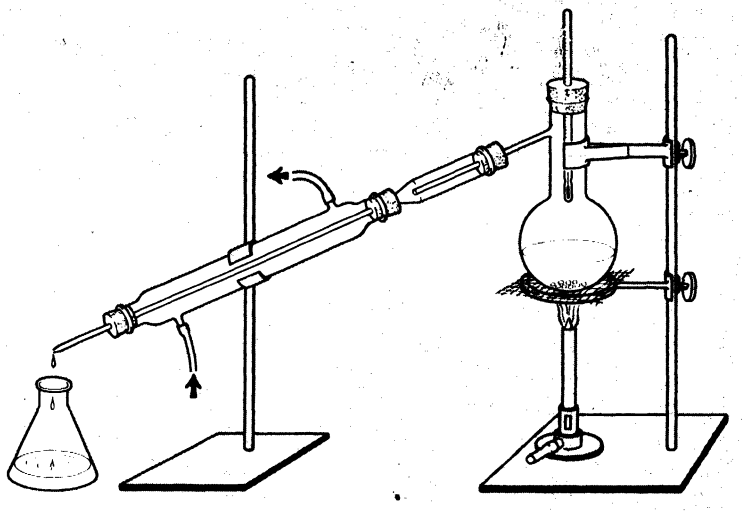


Figure 11–6 Distillation of water.

Distillation is used to purify or concentrate many substances in addition to water.

Chemical properties of water Water is relatively stable; considerable energy is required to decompose it into hydrogen and oxygen. Even at high temperatures, water is only slightly decomposed: little more than 1 per cent at 2000° and about 4 per cent at 2500°.

We learned in the study of hydrogen (Chapter 7) that some of the more active metals act with water to form hydrogen. In the study of oxygen, we learned that metallic oxides, if soluble, act with water to form hydroxides (bases) while nonmetal oxides act to form acids.

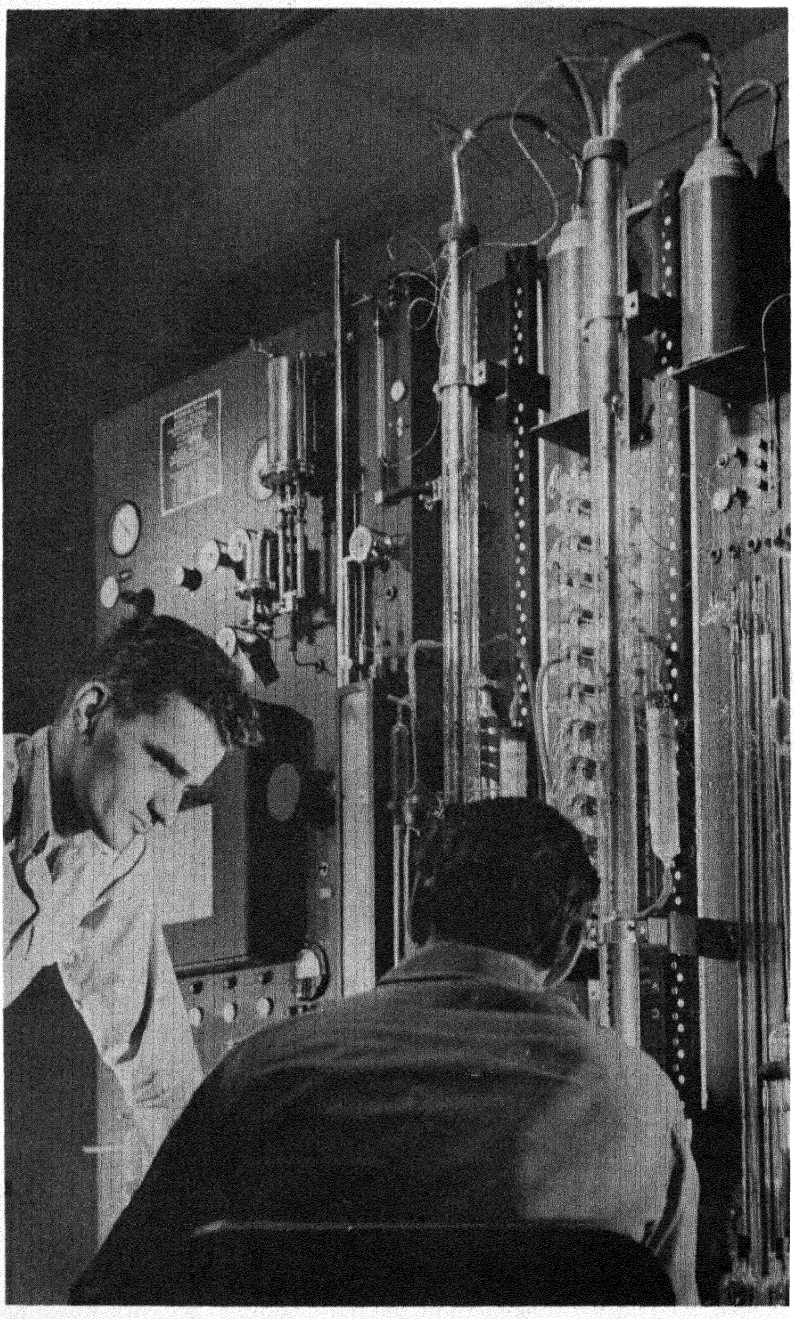


Figure 11–7 Units that may be used to distill as little as one tablespoonful of a liquid.

The molecular structure of water Studies of the molecular structure of water indicate that the hydrogen atoms in the water molecule are not arranged symmetrically about the oxygen atom but rather that they are distributed to one side of the molecule so that the angle between them is about 105° (Figure 11–8).

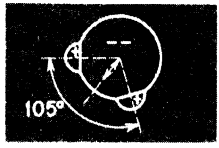


Figure 11–8 Arrangement of hydrogen atoms in the water molecule.

As a result of this arrangement, the center of negative electrical charges (at the center of the oxygen atom) is not the same point as the center of positive electrical charge. Hence, the water molecule acts as a small magnet with one pole positive and the other negative (Figure 11–9, left).

Such electrically unsymmetrical molecules are called *dipoles*. This peculiarity of structure appears to play an important role in the action of liquids as solvents for various types of solutes (see Chapter 15). Because the cohesive forces between these molecules are large, it is likely that the water molecule does not exist as a single dipole; rather, two or more dipoles are associated (Figure 11–9, center and right).

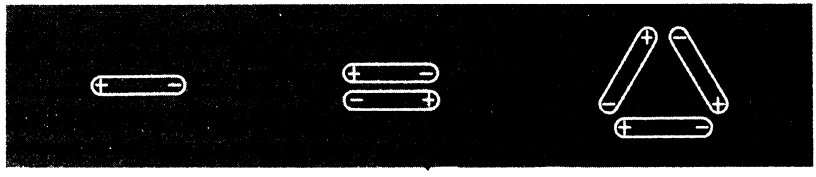


Figure 11–9 Diagrammatic representation of dipoles.

Such association would account for such properties of water as the relatively high heat of vaporization, abnormally high boiling point, and low vapor pressure in view of its low molecular weight.

Heavy water In recent years it has been found that ordinary hydrogen is made up of two isotopes (Figure 11–10). A third isotope of hydrogen is too unstable to be detected normally in nature but may be produced by nuclear reactions (see page 409).

The names deuterium and tritium have been assigned to the heavier

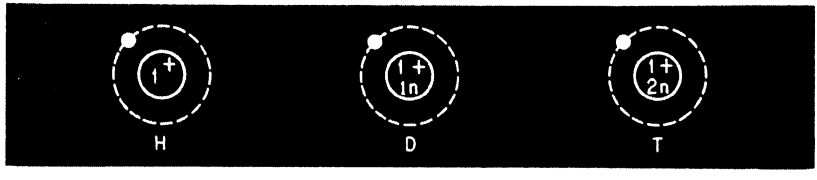


Figure 11–10 The three isotopes of hydrogen.

isotopes, with the symbols D and T. In ordinary hydrogen or its compounds, there is but 1 D atom to 4800 H atoms.

Consider the substitution of atoms of D and T for H in water, so that in addition to H_2O molecules of molecular weight 18, there would be D_2O, T_2O, HOD, HOT, and DOT molecules of molecular weights 20, 22, 19, 20, 21 respectively. In the electrolysis of water, ordinary hydrogen atoms are freed much more readily than hydrogen atoms of atomic weight 2. Accordingly, on long electrolysis the water residue contains a relatively high percentage of D_2O. This water is known as "heavy water"; it differs somewhat from ordinary water in certain physical properties—for example, slightly higher freezing and boiling points. The principal source of heavy water has been the aqueous electrolytic baths which have been used over a long period of time.

The formation of hydrates Many compounds combine chemically with water to form *hydrates*. For example, copper sulfate combines with water to form the hydrate of the composition $CuSO_4 \cdot 5\ H_2O$:

$$CuSO_4 + 5\ H_2O \rightarrow CuSO_4 \cdot 5\ H_2O$$

The hydrate thus formed is a definite chemical compound conforming to the law of definite proportions; exactly five molecules of water, no more and no less, are combined chemically with one formula weight of $CuSO_4$. The ($\cdot$) used in the formula indicates a condition of instability; the compound is readily decomposed by heating. Water held in such a combination is called *water of hydration*, or water of crystallization. Other familiar hydrates are $Na_2CO_3 \cdot 10\ H_2O$ (washing soda), $Na_2SO_4 \cdot 10\ H_2O$ (Glauber's salt), and $KAl(SO_4)_2 \cdot 12\ H_2O$ (alum). All salts do not form hydrates; for example, NaCl, $K_2Cr_2O_7$, and KNO_3 do not form hydrates. When one buys crystalline washing soda ($Na_2CO_3 \cdot 10\ H_2O$), he buys a greater weight of water than of soda.

Hydrates may be decomposed by the application of heat, the water passing off as water vapor, leaving the *anhydrous* (without water) salt:

$$CuSO_4 \cdot 5\ H_2O \rightarrow CuSO_4 + 5\ H_2O$$
$$Na_2CO_3 \cdot 10\ H_2O \rightarrow Na_2CO_3 + 10\ H_2O$$

These changes are reversible, since the hydrates may be re-formed by the addition of water to the anhydrous salt. All hydrates are crystalline but not all crystalline salts are hydrates.

Efflorescence and deliquescence Some hydrates are unstable in contact with the atmosphere. Water of hydration may be released to form a lower hydrate or the anhydrous salt. A hydrated salt exerts a vapor pressure of water, and this vapor pressure is definite for each hydrate. If the pressure of water vapor in the atmosphere is lower than the equi-

librium pressure for a given hydrate, the latter will give up water to the atmosphere. This spontaneous process is termed *efflorescence.* $Na_2CO_3 \cdot 10\ H_2O$ is an example of an effloresecent salt; when exposed to dry air (low humidity), water of hydration is rapidly lost.

Certain soluble substances possess the ability to absorb moisture from the atmosphere and are said to be *hygroscopic.* In this process, water may be absorbed to form a solid hydrate such as

$$CuSO_4 + 5\ H_2O \rightarrow CuSO_4 \cdot 5\ H_2O$$

or a solution of the substance may result. In the latter case, as moisture is absorbed by a crystal, a solution forms about the crystal as it slowly dissolves. The vapor pressure of this concentrated solution will be relatively low. If the pressure of water vapor in the atmosphere is higher than the vapor pressure of this solution, the latter will absorb water and dilute itself until its vapor pressure is equal to the pressure of water vapor in the atmosphere. A crystal which absorbs moisture to form a solution is termed *deliquescent.* Such substances may be used as drying agents, since moisture in the surrounding atmosphere is removed. $CaCl_2$ is often used for this purpose. A specific use of $CaCl_2$ is its application to roadways to keep down dust. The salt takes water from the air and the roadbed becomes somewhat moist. This compound in powder form is also used for dispelling fog around airports.

Figure 11-11 shows a desiccator, an apparatus for drying chemicals or for keeping them dry. Commonly used drying agents are calcium chloride, concentrated sulfuric acid, and magnesium perchlorate.

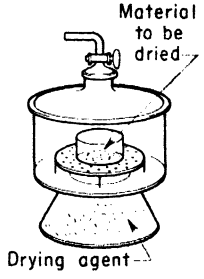


Figure 11-11 A desiccator.

Hydrogen peroxide When certain chemically active metals are heated in oxygen, a peroxide is formed rather than an oxide. A peroxide of a metal contains twice as much oxygen per given weight as its oxide and, in bonding, involves an oxygen-to-oxygen linkage. If a dilute acid is added to a peroxide such as BaO_2, hydrogen peroxide forms:

$$BaO_2 + H_2SO_4\ (\text{dilute}) \rightarrow BaSO_4 + H_2O_2$$

After this chemical change takes place, the $BaSO_4$ may be filtered from a water solution of H_2O_2. By evaporating this water solution of H_2O_2 under reduced pressure, a 30 per cent concentration of the H_2O_2 may be effected. Pharmaceutical hydrogen peroxide is only about 3 per cent H_2O_2. Since hydrogen peroxide has the tendency to decompose to

water and oxygen, various preservatives such as acetanilide are added. Acetanilide acts as a catalyst to decrease the speed of peroxide decomposition; finely divided metals, manganese dioxide, and blood hasten its decomposition.

The mild oxidizing activity of hydrogen peroxide makes it usable in bleaching such substances as feathers, wool, hair, and some silks, which would be injured by more vigorous bleaching agents. Hydrogen peroxide is used as an oxidizing substance in rocket fuels.

EXERCISES

1 Cite evidence to prove that a hydrate is a definite chemical compound.

2 A hundred pounds of washing soda, $Na_2CO_3 \cdot 10\ H_2O$, is purchased at 10 cents per pound. How much money has been invested in water? Ans. \$6.29.

3 What property of calcium chloride makes it useful for laying the dust on roads and highways?

4 Define and illustrate the terms:

(*a*) boiling point	(*d*) efflorescent	(*g*) vapor pressure
(*b*) deliquescence	(*e*) hydrate	(*h*) distillation
(*c*) anhydrous	(*f*) evaporation	(*i*) volatile

5 Suggest a method for detecting the presence of water in kerosene or gasoline.

6 List methods commonly employed for the purification of water.

7 Write equations for the action of water on (*a*) potassium, (*b*) a metallic oxide, (*c*) oxide of a nonmetal, (*d*) zinc.

8 List in order of increasing weight: a 10 cm. cube of Au; a molecule of SO_3; a gram molecular weight of oxygen; a kiloliter of water; a pound of S; a milligram of Pb; a milliliter of alcohol; 22.4 liters of H_2 at standard conditions; a quart of water; an atom of Hg.

9 Below are given temperature and vapor pressure data for the liquid, benzonitrile.

TEMP. °C	VAPOR PRESSURE IN MM. OF Hg
38	1
70	11
90	27
100	43
150	255
180	582
187	700
191	760
195	850

Answer the following questions and give the reason for your answer in each case:

(*a*) Under normal atmospheric pressure, does benzonitrile have a higher or lower boiling point than water?

(*b*) What would be the boiling point of benzonitrile at standard pressure?

(*c*) Would boiling benzonitrile under normal pressure be suitable for processing canned meats and vegetables?

(*d*) At an elevation of 2500 ft. the average air pressure is about 700 mm. Hg. At what temperature would benzonitrile boil at this elevation?

(*e*) At standard pressure, benzonitrile vapor would condense to liquid at what temperature?

10 What weight of water could be heated from 20° to 70° by the heat liberated when 1000 g. of water freezes at 0° C. Ans. 1600 g.

11 What weight of ice could be melted at 0° by the heat liberated on condensing 100 g. of steam at 100° to liquid? Ans. 674 g.

12 A one gram sample of hydrated zinc sulfate on being heated to expel water of hydration leaves a residue of 0.561 g. of anhydrous salt. Determine the formula for the hydrate.

13 List as many types of reactions as you can think of which give water as a product.

14 What quantity of heat would be necessary to convert 100 g. of ice at 0° C. into steam at 100° C.? Ans. 71,900 cal.

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twelve

THE SOLID STATE OF MATTER

Properties of solids In general, the forces of attraction between atoms, molecules, or ions in solids are much stronger than in liquids and gases; thus, a solid possesses rigidity and mechanical strength. Pressure and temperature greatly affect the volume of a gas and to a lesser degree the volume of a liquid but have little effect on the volume of a solid. If a piece of iron is heated, expansion or increase in volume does occur, but the change is relatively small; high pressure would diminish the volume of a piece of iron only slightly.

Solids may be classified as *crystalline* or *amorphous*. A crystalline solid is one in which the atoms are arranged in a definite geometric pattern constantly repeated. An amorphous substance does not possess this orderly arrangement and may be considered as simply an undercooled liquid. When a crystalline solid is heated, the transition from the solid to the liquid state is sharp and distinct; the solid changes state at a definite temperature called the *melting point*. On the other hand, if an amorphous substance such as glass is heated, the glass gradually softens and becomes less viscous as the temperature is raised, but no definite point of transition is recorded. In other words, a crystalline substance possesses a definite melting point; an amorphous substance does not.

Although molecules are held tightly to the surface of solids and there is little freedom of movement, nevertheless a solid may exert an appreciable vapor pressure. Solid iodine, for example, evaporates readily at ordinary temperatures.

Crystal lattice The study of crystal forms and their properties is termed *crystallography*. When a substance crystallizes, the crystals are bounded by plane surfaces and have a definite and characteristic form;

the faces of the crystal meet at definite angles, and the edges are straight lines.

A crystal has a definite shape because of the orderly arrangement of the units that compose it. These units may be ions or molecules, depending upon the electrovalent or covalent nature of the compound. If these units are represented as points, the pattern or configuration of these points which has all the elements of symmetry of the whole crystal is called the *space* or *crystal lattice* for that particular substance.

Types of crystal lattices Many arrangements of the units of a crystal are possible. Suppose we assume that atoms, ions, or molecules are spherical, like marbles. Imagine the ways in which a number of marbles might be grouped or packed together. The tightest packing would result from the arrangement shown in Figure 12–1. In one plane, six marbles will exactly fit around a central one. Three marbles (or spheres) will seat themselves in place above and also below the initial pattern of seven spheres, so that twelve spheres are now spatially placed and touching the thirteenth or central sphere. This central sphere is said to have a *coordination number* of twelve—it has twelve spatially placed intermass contacts.

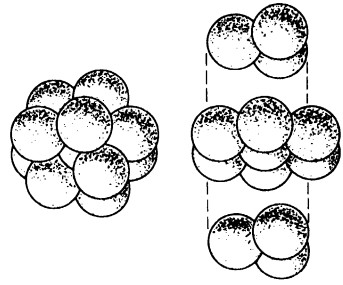


Figure 12–1 Hexagonal close packing. Left, twelve spheres are touching the central sphere. Right, enlarged view showing how the contact with the central sphere is achieved.

In another arrangement, a unit of the crystal lattice may be at the center of a cube with each of the eight corners occupied by another unit, in which case the coordination number is eight. Similarly, a unit in the center of an octahedron will have a coordination number of six; a unit in the center of a tetrahedron will have a coordination number of four.

The lattice arrangements become more complex when crystals of compounds are composed of ions or molecules rather than of like atoms. Factors contributing to complexity are: (1) Ionic diameters of positive and negative ions comprising a compound may vary markedly (see Figure 4–3), especially with crystals involving radical ions. Such ions may not have a spherical shape; for example, SO_3^{--}, NO_3^{-}, OH^{-}. (2) Valence may dictate a ratio other than 1 to 1 of ions in the compound. (3) Ionic bonds differ from intermetallic or intermolecular bonds, causing differences in crystal structure as well as in solubility, melting points, and other physical properties. (4) The charge density of ions influences interion distances. Lithium and fluorine ions are compara-

tively small, and their charge is concentrated on a fairly small sphere. They attract their neighbors strongly. (5) Molecules may vary from simple ones such as CCl_4 to very complex ones such as proteins (Figure 12–4, page 162).

Six crystal systems In spite of the many complex patterns which the solid state may assume, all crystal forms may be resolved into six fundamental types, as shown in Figure 12–2. In these diagrams, the plane

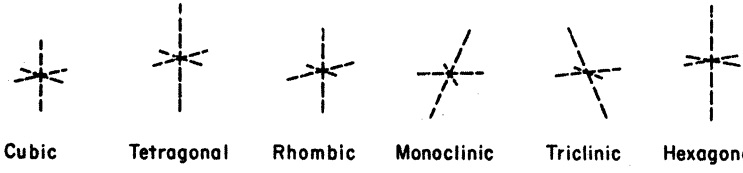


Figure 12–2 Crystal systems.

surfaces of crystals are referred to imaginary lines or axes drawn through them.

1 *Cubic or regular system:* Three axes of equal length and all at right angles to each other.
2 *Tetragonal system:* Three axes, two of equal length, all intersecting at right angles.
3 *Rhombic system:* Three axes of unequal length, all intersecting each other at right angles.
4 *Monoclinic system:* Three axes of unequal length, two of which intersect obliquely, while the third intersects the other two at right angles.
5 *Triclinic system:* Three axes of unequal length, none of which intersect at right angles.
6 *Hexagonal system:* Three axes of equal length in one plane intersecting each other at 60° angles; and a fourth axis at right angles to the plane of the other three.

Isomorphous, polymorphous Two substances which crystallize in the same system and have corresponding axes of approximately the same dimensions and equal angles between corresponding faces are said to be *isomorphous;* for example, the alums (Chapter 35). A substance may sometimes crystallize in more than one form; sulfur, for example, may crystallize in the rhombic or the monoclinic system, depending upon the temperature. Such a substance is said to be *polymorphous.* Each of the

crystal forms that a substance may exhibit is termed an *allotropic* form.

Cubic lattices The smallest portion of the crystal which shows the complete pattern of the particles in their relative positions is called a *unit cell.* While the cubic system is the simplest of the six crystal systems listed above, three arrangements of the particles in a crystal belonging to the cubic system are possible:

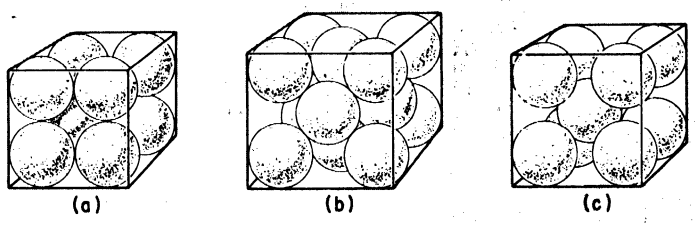


Figure 12–3 *a,* simple cubic lattice; *b,* face-centered lattice; *c,* body-centered lattice.

1 Simple cubic lattice (Figure 12–3a), in which atoms, ions, or molecules are located only at the corners of the cube.
2 Face-centered lattice (Figure 12–3b), in which the unit particles are located at each corner and the center of each face of a cube. Gold, silver, and copper crystallize in this pattern.
3 Body-centered lattice (Figure 12–3c), in which a unit particle is located at each of the corners of a cube and also in the center of the cube, equidistant from the eight corners. Iron, sodium, and potassium are examples of this type.

Salts of the alkali metals with halogens commonly crystallize as cubes. Thus sodium chloride crystallizes in the face-centered cubic system; the arrangement of sodium and chlorine ions in the crystal lattice is shown in Figure 12–5. If we select a unit of the crystal in which a sodium ion appears at each corner of the cube, then a sodium ion also appears in the center of each of the six faces. Six chlorine ions are equidistant from each sodium ion, and likewise six sodium ions surround and are equidistant from each chlorine ion.

Some covalent compounds crystallize in the cubic system, particularly if the molecules can approach a spherical shape; however, the more complex substances usually crystallize in some pattern other than cubic. Certain ring structure organic compounds favor the hexagonal system. The unit cell of cellulose, asbestos, and other fibrous materials has been shown by X rays to possess a long bar or stringlike structure.

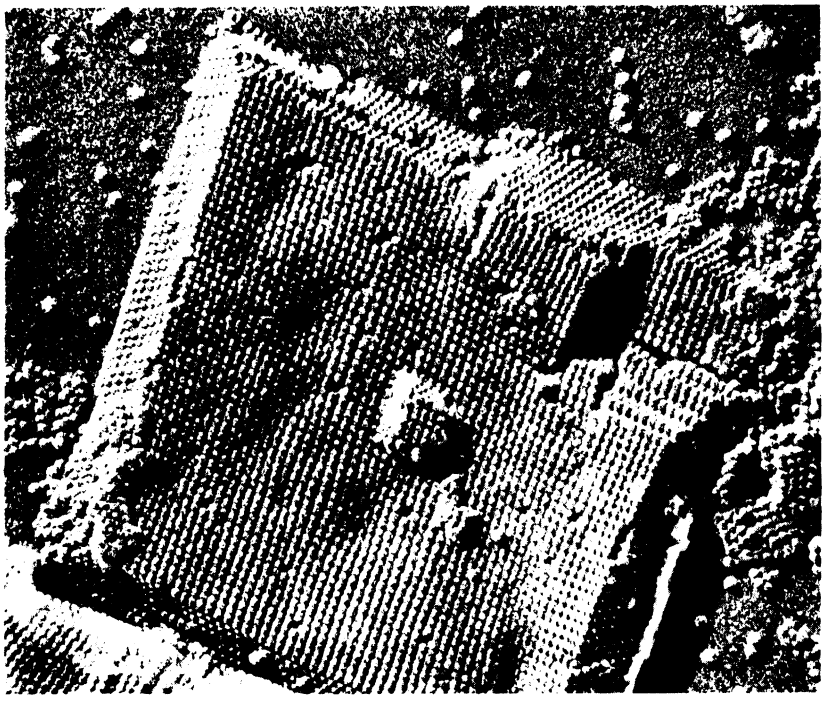


Figure 12–4 Electron microscope view of virus protein crystal showing its molecularly well-ordered structure. Magnification 50,000X.

The use of X rays to study crystal structure Diffraction gratings, which are made by ruling parallel lines equidistant and very close together on a glass surface, are used to study spectra and other phenomena connected with light. When light passes through the small spaces between the lines on such a grating, it is spread out or dispersed—an effect that is known as *diffraction*. A diffraction grating may have as many as 20,000 or 30,000 lines per inch.

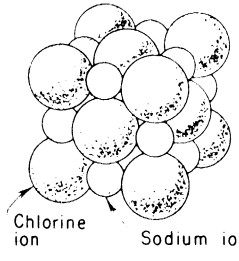


Figure 12–5 Crystal lattice of sodium chloride.

In a crystal, the regular arrangement of atoms constitutes a natural diffraction grating. The distance between planes in a crystal is very small, yet great enough to diffract the extremely short waves of X rays. If monochromatic X rays (X rays of a single wave length) are passed through a crystal from above, they will be diffracted by the inner planes of the crystal and will form a pattern of light spots on a photographic plate beneath the crystal. These spots corre-

spond to a definite arrangement of the units in the crystal, and from the nature of the arrangement, facts concerning the structure of the crystal may be deduced. Figure 12–6 shows such an X-ray diffraction pattern.

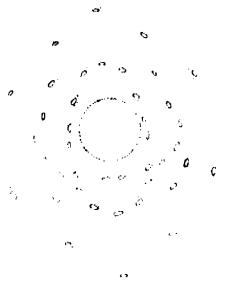


Figure 12–6 X-ray diffraction pattern of magnesium oxide.

With the *X-ray spectrometer,* the distance between the planes in a crystal may be calculated. In this apparatus, a beam of monochromatic X rays of known wave length strikes the surface of the crystal at an angle so that the beam is "reflected." Since X rays are much more penetrating than visible light, the beam will be reflected by the inner planes as well as by the surface of the crystal. If the angle at which the X rays strike the crystal is varied, the reflections from the different planes can be brought into phase so that they reinforce each other, resulting in a reflected beam of high intensity. Variations of intensity of the reflected beam as the angle is changed are measured, and the results are plotted on a graph as a curve showing a series of peaks. Similar graphs are plotted for each of the principal planes of the crystal by turning the crystal and taking reflections from the other faces. From a study of these graphs, knowledge of the arrangement of the atoms in the crystal may be obtained.

Crystal structure and physical properties The crystal structure of a substance will often account for certain of its physical properties. For example, the element carbon may crystallize in two forms, diamond and graphite. In the diamond (Figure 12–7), the carbon atoms are arranged as in a tetrahedron, with one atom at each of the four corners and one atom in the center of the tetrahedron. The atoms are held together by strong covalent forces and, as a result, the diamond is hard, strong, and possesses a high melting point. In graphite (Figure 12–8), the unit cell possesses a two-dimensional structure in which carbon atoms are arranged in the form of hexagons in planes. The atoms in a given plane are held together by strong covalent linkages, but the forces between planes are weak. As a result, the planes can readily slide past one

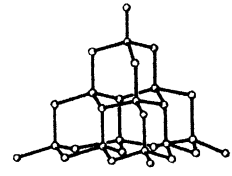


Figure 12–7 Structure of diamond. Each carbon atom is bound to four other carbon atoms in a close-packed arrangement.

another, thus explaining the flaky character and lubricating properties of graphite.

The density of a solid is a function of the weight and radius of the atomic units in a crystal and also of the interatomic or interionic distances between these units in the crystal lattice of the solid. Table 12–1 shows these distances in angstrom units for a few simple crystals.

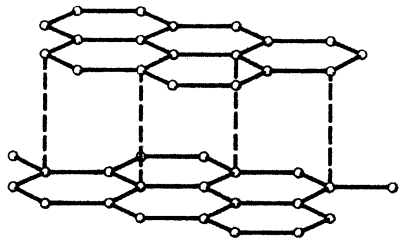


Figure 12–8 Structure of graphite.

Melting points are also related to crystal structure. For example, diamond with its close packed tetrahedral structure has a very high melting point—more than 3500° C. Sodium, with greater interatomic distances and weak metallic bonding, melts at 97° C. Crystals composed of molecules are likely to have lower melting points than electrovalent substances. Melting points are affected by pressure only to a small degree. A pressure of one atmosphere lowers the melting point of ice only 0.0076° C., and it would require a pressure of 132 atmospheres to lower it by 1° C.

TABLE 12–1 Distances Between Units in Crystal Lattices

SUBSTANCE	TYPE OF LATTICE	LENGTH OF SIDE OF UNIT CELL (angstroms)	DISTANCE BETWEEN ATOMS OR IONS* (angstroms)
Na	body-centered	4.30	3.72
Cu	face-centered	3.60	2.54
Diamond	tetrahedral	3.56	1.54
NaCl	face-centered	5.63	2.81
ZnS	face-centered	5.56	2.41

*A crystal of a metal only 1 mm. on an edge would have about 4,000,000 atoms in a row.

Heat is a manifestation of atoms and molecules in motion. When a solid is melted, a considerable amount of heat is required (heat of fusion). In the solid, motion of the unit particles is highly restricted because of the quite fixed positions in the crystal lattice. There is evidence that some random motion or vibration occurs in the solid, since X-ray photos become increasingly "fuzzy" as the melting point is approached.

Specific heats (number of calories required to raise the temperature of 1 gram of a substance 1° C.) of solids are in general much lower than for liquids. Apparently a smaller mass motion factor is involved per

1° C. change in the solid state. The specific heat of a given solid varies considerably with temperature, but the specific heat of all solids approaches zero at absolute zero temperature.

Most solids expand when heated, and this thermal expansion is a further index of increased motion or vibration around fixed positions. Heat conduction, which varies with different solids, is also related to the transfer of energy of motion from particles in one part to particles in other parts of a solid.

Giant molecules In many solids such as diamond, silicon carbide, and boron nitride, a tight covalent bonding links all atoms together in a three-dimensional space pattern. A single crystal of such a solid may be regarded as a giant molecule. Inasmuch as such bonds are not easily broken, these substances possess qualities of low solubility, high melting and boiling points, poor electrical conduction, and marked hardness.

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MOLECULAR AND ATOMIC WEIGHTS

Experimental determination of molecular weights Since a mole (gram molecular weight) of any gas at standard conditions occupies a volume of 22.4 liters, the molecular weight of a gas is easily obtained by determining the weight of a given volume of the gas at any suitable temperature and pressure and then calculating the weight of gas which would occupy 22.4 liters at standard conditions. The weight in grams of this volume is the gram molecular weight and is numerically equal to the molecular weight. The molecular weight of solids and liquids which are easily vaporized without decomposition may also be determined by this method. For example, an experiment showed that 6 grams of chloroform, $CHCl_3$ (boiling point 61°) occupied a volume of 1.53 liters at 100° and 760 mm. pressure. At standard conditions, the volume would be

$$1.53 \times \frac{273}{373} = 1.12 \text{ l.}$$

Since the gram molecular weight (x) is the weight of 22.4 liters at standard conditions:

$$\frac{x}{6} = \frac{22.4}{1.12}$$

$$x = 120$$

Since the accurate molecular weight of chloroform is 119.37, the experimental error by this method may be less than 1 per cent.

The method is limited in its application, since many substances are either nonvolatile or may decompose when an attempt is made to vaporize them. However, we shall learn in Chapter 15 that molecular

weights of solids may be determined by accurately measuring the boiling and freezing points of aqueous and nonaqueous solutions.

Atomic weights Atomic weights are determined by analysis of pure chemical compounds. Since the atom is the reactive unit in chemical change, the smallest weight of an element in a molecular weight of any of its compounds should be its atomic weight. If the molecular weight of a compound of an element is known, the weight of the element present in a mole of the compound can be determined by chemical analysis. It is unnecessary to analyze all the compounds of the element; a representative number of them will be enough to arrive at the atomic weight. Table 13–1 shows the percentage and parts by weight of chlorine in molecular weights of several of its compounds. The smallest weight of chlorine in a molecular weight of these compounds is 35.46. Since no compound of chlorine has ever been found with a molecular weight containing less than 35.46 parts by weight of chlorine, this value must be its atomic weight.

TABLE 13–1 Analysis of Several Chlorine Compounds

COMPOUND	MOLECULAR WEIGHT	PERCENTAGE OF CHLORINE	PARTS BY WEIGHT OF CHLORINE
Hydrogen chloride	36.46	97.26	35.46
Methylene chloride	84.95	83.49	70.92
Chloroform	119.40	89.10	106.38
Carbon tetrachloride	153.85	92.19	141.84
Thionyl chloride	118.98	59.69	70.92
Phosphorus pentachloride	208.28	85.13	177.30
Butyl chloride	92.57	38.31	35.46
Carbonyl chloride	98.93	71.69	70.92

This method of determining atomic weight depends on molecular weights which cannot be determined with a high degree of accuracy. The accuracy of the atomic weight of the element is thus limited to the accuracy of the molecular weight determinations.

Precise atomic weights Precise atomic weights are obtained from equivalent weights, which in turn are obtained from accurate analysis and synthesis of pure chemical compounds. The equivalent weight of an element is that weight of the element which will combine with 8 grams of oxygen or which will displace 1.008 grams of hydrogen from an acid. A simple relationship (see page 27) exists between the equivalent weight and the atomic weight of an element:

$$\text{Atomic weight} = \text{Equivalent weight} \times X$$

X is a small integral number that represents the valence of the element

in the compound from which the equivalent weight was obtained. Our next problem, then, is to find the value of X.

Fortunately, we have an empirical method for the determination of the approximate atomic weight of an element. If we have the approximate atomic weight, it will be an easy matter to determine the value of X in the above relationship. DuLong and Petit found that the product of the specific heat of a solid element and its atomic weight gave a value between 6 and 7, the average value being about 6.4. They therefore stated the general rule:

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

Examination of Table 13–2 will show the validity of this rule.

If the specific heat of an element is known, its approximate atomic weight may be obtained by dividing 6.4 by its specific heat. The following examples illustrate how atomic weights are obtained from equivalent weights, and the DuLong and Petit rule:

TABLE 13–2 Illustrations of the DuLong and Petit Rule

ELEMENT	SPECIFIC HEAT	ATOMIC WEIGHT	ATOMIC WEIGHT × SPECIFIC HEAT
Iron	.12	55.85	6.7
Tin	.054	118.7	6.4
Phosphorus (white)	.20	31.0	6.2
Silver	.056	107.0	6.0
Mercury	.034	200.6	6.8
Magnesium	.25	24.3	6.1
Zinc	.093	65.38	6.1
Gold	.032	197.2	6.3
Sodium	.29	23.0	6.7

EXAMPLE 1. Analysis of an oxide of iron shows that 18.61 g. of iron is combined with 8 g. of oxygen. 18.61 is therefore the equivalent weight of iron in this compound.

The specific heat of iron is .12; thus, the approximate atomic weight of iron by the DuLong and Petit rule is:

$$\text{Approximate Atomic Weight} = \frac{6.4}{.12} = 54$$

It is evident from inspection that the multiple of the equivalent weight (18.61) which most nearly gives 54 is 3. The precise atomic weight must therefore be

$$3 \times 18.61 = 55.83$$

EXAMPLE 2. A compound analyzes 21.23 per cent oxygen and 78.77 per cent tin.

We may calculate the equivalent weight of tin (the weight of tin combining with 8 parts by weight of oxygen) from the proportion

$$\frac{21.23}{78.77} = \frac{8}{x} \qquad x = 29.68$$

The specific heat of tin is .054, and the approximate atomic weight is $\frac{6.4}{.054} = 118$. The smallest integral number which most nearly gives this value when multiplied by the equivalent weight is 4. The precise atomic weight, then, must be $4 \times 29.68 = 118.72$. The valence of tin in this compound must be 4.

EXAMPLE 3. The analysis of a compound gives 24.76 per cent chlorine and 75.24 per cent silver.

While we cannot calculate directly from these data the weight of silver which combines with 8 grams of oxygen, we can calculate the weight of silver which combines with 35.46 parts by weight of chlorine. This value, then, must be the equivalent weight of silver since we know that 35.46 is the equivalent weight of chlorine. By proportion

$$\frac{24.76}{75.24} = \frac{35.46}{x} \qquad x = 107.88$$

The specific heat of silver is .056; therefore, the approximate atomic weight of silver is $\frac{6.4}{.056} = 114$.

It is evident that the valence of silver must be 1 and the atomic weight is, then, the same as the equivalent weight; namely, 107.88.

Atomic weights from the mass spectrograph As pointed out on page 45, isotopic masses may be determined accurately with the mass spectrograph. In the case of an element with only one isotope—such as gold—the mass determined with the mass spectrograph is its atomic weight. But for elements with more than one isotope, it is necessary to know not only the mass of each isotope but also the percentage of each isotope present in the naturally occurring form of the element, since atomic weights as we use them are based on the average mass of the atoms in the naturally occurring mixture. Fortunately, this information can be derived from mass spectrographic data and the atomic weight can be calculated. For example, a mass spectrogram for chlorine (Figure 13–1) shows that in ordinary chlorine the two isotopes occur in the proportions of

	% ABUNDANCE	ACTUAL MASS
Cl^{35}	75.4	34.979
Cl^{37}	24.6	36.978

The atomic weight of naturally occurring chlorine may then be obtained in the following manner:

$$(.754)\,(34.979) + (.246)\,(36.978) = 35.471$$

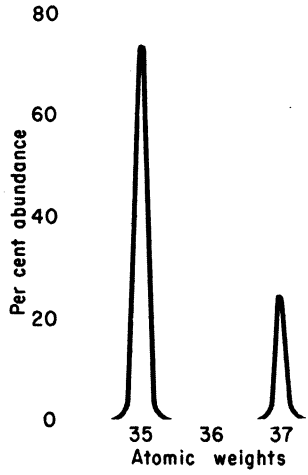


Figure 13–1 Mass spectrogram for naturally occurring chlorine.

Because of its great accuracy, the mass spectrographic method of determining atomic weights is almost certain to be more important in the future than methods based on chemical analysis.

Physical and chemical atomic weights Atomic weights as determined by the mass spectrograph are based on the most abundant isotope of oxygen, O^{16}, taken as 16.0000. These are termed atomic weights on the *physicist's scale.* Chemical atomic weights are based on naturally occurring oxygen (taken as 16.0000) which is made up of the three isotopes, O^{16}, O^{17} (.04%) and O^{18} (0.2%). The relationship between the physical and chemical scales is given by the expression:

$$\text{Chemical atomic weight} = \frac{\text{physical atomic weight}}{1.000272}$$

EXERCISES

1 56 ml. of a gaseous compound measured at standard conditions weighed 0.26 g. What is the molecular weight of the compound? Ans. 104.

2 .532 g. of a solid substance when vaporized occupied a volume of 118 ml. at a pressure of 694 mm. and a temperature of 94° C. Calculate the molecular weight of the substance. Ans. 149.

3 Calculate the approximate atomic weight of an element leaving a specific heat of 0.32.

4 If the atomic weight of oxygen were 100, what would its equivalent weight be?

5 0.134 g. of aluminum combines with 0.532 g. of chlorine. The specific heat of aluminum is .217. Calculate the valence and atomic weight of aluminum.

6 2.25 g. of a metal of atomic weight 27 yielded 2800 ml. of H_2 gas at standard conditions. What is the valence of the metal? Ans. 3.

7 50 ml. of a gaseous oxide of sulfur at standard conditions weighs 0.143 g. What is its molecular weight and formula? Ans. SO_2.

8 373 ml. of vapor at 100° and 760 mm. pressure on condensing forms 0.45 ml. of liquid with a density of 1.2 g./ml. Calculate the molecular weight of the vapor. Ans. 44.

9 2.0 g. of copper is displaced from $CuSO_4$ by 0.76 g. of an unknown metal. What is the equivalent weight of the unknown metal? Equivalent weight of Cu = 31.8. Ans. 12.1.

10 2.5 g. of a metallic oxide contains 1.4 g. of metal. The specific heat of this metal is 0.128. Calculate the exact atomic weight Ans. 50.91.

11 0.4 g. of O_2 combines with 0.6 g. of Mg. 0.4 g. of Mg displaces 1.05 g. of Cu from a copper salt. What is the equivalent weight of copper? Ans. 31.5.

12 Suppose 0.563 g. of metal displaces 700 ml. of hydrogen at STP. What is the equivalent weight of the metal? Ans. 9.

13 Element X forms a series of chlorides of approximate molecular weights 126; 161; 197. These compounds contain 56%, 66% and 72% of chlorine, respectively. An oxide of X contains precisely 36.81% oxygen. Calculate the precise atomic weight of X.

14 Element X forms a chloride which contains 74.82% chlorine. The specific heat of X is 0.12. Determine (*a*) the precise atomic weight of X; (*b*) the formula for the chloride. Ans. (*a*) 47.54 (*b*) XCl_4.

fourteen

WEIGHT AND VOLUME RELATIONS BETWEEN SUBSTANCES IN CHEMICAL CHANGE

For a person working with chemicals, it is important to know not only the behavior of substances entering into or resulting from chemical change but also the proportionate *amounts* of these chemicals which react with one another and the amounts of products formed as a result of a chemical change. Since amounts of substances may be measured by volume or by weight, and by either the metric or English system, one must carefully designate the units of measurement used. Solids and liquids are weighed; gases are usually measured by volume.

Volume-volume relations Some of the simplest problems of chemistry are of a volume-to-volume nature. Their solution is based on Gay-Lussac's law of combining volumes (Chapter 8), which states, "in a chemical change the comparative volumes of gases involved (measured under the same conditions of temperature and pressure), bear to each other a small whole-number relationship." For example, in the reaction

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

reactants and products are gases. The coefficients of the formulas give the volume relations; in this case, 2 unit volumes of CO react with 1 unit volume of O_2 to give 2 unit volumes of CO_2. We might use any unit of volume—liters, gallons, cubic feet; the proportions remain the same.

The following examples will illustrate the solution of typical volume-volume problems. (It is assumed that all gases are under the same conditions of temperature and pressure.)

EXAMPLE 1. Calculate the volume of oxygen necessary to burn 50 liters of CO. According to the equation above, 2 liters of CO would require 1 liter of oxygen (the numbers 2 and 1 are the coefficients of CO and O_2 respectively); therefore we might set up the proportion

$$\frac{2 \text{ liters}}{50 \text{ liters}} = \frac{1 \text{ liter}}{x \text{ liters}} \qquad x = 25 \text{ liters}$$

What volume of CO_2 would be formed?

The equation tells us that 2 liters of CO would produce 2 liters of CO_2; hence, 50 liters of CO would produce 50 liters of CO_2.

EXAMPLE 2. Calculate the volume of oxygen necessary to produce 1000 cubic feet of SO_2 according to the equation:

$$S + O_2 \rightarrow SO_2$$

The coefficients of oxygen and sulfur dioxide are 1 and 1; therefore

$$\frac{1 \text{ cu. ft.}}{x} = \frac{1 \text{ cu. ft.}}{1000 \text{ cu. ft.}} \qquad x = 1000 \text{ cu. ft.}$$

We should keep in mind that Gay-Lussac's law applies *only* to substances in the gaseous state and cannot be used with those substances which may be present as liquids or solids. Thus, in Example 2, we cannot calculate the volume relationship between sulfur and oxygen or sulfur dioxide, since sulfur is a solid at the conditions under which this reaction is carried out.

EXAMPLE 3. How much oxygen is required for the complete combustion of 1000 cu. ft. of NH_3 according to the equation given below? Calculate also the volume of nitric oxide formed.

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$$

According to the equation, 4 unit volumes of ammonia react with 5 unit volumes of oxygen to give 4 unit volumes of nitric oxide and 6 unit volumes of water (vapor). Since the ratio of NH_3 to O_2 is 4 to 5 by volume, we can set up the proportion

$$\frac{4}{1000 \text{ cu. ft.}} = \frac{5}{x} \qquad x = 1250 \text{ cu. ft.}$$

To calculate the volume of NO formed, we may use the proportion

$$\frac{4}{1000 \text{ cu. ft.}} = \frac{4}{x} \qquad x = 1000 \text{ cu. ft.}$$

Note that the sums of the volumes on both sides of the equation for this reaction are not equal: on the left side, there is a total of 9 unit volumes; on the right side, 10 unit volumes. Many chemical changes involving gases may show increase or decrease of volume of products over initial volume.

Weight-weight relations In considering reactants and products of a chemical change, such questions as these may arise: In what proportion should one mix the initial substances? What weight of product or products will result after chemical change from certain weights of reacting substances? Such problems are solved with the balanced chemical equation as a guide. Just as a formula tells us very definitely the ratio of weights of the different elements present in a compound, so an equation tells us the relationship of the weights of the reactants to one another and to the products. The calculation of weights from equations can be illustrated with examples.

EXAMPLE 1. What weight of oxygen may be obtained by heating 30 grams of potassium chlorate?

The balanced equation is

$$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$$

ATOMIC WEIGHTS
K = 39
O = 16
Cl = 35.5

The equation tells us that 2 formula weights (2 moles) of potassium chlorate will give 2 formula weights (2 moles) of KCl and 3 formula weights (3 moles) of O_2; or $2 \times (39 + 35.5 + 48)$ parts by weight of $KClO_3$ will produce $2 \times (39 + 35.5)$ parts by weight of KCl and $3 \times (32)$ parts by weight of oxygen.

It is convenient to make a brief statement of the problem by putting written notes just above the formulas of the substances under consideration; thus

$$\underset{2(122.5)}{2\ KClO_3} \rightarrow \underset{}{2\ KCl} + \underset{3(32)}{3\ O_2}$$

(30 g. above $KClO_3$; x g. above $3\ O_2$)

The formula weights multiplied by the proper coefficients are then placed directly beneath the formulas. We are not concerned with KCl in this problem so it is unnecessary to calculate its formula weight. (In

this problem the formula weight of KCl was calculated simply to show the full meaning of the balanced equation; but, in subsequent calculations, only those formula weights which actually are needed in the solution of the problem will be used.) The proportion may be formulated:

$$\frac{30}{2(122.5)} = \frac{x}{3(32)} \qquad x = 11.75 \text{ g. of oxygen}$$

Alternate methods of solution The solution of most problems may be approached in several ways. In addition to the proportion method shown above, weight relation problems are often solved by the *factor* method and by the *mole* method. Solution of the problem in Example 1 on page 174 by these two other methods is as follows:

Factor method: According to the equation, 245 g. of $KClO_3$ yields 96 g. of O_2; therefore, 1 g. of $KClO_3$ will yield 96/245 g. of O_2. Hence 30 g. of $KClO_3$ will yield

$$30 \text{ g. } \cancel{KClO_3} \times \frac{96 \text{ g. oxygen}}{245 \text{ g. } \cancel{KClO_3}} = 11.75 \text{ g. oxygen}$$

Mole method: The equation tells us that 2 moles of $KClO_3$ will yield 3 moles of oxygen; therefore 1 mole of $KClO_3$ will give 3/2 moles of oxygen. 30 g. of $KClO_3$ = 30/122.5 = 0.245 moles. 0.245 moles of $KClO_3$ will then yield 0.245 × 3/2 = 0.367 moles of oxygen. 0.367 moles of oxygen weighs (0.367) × (32) = 11.75 g.

EXAMPLE 2. What weight of sulfur must combine with aluminum to prepare 600 pounds of aluminum sulfide?

This problem can be solved as a percentage composition problem or as a weight-weight problem. If we calculate the percentage of sulfur in Al_2S_3 and multiply by 600 pounds, we will determine the needed amount of sulfur. As a weight-weight problem, the usual procedure is best followed:

$$2\,Al + \underset{3(32)}{\overset{x \text{ lb.}}{3\,S}} \rightarrow \underset{150}{\overset{600 \text{ lb.}}{Al_2S_3}}$$

$$\frac{x}{96} = \frac{600}{150} \qquad x = 384 \text{ lb. sulfur}$$

Factor method: 150 lb. of Al_2S_3 requires 96 lb. of S; therefore, 1 lb. of Al_2S_3 requires 96/150 lb. of S. Thus, 600 lb. of Al_2S_3 would require:

$$600 \text{ lb. } \cancel{Al_2S_3} \times \frac{96 \text{ lb. S}}{150 \text{ lb. } \cancel{Al_2S_3}} = 384 \text{ lb. S}$$

Mole method: One mole (in lbs.) of Al_2S_3 requires 3 moles (in lbs.) of S. 600 lb. of Al_2S_3 = 600/150 = 4 pound moles. 4 lb. moles of Al_2S_3 will require 4 × 3 = 12 lb. moles of sulfur. 12 pound moles of S = 12 × 32 = 384 lbs.

EXAMPLE 3. What weight of arsenic acid should a company use on lime to prepare a thousand pounds of calcium arsenate insecticide material?

Once we have the balanced chemical equation for this commercial preparation, the weight-weight problem readily follows the usual pattern:

$$3\ CaO + 2\ \underset{2(142)}{\overset{x\ \text{lb.}}{H_3AsO_4}} \rightarrow \underset{398}{\overset{1000\ \text{lb.}}{Ca_3(AsO_4)_2}} + 3\ H_2O$$

$$\frac{x}{284} = \frac{1000}{398} \qquad x = 714\ \text{lb. } H_3AsO_4$$

The student should solve this problem by both the factor and the mole methods.

Weight-volume relations Gases are most commonly measured by volume, whereas liquids and solids are usually measured by weight. At times it is desirable to calculate the relationship of weight to volume in chemical changes where a gas is involved.

The fact that *22.4 liters* of any gas at standard conditions weighs *its gram molecular weight* allows one to interchange weight and volume units for a gas. By a mathematical coincidence, *22.4 cubic feet* of any gas at standard conditions weighs *its ounce molecular weight.* These facts allow calculation of the weight from volume or volume from weight of any amount of pure gas. When a gas is at other than standard conditions, gas law calculations of volume at standard conditions are necessary, since the equality of 22.4 liters and gram molecular weight holds only for standard conditions. The following examples will illustrate the usefulness of this relation between the weight of a gas and its volume at standard conditions:

EXAMPLE 1. What is the weight of one liter of carbon monoxide, CO, at standard conditions?

The molecular weight of CO is 28; consequently

22.4 liters of CO at S.T.P. = 28 grams (gram molecular weight)
1 liter of CO at S.T.P. = x grams

$$\frac{22.4}{1} = \frac{28}{x} \qquad x = 1.25\ \text{g.}$$

EXAMPLE 2. What is the weight of one thousand cubic feet of carbon monoxide at standard conditions?

22.4 cu. ft. of CO at S.T.P. = 28 ounces (ounce molecular weight)
1000 cu. ft. of CO at S.T.P. = x ounces

$$\frac{22.4}{1000} = \frac{28}{x} \qquad x = 1250\ \text{ounces}$$

EXAMPLE 3. As sulfuric acid chemically acts on 120 grams of metallic calcium, what volume of hydrogen at standard conditions is produced?

The problem may be solved almost like a weight-weight problem, except that for the gas we can substitute 22.4 liters in place of its gram molecular weight:

$$\underset{40\text{ g.}}{\overset{120\text{ g.}}{Ca}} + H_2SO_4 \rightarrow CaSO_4 + \underset{22.4\text{ l.}}{\overset{x\text{ liters}}{H_2}}$$

$$\frac{120}{40} = \frac{x}{22.4} \qquad x = 67.2 \text{ liters}$$

Factor method: According to the equation, 40 g. of Ca yields 22.4 liters of hydrogen. Thus, 1 g. of Ca would give $\frac{22.4}{40}$ liters. 120 g. of Ca would give:

$$120 \text{ g. Ca} \times \frac{22.4 \text{ liters } H_2}{40 \text{ g. Ca}} = 67.2 \text{ liters } H_2$$

Mole method: One mole of Ca gives one mole of H_2. 140 g. of Ca = 120/40 = 3 moles. Three moles of Ca would give 3 moles of H_2. Three moles of H_2 at STP = 3 × 22.4 liters = 67.2 liters.

EXAMPLE 4. What volume of ammonia at standard conditions can be obtained when steam is passed over 4000 grams of calcium cyanamide?

$$\underset{80\text{ g.}}{\overset{4000\text{ g.}}{CaCN_2}} + 3\ H_2O \rightarrow \underset{2(22.4)\text{ liters}}{\overset{x\text{ liters}}{2\ NH_3}} + CaCO_3$$

$$\frac{4000}{80} = \frac{x}{2(22.4)} \qquad x = 2240 \text{ liters}$$

EXAMPLE 5. What volume of oxygen is needed in the complete burning of 100 ounces of octane liquid?

$$\underset{2(114)\text{ oz.}}{\overset{100\text{ oz.}}{2\ C_8H_{18}}} + \underset{25(22.4)\text{ cu. ft.}}{\overset{x\text{ cu. ft.}}{25\ O_2}} \rightarrow 16\ CO_2 + 18\ H_2O$$

$$\frac{100}{2(114)} = \frac{x}{25(22.4)} \qquad x = 245.6 \text{ cu. ft.}$$

The volume of air required for the combustion would be 5 × 245.6 or 1228 cu. ft., since air is approximately $\frac{1}{5}$ oxygen. One hundred ounces of octane liquid (octane approximates the average composition of gasoline) occupies a volume of about 1 gallon. It is surprising that as much as 1228 cu. ft. of air is needed in the complete combustion of 1 gallon of gasoline.

EXERCISES

1 (*a*) What volume of oxygen is needed to burn completely 20 liters of CH_4 gas? (Consider gases at same conditions.) (*b*) What volume of products will be formed? Ans. (*a*) 40 l.; (*b*) 60 l.

2 A balloon contains 1000 cu. ft. of hydrogen. What volume of air would be used in burning the hydrogen? Ans. 2500 cu. ft.

3 Given 0.4 liter of C_8H_{18} (octane) vapor at 100° C. (*a*) What volume of oxygen at 100° will be required to completely burn the gas? Products of combustion are carbon dioxide and water. (*b*) What volume of air (20 per cent oxygen) would be necessary? (*c*) What would be the total volume of the gaseous products at 100°? Ans. (*a*) 5 l.

4 Four liters of nitrogen and 14 liters of hydrogen gases are mixed. If all the nitrogen reacts to produce ammonia gas, what gases and what volume of each would be present? Assume no change in temperature.

5 Most mercury is obtained from cinnabar, which chemically is HgS. What weight of mercury should be obtained from 1000 pounds of HgS?

6 What weight of chromium could theoretically be electrodeposited from a solution containing a kilogram of $Cr_2(SO_4)_3$? Ans. 265 g.

7 (*a*) Calculate the volumes of hydrogen and oxygen, respectively, produced at standard conditions, when 100 grams of water is electrolyzed. (*b*) Calculate the weights of these gases. Ans. (*b*) H_2, 11.1 g.; O_2, 88.9 g.

8 What weight of H_3PO_4 can be prepared as H_2SO_4 acts on 400 pounds of $Ca_3(PO_4)_2$? Ans. 253 lb.

9 How many pounds of silver sulfate must be used in the reaction with KBr to produce 94 pounds of silver bromide for photographic use?

10 $Bi_2(CO_3)_3$ is treated with HNO_3 to obtain $Bi(NO_3)_3$ in a step in making the medicinal bismuth subnitrate. What weight of $Bi(NO_3)_3$ can be made as excess HNO_3 acts on 2 gram moles of $Bi_2(CO_3)_3$?

11 What weight of 10 per cent sulfuric acid should be used with Al_2O_3 to prepare 2 gram moles of $Al_2(SO_4)_3$?

12 What weight of lime (CaO) should be added to excess 10 per cent nitric acid to prepare 4920 pounds of $Ca(NO_3)_2$? Ans. 1680 lb.

13 What is the weight of 10 liters of SiF_4 at standard conditions?

14 As hydrochloric acid acts on 500 grams of iron filings, what volume of hydrogen is produced at standard conditions? Ans. 200 l.

15 How many cubic feet of H_2S gas at standard conditions must be bubbled into a solution of $SbCl_3$ to produce 1000 pounds of the insoluble substance Sb_2S_3? (Antimony sulfide is used as a combustible substance in the preparation of matches.)

$$2\ SbCl_3 + 3\ H_2S \rightarrow Sb_2S_3 \downarrow + 6\ HCl$$

Ans. 3170 cu. ft.

16 What volume of CO_2 measured at standard conditions would have to be cooled to produce 220 grams (about ½ pound) of "dry ice" (solid CO_2)? Ans. 112 l.

17 Eighty liters of ammonia gas at standard conditions was dissolved in water. How many grams of sodium nitrate must be treated with sulfuric acid in order to prepare enough HNO_3 to neutralize the solution?

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$
$$2\ NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HNO_3$$

Ans. 304 g.

18 How many grams of nitrogen are there in 500 liters of NO_2 at standard conditions? Ans. 313.

19 One kilogram of oxygen is pumped into a tank of 100 liters capacity. Calculate the pressure of oxygen in the tank, assuming a temperature of 0° C.
Ans. 7 Atm.

20 When Ca_3As_2 is treated with dilute hydrochloric acid, arsine gas (AsH_3) is evolved. The residue is calcium chloride. Write the balanced equation for this reaction and then calculate the volume of arsine gas (at standard conditions) produced by the action of acid on 90 g. of Ca_3As_2 (calcium arsenide).
Ans. 14.9 l.

21 How many moles of HBr gas may be prepared as 1200 grams of $CaBr_2$ is acted on by H_3PO_4?

22 Determine the volume of acetylene gas (C_2H_2) at standard conditions produced from two gram moles of calcium carbide according to the equation:

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

Ans. 44.8 l.

23 Potassium chlorate may be prepared by passing chlorine gas into a hot solution of KOH, then cooling and crystallizing the salt. If the reaction takes place according to the equation

$$3\ Cl_2 + 6\ KOH \rightarrow KClO_3 + 5\ KCl + 3\ H_2O$$

what weight of $KClO_3$ could be produced by action of 100 l. of chlorine (at standard conditions) on an excess of KOH solution? Ans. 182 g.

24 14.5 g. of an impure sample of ferrous sulfide yields 3.09 liters of H_2S (standard conditions) when treated with dilute HCl:

$$FeS + 2\ HCl \rightarrow FeCl_2 + H_2S$$

Determine the percentage of FeS in the sample. Ans. 83.

25 In the presence of a platinum catalyst and at a temperature of 900° C., ammonia gas burns according to the equation:

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

Assuming all gases are at the same conditions of temperature and pressure (*a*) what volume of air (20% oxygen) would be required to burn 200 cubic feet of ammonia? (*b*) What total volume of products would remain?
Ans. (*a*) 1250 cu. ft.; (*b*) 1500 cu. ft.

26 What weight of carbon is contained in 100 liters of CO_2 at a temperature of 10° C. and a pressure of 2 atmospheres? Ans. 93.5 g.

27 One pound of dry ice (CO_2) will occupy what volume on evaporation at standard conditions? Ans. 8.15 cu. ft.

28 A 1 g. sample of Epsom salts ($MgSO_4 \cdot 7\ H_2O$) analyzed for magnesium gave 0.429 g. of $Mg_2P_2O_7$. (*a*) What was the percentage of magnesium in the sample? (*b*) If all the magnesium is present as $MgSO_4 \cdot 7\ H_2O$, what is the purity of the sample? Ans. (*a*) 9.4; (*b*) 95 per cent.

29 Calculate the weight of each of the products of the complete electrolysis of 1 kg. of a 20% aqueous solution of NaCl according to the equation:

$$2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + H_2 + Cl_2$$

Ans. NaOH 137 g.; H_2 3.4 g.; Cl_2 121 g.

30 In the reaction $H_2 + Cl_2 \rightarrow 2\ HCl$, all substances are gaseous. In the following, assume STP.

(*a*) What volume of hydrogen is necessary to produce 10 cubic feet of HCl? (*b*) What volume of chlorine is necessary to obtain 10 gram moles of HCl? (*c*) How many grams of hydrogen is necessary to obtain 22.4 liters of HCl? (*d*) What volume of HCl will be produced if 6×10^{23} molecules of chlorine react? (*e*) How many grams of HCl can be prepared from 35.5 g. of chlorine?

fifteen SOLUTIONS

Solutions are familiar to all of us from everyday life. The water we drink is a solution of various minerals dissolved in water. Plants derive their food, in part, from the water-soluble constituents of the soil. In the digestion of food, a chemical change takes place whereby constituents of food are converted into soluble substances which can be absorbed by the blood and carried to various tissues in the body. The atmosphere we breathe is a solution of nitrogen and oxygen gases. Fish and marine life derive oxygen necessary for their life processes from oxygen dissolved in the water.

Many chemical changes are brought about in solution, since the rate of reaction may be faster than between the substances in the pure state. This is probably due to the better contact of the reacting substances.

What is a solution? Solutions are like compounds in that they are homogeneous, and they are like mixtures in that the relative proportions of the constituents are variable. We may, therefore, classify solutions between mixtures and compounds:

MIXTURES	SOLUTIONS	COMPOUNDS
1. Not homogeneous	Homogeneous	Homogeneous
2. Variable proportions of constituents	Variable proportions of constituents	Fixed proportions of elements

A solution is formed when sugar is dissolved in water. It is perfectly uniform or homogeneous; if we should taste samples taken from various parts of the solution, we should find that each sample has the same degree of sweetness. The amount of sugar which we can dissolve in 100 ml. of water is variable; we may dissolve 1 gram, 10 grams, or 50 grams of sugar in the water. There is a limit, though, to the amount of sugar we can dissolve in a given amount of water at a certain temperature. This limiting amount is termed the *solubility* of sugar in water at that temperature.

If we could observe the molecules in the sugar solution, we would probably see that individual molecules of sugar are scattered throughout

the solution in a uniform distribution; each unit volume of solution would contain the same number of sugar molecules. The particles of sugar are dispersed in the solution as individual molecules; the solid is said to be *molecularly dispersed.* Molecular dispersion is a characteristic of a true solution. We shall learn later (Chapter 27) that aggregates or groups of molecules may be dispersed in a *colloidal* solution.

The above properties of a solution may be summarized in the definition: *A solution is a homogeneous mixture of two or more substances, the relative proportions of which may vary continuously within certain limits.*

Solute and solvent The dissolved material in a solution is termed the *solute* and the dissolving medium the *solvent.* Thus in a solution of sugar in water, the sugar would be the solute and the water the solvent. These terms, however, are arbitrary and lose their significance when applied to certain solutions. For example, in a solution of two liquids, such as alcohol and water, either the water or the alcohol might be properly classified as the solute. In situations of this kind, the constituent of the solution present in the smaller amount is usually designated as the solute.

Types of solutions When we speak of a solution, we usually think of a solid dissolved in water. While water is the most common of solvents, other liquids are frequently employed as solvents for certain substances; for example wax may be dissolved in gasoline, oil in turpentine, and sulfur in carbon disulfide. Solutions, however, are not confined to the solution of solids in liquids. Since there are three physical states of matter—gas, liquid, and solid—nine possibilities suggest themselves:

1. *Gases in gases.* Gases mix in all proportions, and since the particles of the gases exist as individual molecules, a mixture of any gases may be regarded as a solution. Air is essentially a solution of nitrogen and oxygen gases. Actually other gases are present in the atmosphere, and the entire system constitutes a complex solution.

2. *Gases in liquids.* The solution of oxygen in water and the solution of carbon dioxide in water (carbonated water) are examples of this type.

3. *Gases in solids.* Certain metals (platinum, palladium) absorb large volumes of hydrogen gas. In these cases, the gas may be considered as being dissolved in a solid.

4. *Liquids in gases.* Doubtful.

5. *Liquids in liquids.* Examples of this type are well known. Alcohol and water are completely *miscible* (mix with one another in all proportions); gasoline and kerosene dissolve in one another in all proportions. Certain liquids show incomplete solubility in one another. For example, ether and water are only partially miscible.

6. *Liquids in solids.* The solution of mercury in certain metals (amalgams) might be considered an example of this type.

7. *Solids in gases.* Doubtful.

8. *Solids in liquids.* This is the most common type of solution.

9. *Solids in solids.* If two solids are held tightly together, diffusion of each solid into the other occurs very slowly. To demonstrate this, a piece of lead and a piece of gold were tightly clamped together for several years. On analysis, it was found that the lead contained gold in the part that had been adjacent to the piece of gold, and the gold contained a small amount of lead. This experiment indicates that, while diffusion in the solid state is extremely slow, nevertheless it does occur. Certain alloys are sometimes classed as solid solutions.

Polar and nonpolar solvents We know that liquids differ greatly in solvent action. Water is a good solvent for acids, bases, and salts—those substances that are ionic or that produce ions in solution—but it is almost completely immiscible with such liquids as benzene, carbon disulfide, and carbon tetrachloride. However, these three liquids readily dissolve such substances as sulfur, phosphorus, and wax, which are insoluble in water.

On the basis of molecular structure, solvents are classed as *polar* and *nonpolar*. A polar solvent consists of dipoles (see Chapter 11): molecules in which constituent atoms are unsymmetrically arranged so that the centers of positive and negative electrical charges are not located at the same point in the molecule. (Of course, the molecule as a whole is electrically neutral.) Water and liquid ammonia are polar solvents. Nonpolar solvents consist of symmetrical molecules with the center of positive and negative electrical charge at the same point within the molecule; benzene and carbon tetrachloride are nonpolar liquids. Cohesive forces between molecules of polar liquids are large as compared to forces tending to hold molecules of nonpolar liquids together, since positive ends of the dipoles will tend to attract negative ends of other dipoles and hold the molecules together.

Water acts as a good solvent for electrovalent compounds since there is a definite attraction between the ions present and the dipoles of the water molecules. In crystalline sodium chloride, sodium and chloride ions are oriented in a definite pattern by electrostatic forces acting between the oppositely charged ions; thus the crystals of the compound exhibit a definite geometric pattern (NaCl crystallizes in the cubic system; see Chapter 12). When NaCl dissolves, the forces holding the ions together must be overcome, so that the ions are free to move in solution. Water weakens inter-ion forces to some extent, probably by attraction between the dipoles and ions in some such fashion as is represented by Figure 15–1.

These electrovalent compounds are insoluble in nonpolar liquids like

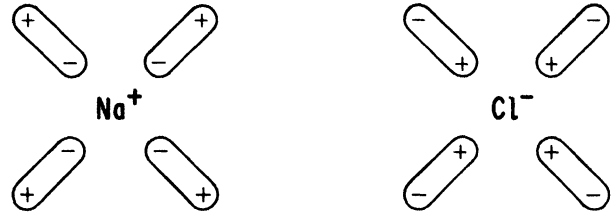


Figure 15–1 Attraction between ions and water dipoles.

benzene, since there is no electrical attraction between the ions in the compounds and the solvent molecules.

Equilibrium in solutions When a solid is dissolved in a liquid, molecules (or ions) break away from the surface of the solid and pass into the solvent, where they diffuse until a uniform distribution has been effected. Stirring or agitation will speed up the solution process. As the molecules find their way into the solvent, some of them are deflected back toward the solid due to collision with other molecules. Some of these particles which strike the solid will deposit out on the solid surface and are converted back to the solid form. There are, then, two processes occurring: (1) the solution of molecules from the surface of the solid, (2) the deposition of molecules on the surface of the solid. If the amount of solid present is insufficient to saturate the solution, process (1) will continue until all of the solid dissolves. If there is sufficient solid to saturate the solution, the two opposing forces (1) and (2) will eventually equalize each other, and the number of molecules passing into solution will be the same as the number coming out of the solution. When the speed of these two processes is the same, a condition of equilibrium is reached and the solution is said to be saturated (Figure 15–2). *A saturated solution, then, is one in which the solution is in equilibrium with the undissolved solute.*

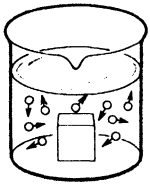


Figure 15–2 Equilibrium between solid and solution.

The passage of a solid into solution is analogous to the passage of liquid to vapor. Molecules of liquid break away from the surface of the liquid and pass into the atmosphere above the liquid. Molecules from the vapor may strike the liquid and condense to the liquid state. When the rate of evaporation is equal to the rate of condensation, a condition of equilibrium results. Just as a certain amount of vapor (vapor pressure) can exist in equilibrium with the liquid, so in the case of a solid dissolved in a liquid, a certain amount of solid can

be present in the solution in equilibrium with the undissolved solid.

We must not think of the processes of solution and deposition (precipitation) as stopping when equilibrium has been attained. Actually the equilibrium is a dynamic one; the two opposing processes are occurring continuously. To demonstrate the dynamic nature of this equilibrium we may perform the following experiment: A hole is bored in a crystal of solid which is in equilibrium with its saturated solution. After a time the hole becomes filled with solid and the crystal is perfectly repaired. This would seem to demonstrate that molecules are continuously passing from the solution to the solid. For every molecule which returns, a molecule passes into solution so that the number in the solution remains a constant. Thus the solubility of a substance is a constant value at a given temperature. As the temperature is raised, relatively more molecules of the solid may pass into solution than precipitate out, and a new condition of equilibrium is established at the higher temperature.[1]

Supersaturation Ordinarily when a saturated solution is cooled, excess solute will crystallize out at the lower temperature. However, with certain substances it is possible to cool a saturated solution in the *absence of solid solute* without the separation of the excess solute. The cooled solution then contains more of the solute than is present in a saturated solution at that particular temperature. Such a solution is said to be *supersaturated.* These solutions are very unstable, and the excess solute immediately separates out if a tiny crystal of the solid solute is added to the solution.

Supersaturation may be demonstrated by preparing a saturated solution of sodium thiosulfate at an elevated temperature and allowing the solution to cool carefully in the absence of undissolved solute. The solution remains perfectly clear at the lower temperature until a crystal of sodium thiosulfate is added, after which a large mass of crystals forms slowly in the solution. The solution which remains in contact with the excess solid is saturated.

To determine whether a given solution is saturated, unsaturated, or supersaturated, we can add a crystal of the dissolved substance. If the crystal dissolves, the solution is unsaturated; if it remains the same, the solution is saturated; and if the crystal causes the formation of more crystals, the solution is supersaturated.

Solubility The weight of a substance dissolved by a given weight or volume of solvent at a given temperature is termed the solubility of the substance. Solubility varies greatly with the nature of the dissolved substances: 100 grams of water will dissolve 179 grams of sugar, or 35.7 grams of sodium chloride, or 3 grams of potassium chlorate, or 0.00009

[1] The solubility of a few substances decreases with increasing temperature.

gram of silver chloride at 0°. Sugar would be classed as very soluble, sodium chloride as moderately soluble, potassium chlorate as slightly soluble, and silver chloride as practically insoluble.

General rules for solubility of salts and hydroxides in water are:

1 All nitrates, acetates, and chlorates are soluble.
2 All chlorides, bromides, and iodides are soluble except those of Pb, Hg (ous), and Ag.
3 All sulfates are soluble except those of Ba, Sr, Pb, and Ca ($CaSO_4$ is slightly soluble).
4 All sulfides are insoluble except those of Na, K, NH_4, Mg, Ca, Sr, Ba.
5 All oxides and hydroxides are insoluble except those of Na, K, NH_4. (Ca, Ba, Sr are slightly soluble.)
6 All phosphates, carbonates, and chromates are insoluble except those of Na, K, NH_4.
7 Nearly all Na, K, and NH_4 salts are soluble.

The solubility of gases in liquids The solubility of a gas is often expressed as the volume of gas dissolved by a certain volume of liquid. For example, .021 volume of hydrogen dissolves in 1 volume of water, or 1.71 volumes of carbon dioxide dissolve in 1 volume of water. The solubility of gases in liquids varies over a wide range and depends upon the nature of the solute and solvent. At 0°, 1 volume of water may dissolve .021 volume of hydrogen, 1.71 volumes of carbon dioxide, 506 volumes of hydrogen chloride, or 1175 volumes of ammonia. Gases which are very soluble in water may be nearly insoluble in some other solvent.

The weight of a gas dissolved by a given weight of liquid at constant temperature is directly proportional to the pressure of the gas over the liquid. This is a statement of Henry's Law. If a certain weight of gas is dissolved by a liquid at a pressure of 1 atmosphere, then ten times that weight will dissolve if the pressure is increased to 10 atmospheres. A practical application of this law is the preparation of carbonated beverages. Carbon dioxide gas is dissolved in the liquid under pressure. When the cap of the bottle is removed, the solution effervesces (gives off gas from solution) rapidly, since the pressure has been reduced.

The solubility of a gas in a liquid is also dependent upon the temperature. The quantity of gas dissolved by a given weight of liquid usually decreases as the temperature is raised. If water containing dissolved air is warmed, bubbles of the air escape from the solution as the temperature increases. At the boiling point of the solvent, the gas is practically insoluble.

Effect of temperature on solubility of solids in liquids Although the

TABLE 15–1 **Solubility of Salts at Various Temperatures (g./100 g. H_2O)**

TEMPERATURE ° C.	POTASSIUM NITRATE	SODIUM CHLORIDE	POTASSIUM ALUM	CALCIUM CHROMATE	POTASSIUM CHLORIDE	SODIUM SULFATE	SODIUM NITRATE
0	13	35.7	4	13	28	4.8	73
10	21	35.8	10	12		9.0	80
20	31	36	15	10.4	34	19.5	85
30	45	36.3	23	9.1		40.9	92
40	64	36.6	31	8.5	40	48.8	98
50	86	37	49	7.3		46.7	104
60	111	37.3	67	6	46	45.3	
70	139	37.9	101	5.3		44.4	
80		38.4	135	4.4	51	43.7	133
90		39.1		3.8		43.1	
100	249	39.8		3	57	42.5	163

solubility of a solid in a liquid is usually increased with an increase in temperature, this is not always true. The solubilities of several salts in water are shown in Table 15–1 and represented graphically in Figure 15–3.

It may be noted that in some cases an increase in temperature greatly changes the solubility, while in other cases there is very little change. The solubility of potassium nitrate increases from about 13 grams per 100 grams of water at 0° to about 139 grams at 70°. Sodium chloride increases only from 35.7 to 37.9 for the same temperature range. Calcium chromate actually decreases in solubility as the temperature is raised. A break in the solubility curve for sodium sulfate appears at a temperature of 32.7°. The solubility curve below this temperature is for the hydrated salt and above this temperature for the anhydrous salt. A transition from the hydrate to the anhydrous form takes place at this temperature which is known as a *transition point*. The

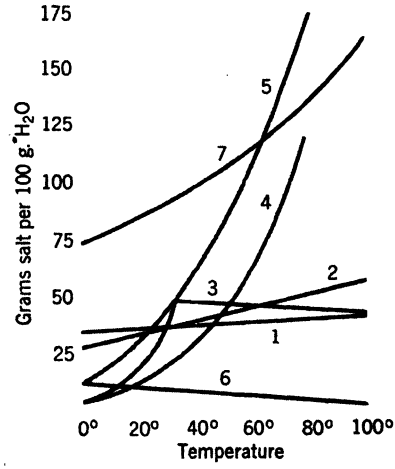


Figure 15–3 Solubility curves. (1) NaCl; (2) KCl; (3) Na_2SO_4; (4) alum; (5) KNO_3; (6) $CaCrO_4$; (7) $NaNO_3$.

transition point of sodium sulfate is so definite that it is often used for the standardization of thermometers.

Fractional crystallization Differences of solubility at various temperatures form the basis for the selective separation of salts from a solution containing two or more dissolved salts. Consider the evaporation of a solution containing 50 g. KNO_3, 50 g. KCl, and 200 g. H_2O. If the solution is evaporated at 100° to a weight of 100 g. H_2O, no crystallization would be effected, since according to Table 15-1 the solubilities are 249 g. KNO_3 and 57 g. KCl, respectively. However, suppose the solution is evaporated at 100° to a weight of 50 g. H_2O. All of the KNO_3 would remain in solution, but only $\frac{57}{2}$ or 28.5 g. KCl would remain in solution. The excess KCl above a saturated solution—namely, 50 − 28.5 = 21.5 g. KCl—would crystallize out. If the hot liquid was poured off from the crystallized KCl, 21.5 g. of fairly pure KCl would be left; not entirely pure since the adhering liquid would still contain a small amount of KNO_3. If the crystals were redissolved in water and the process repeated, a purer fraction of KCl crystals could be obtained. Such a process is an example of fractional crystallization.

Concentration Sometimes we speak of a solution as being "dilute" or "concentrated." These are qualitative terms to designate whether a solution contains relatively little solute or a relatively large amount. For example, a solution containing 1 gram of sugar in 100 ml. of water would be "dilute" while a solution containing 50 g. of sugar in 100 ml. of water would be "concentrated." The concentration of a solution represents the weight of solute dissolved in a given weight or volume of the solution. Several methods are available for expressing the concentration of a solution. The weight of a solute in a given weight of the solution may be expressed in terms of percentage. Thus, a solution containing 5 grams of solute and 95 grams of solvent would be a 5 per cent solution, since 5 parts of 100 are solute.

Molarity Another means of expressing concentration which has been adopted by the chemist involves expression of the concentration in terms of moles of solute in 1 liter of the solution. A solution containing one mole of solute in 1 liter of solution is termed a *molar* (1 *M*) solution. Thus, a solution containing 2 moles of solute in 1 liter of solution would be 2 molar (2 *M*), one containing 0.5 mole in 1 liter would be 0.5 molar (0.5 *M*), and so on. In other words,

$$\text{Molarity} = \frac{\text{Number of Moles}}{\text{Number of Liters}}$$

In order to become more familiar with this method of expressing concentration, consider the following illustrative problems.

PROBLEM 1. · Calculate the molarity of a solution containing 10 grams of sulfuric acid in 500 ml. of solution.

Since molarity is defined in terms of moles, we must first convert grams to moles. A mole is the molecular weight in grams, so to convert grams to moles we divide weight in grams by molecular weight. Since the molecular weight of sulfuric acid is 98,

$$10 \text{ g.} = \tfrac{10}{98} = 0.102 \text{ mole}$$

0.102 mole of sulfuric acid in 500 ml. would be the same as 0.204 mole in 1000 ml. or 1 liter. The molarity is thus 0.204.

PROBLEM 2. Calculate the weight in grams of sulfuric acid in 2 liters of 0.1 molar solution.

One liter of a molar solution of sulfuric acid would contain 1 mole of sulfuric acid or 98 grams. One liter of a $\frac{1}{10}$ molar solution would contain $\frac{1}{10}$ of 98 or 9.8 grams. Two liters of the solution, then, would contain $2 \times 9.8 = 19.6$ g.

Normal solutions The equation

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$$

shows that one mole of sulfuric acid reacts with two moles of sodium hydroxide. It is evident that if the solutions of H_2SO_4 and NaOH were of the same molarity, it would require twice the volume of NaOH as of H_2SO_4 for the neutralization. One liter of 1 *M* H_2SO_4 will require 2 liters of 1 *M* NaOH, or 1 liter of 2 *M* NaOH.

In the reaction of NaOH and HCl, equal volumes of molar solutions will exactly neutralize one another. The difficulty of working with equal volumes in some reactions and different volumes in other reactions can be avoided by making up the solutions in terms of equivalent weights rather than molecular weights.

One equivalent of a substance is the weight (1) which (as an acid) contains 1 gram atom of replaceable hydrogen, or (2) which (as a base) reacts with a gram atom of hydrogen, or (3) which (as a salt) is produced in a reaction involving 1 gram atom of hydrogen. Thus, 36.5 g. of HCl contains 1 g. atom of replaceable hydrogen, hence is an equivalent weight; 40 g. of NaOH will react with 36.5 g. of HCl which contains 1 g. atom of hydrogen; hence 40 g. of NaOH is an equivalent weight; 58.5 g. of NaCl is formed in the reaction involving 36.5 g. of HCl, hence is an equivalent weight. 98 g. of H_2SO_4 contains two gram atoms of hydrogen, so $\frac{98}{2} = 49$ g. is one equivalent.

A solution containing one equivalent of a solute in 1 liter of solution

is a *normal* solution; one containing 2 equivalents in 1 liter is 2 normal (2 N), etc. Normality of any solution is given by

$$\text{Normality} = \frac{\text{Equivalents of Solute}}{\text{Liters of Solution}}$$

Equal volumes of solutions of the same normality are equivalent, for example, 1 liter of a normal solution of any acid will react with exactly 1 liter of a normal solution of any base.

Following are examples involving calculation of normalities.

EXAMPLE 1. Calculate the normality of a solution containing 2.45 grams of sulfuric acid in 2 liters of solution.

One equivalent of H_2SO_4 (mol. wt. 98) would be 49 grams, since one molecule of acid contains two atoms of replaceable hydrogen. The solution in this problem contains 2.45 g in 2 liters, or 1.225 g per liter. The normality would then be $\frac{1.225}{49} = 0.025$ N.

EXAMPLE 2. How many grams of sulfuric acid is contained in 3 liters of 0.5 N solution?

There are 49 grams of H_2SO_4 (one equivalent) in 1 liter of a normal solution. In 1 liter of .5 N solution there would be 24.5 g, in 3 liters, $3 \times 24.5 = 73.5$ g.

Standard solutions and titrations. Very often in analytical work it is necessary to determine the acidity or basicity of an unknown solution. This may be accomplished with the aid of a *standard solution* of an acid or a base—a solution whose concentration is accurately known. The operation of analyzing an unknown solution by means of a standard solution is known as *titration*. The determinations are usually carried out with the aid of burets (Figure 15–4), which are devices for accurately measuring the volumes of solutions used. Acids neutralize bases, and the endpoint of a titration is reached when *equivalent quantities* of acid and base have been brought together. A certain volume of solution from one buret is collected in a beaker, then solution from the other buret is added carefully until equivalent quantities of the two solutions have been brought together. The point at which equivalent quantities have been brought together is determined by an indicator which changes in color at the endpoint. Knowing the volumes of the two solutions used and the normality of either the acid or base, we may calculate the normality of the other solution and thereby determine its acidity or basicity.

The concentration of a standard solution is usually expressed in terms of normality:

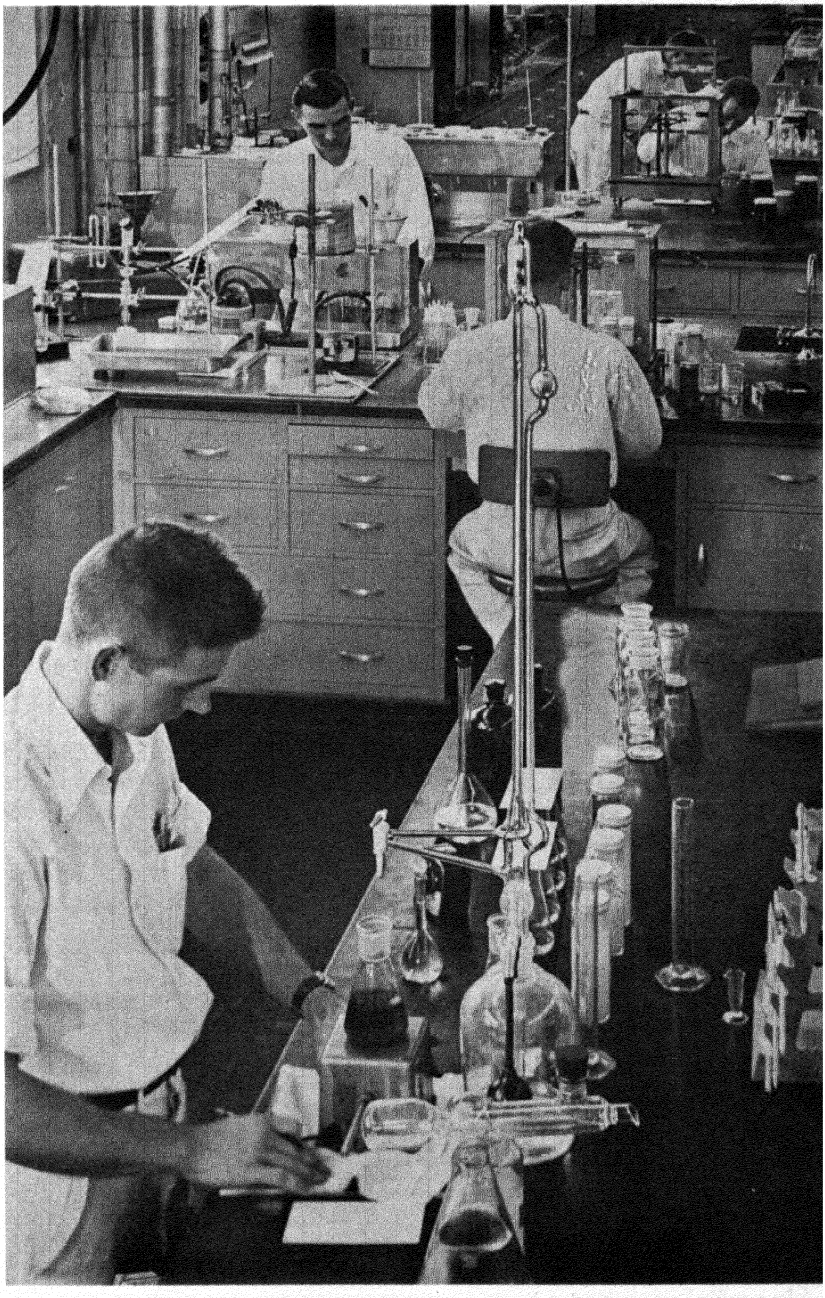


Figure 15–4 Titrating solutions in an industrial laboratory.

$$\text{Normality } (N) = \frac{\text{Equivalents } (E)}{\text{Liters } (L)}$$

or

$$E = N \times L$$

Since equivalent quantities of acid and base must be present at the endpoint of the titration, $E_{\text{acid}} = E_{\text{base}}$; therefore

Normality of Acid × Volume of Acid = Normality of Base × Volume of Base

or

$$N_1V_1 = N_2V_2$$

If three of the above four factors are known, the fourth may be calculated. Volumes may be expressed in milliliters or liters. Study the following sample calculations.

EXAMPLE 1. Calculate the volume of 0.3 N base necessary to neutralize 3 liters of .01 N acid.

Substituting in the formula

$$N_1V_1 = N_2V_2$$
$$.01 \times 3 \text{ liters} = 0.3 \times V_2$$
$$V_2 = \frac{.01 \times 3}{.3} = 0.1 \text{ liter or } 100 \text{ ml.}$$

EXAMPLE 2. If 20 ml. of 0.50 N salt solution is diluted to 1 liter, what is the new concentration?

$$N_1V_1 = N_2V_2$$
$$.50 \times 20 \text{ ml.} = N_2 \times 1000 \text{ ml.}$$
$$N_2 = \frac{.50 \times 20}{1000} = .01$$

Molal solutions In the study of colligative properties—properties of solutions which depend upon the ratio of number of solute particles to number of solvent particles—concentrations are expressed in terms of *molality*. A molal solution is one which contains 1 mole of solute in 1000 g. of solvent. Such solutions are independent of temperature changes. In dilute solutions molar and molal solutions are very nearly identical, but in more concentrated solutions wide differences may be expected.

The boiling point of solutions We have learned that the boiling point of a liquid is the temperature at which the vapor pressure of the liquid is equal to the external pressure (usually the atmospheric pressure). The addition of a substance like sugar or salt lowers the vapor pressure of the liquid because the solute molecules interfere with the escape of molecules of the solvent from the liquid to the vapor state. Molecules of the solvent

will collide with solute molecules; thus, the speed at which the solvent molecules escape from solution is diminished, resulting in a decreased vapor pressure. *At constant temperature the lowering of the vapor pressure by a nonvolatile solute is proportional to the concentration of the solute in the solution.* This is a statement of Raoult's Law.

A decreased vapor pressure means a rise in the boiling point of the liquid, since a higher temperature will be necessary to bring the vapor pressure up to the external pressure. From a kinetic standpoint, it would seem that the rise of the boiling point would depend directly upon the number of solute particles, since the escape of solvent molecules (the vapor pressure) is influenced by the number of solute particles. The following facts indicate the validity of this speculation. 342 grams of sugar (1 gram molecular weight) dissolved in 1000 grams of water raises the boiling point 0.52° (in other words, the solution would boil at 100.52°); 60 grams of urea (1 gram molecular weight) dissolved in 1000 grams of water gives exactly the *same* elevation of the boiling point. It has been found that 1 gram molecular weight of other substances gives the same elevation of the boiling point. There is no relation between the weight in grams of substance and the boiling point elevation, since 60 grams of urea produces the same effect as 342 grams of sugar. However, a gram molecular weight of each of these substances contains exactly the same number of molecules. This seems to indicate beyond doubt that the boiling point of a solution is dependent upon the number of solute particles in solution. The normal elevation of the boiling point of a liquid containing 1 gram molecular weight of dissolved substance in 1000 grams is called the boiling point constant. For water, this constant is 0.52°. The elevation of the boiling point of water containing 3 moles of solute in 1000 grams of water would be 3×0.52 or 1.56°.

We shall find in the study of ionization (Chapter 18) that solutions of acids, bases, and salts have abnormal boiling points. These abnormalities will be explained at that time.

Solutions of volatile solutes Raoult's Law does not apply to solutions in which the solute has a vapor pressure of its own. A solution of alcohol and water boils below the boiling point of water. Probably the vapor pressures of alcohol and water are separately reduced by the presence of the other, but the additive reduced vapor pressures exceed the vapor pressure of water alone.

In Figure 15–5, the liquid and vapor curves for solutions of two volatile liquids *A* and *B* are shown. The lower curve shows the boiling points of solutions of *A* and *B* of varying composition from 100 per cent *A* to 100 per cent *B*. *O* is the boiling point of pure *A*, and *P* the boiling point of pure *B*. The broken curve shows the compositions of vapor in equi-

librium with various solutions of A and B. The composition can be determined by a perpendicular drawn to the composition axis.

Suppose a solution of composition X is distilled. The composition of the vapor is represented by Y—the vapor is richer in the lower boiling component B. As the solution is boiled, the temperature rises and the solution becomes richer in the higher boiling component A. If the vapor at Y is condensed to liquid and subsequently redistilled, the composition of the vapor would be that represented by point Z. Thus by distilling a solution and collecting several fractions boiling at different temperatures and repeating the distillation of the fractions perhaps several times, an almost complete separation of the two components may be effected. This process is termed *fractional distillation* and is invaluable in separation of the components of such complex mixtures as petroleum.

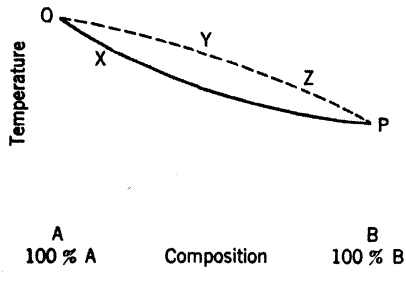


Figure 15–5 Boiling point diagram of two volatile liquids.

The freezing point of solutions Solutes lower the freezing point of water. Alcohol and other antifreeze mixtures are added to water in car radiators to prevent them from freezing. Just as the boiling point of a solution is dependent upon the number of solute particles, so the freezing point of a solution is a function of the number of particles in solution. 1 mole of a substance (except those substances which ionize) dissolved in 1000 grams of water lowers the freezing point 1.86°. This number 1.86 is called the freezing point constant for water. Thus a solution containing 1 gram molecular weight of alcohol (46 grams) in 1000 grams of water will freeze 1.86° below the freezing point of water (0°)—that is, at −1.86°; a solution containing 2 moles of alcohol in 1000 grams of water would freeze at $-(2 \times 1.86) = -3.72°$, etc. From these facts,[2] we can calculate the concentration of an antifreeze necessary to prevent our car radiator from freezing at a given temperature.

PROBLEM. Calculate the composition of an alcohol-water mixture which will not freeze above a temperature of −30° C. Molecular weight of alcohol is 46.

[2] It should be pointed out that this relationship between freezing point and concentration does not hold very well for concentrated solutions.

Let x = number of moles of alcohol per 1000 g. H_2O in mixture.
Since 1 mole alcohol in 1000 g. H_2O freezes at $-1.86°$
then x moles alcohol in 1000 g. H_2O freezes at $-30°$.

$$\frac{1}{x} = \frac{-1.86}{-30} \quad x = \frac{-30}{-1.86} = 16.1 \text{ moles}$$

16.1 moles = 16.1 × 46 g. = 741 g. alcohol per 1000 g. H_2O

Osmotic pressure If the U-shaped tube shown in Figure 15–6 were filled with water on one side and a sugar solution on the other side, in time the sugar molecules would have diffused throughout so that a uniform concentration of sugar would be present on both sides of the tube. If, however, a semipermeable membrane—such as an animal or vegetable membrane that will allow water to pass through it but not the solute molecules—is placed across the bottom of the U-tube and the U-tube is again filled with water on one side and sugar solution on the other to the same level, then it will be noted that water will flow through the semipermeable membrane from the water side of the tube to dilute the sugar solution on the other side. As a result, the level of solution on the sugar side will rise while the level on the pure water side will be depressed. If evaporation is prevented, the system will remain indefinitely at these new levels. The difference in levels between the two arms of the U-tube, h, is a measure of the pressure tendency of the water to go through the membrane and dilute the solution. This pressure, which is the pressure sufficient to prevent the flow of pure solvent through a semipermeable membrane into a solution, is called *osmotic pressure.* At constant temperatures this pressure is proportional to the concentration of the solution. Like the boiling point elevation and freezing point depression of a solvent as well as the vapor pressure of a solution, the osmotic pressure is a property dependent upon the *number* of dissolved particles and is independent of the nature of the dissolved particles. Such properties which are dependent upon *number* but *not kind* of dissolved particles are termed *colligative* properties.

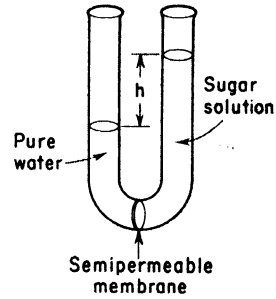


Figure 15–6 Apparatus for demonstrating osmotic pressure.

Osmosis is the passage of a solvent through a semipermeable membrane from a solution of lesser concentration to one of higher concentration. Osmosis through plant and animal membranes is of prime importance in many physiological processes.

Determination of molecular weights of dissolved substances Since a

mole (molecular weight in grams) of a substance in 1000 grams of water gives a definite and known lowering of the freezing point (1.86°), we can, by determining the freezing point of a solution of known concentration, calculate the molecular weight of the dissolved substance. For example, suppose the freezing point of a solution containing 30 grams of solute in 1000 grams of water is $-.62°$. The molecular weight of the dissolved substance must be $\frac{1.86}{.62} \times 30 = 90$.

Molecular weights may also be determined in similar manner from boiling point elevations. However, since the effect is less (0.52 as compared with 1.86) and since the effect of pressure is much greater on boiling points than freezing points, molecular weights are usually determined from freezing point determinations.

EXERCISES

1 Differentiate clearly between unsaturated, saturated, and supersaturated solutions.

2 Two beakers contain sugar solutions (*a*) and (*b*). A lump of sugar is dropped into each and thoroughly stirred. In (*a*) the lump disappears and in (*b*) it grows larger. Give the appropriate terms descriptive of solutions (*a*) and (*b*).

3 Would it be possible for a certain solution to be both *saturated* and *dilute?* Explain briefly.

4 The concentration of dissolved air in the waters of a mountain lake is not the same as in a lake at sea level at the same temperature. In which is the concentration greater? Explain.

5 Indicate in a general way how you would proceed to separate the components of a

(*a*) mixture of two immiscible liquids.
(*b*) solution of a nonvolatile solute.
(*c*) solution of volatile solute.
(*d*) solution of gases.

6 What properties of compounds are useful in predicting solubilities in polar and nonpolar solvents?

7 From the following list of water soluble compounds, select (*a*) 5 pairs which, when brought together in aqueous solution, will not form a precipitate; (*b*) 5 pairs which will give a precipitate. Write equations for part (*b*) reactions. $AgNO_3$; NaCl; K_3PO_4; $BaCl_2$; NH_4OH; HBr; $CuSO_4$; KOH; Na_2CrO_4; $(NH_4)_2CO_3$; $Zn(C_2H_3O_2)_2$; $Ca(ClO_3)_2$; $NaNO_3$; K_2S.

8 Refer to the solubility data on page 187. A solution containing 40 g. NaCl, 100 g. $NaNO_3$ and 150 g. H_2O is evaporated to 100 g. H_2O at 100°. (*a*) What solid will crystallize from solution and how much? (*b*) If the solution is allowed to cool to 50°, what solid will crystallize and how much? (*c*) If the solution from (*b*), after filtering off the solid, is concentrated to 50 g. H_2O and cooled to 20°, what would be the composition of the solid crystallizing out? Ans. (*a*) NaCl, 0.2 g. (*c*) NaCl, 19 g.; $NaNO_3$, 57.5 g.

9 With the aid of the solubility curves on page 187, answer the following questions:

(*a*) At what approximate temperature would the solubilities of NaCl and KCl be the same?

(*b*) At what approximate temperature would the solubilities of KCl and KNO_3 be the same?
(*c*) Under what conditions would KCl exhibit a greater solubility than KNO_3?
(*d*) If separate saturated solutions of $NaNO_3$ and NaCl are made up at 50° and cooled to 0°, will the weight of $NaNO_3$ separating out be less or greater than the weight of NaCl crystallizing out?
(*e*) Which of the salts in the diagram is most soluble at 50°?
(*f*) If a saturated solution of $CaCrO_4$ at 50° is cooled at 20°, will solid crystallize? If this solution is heated to 100°, what happens?
(*g*) If separate saturated solutions of the salts NaCl, KCl, KNO_3, and $NaNO_3$ are made up at 100° in 100 g. H_2O, what weight of each salt would be crystallized from solution on cooling to 20°?
(*h*) How would you proceed to prepare a supersaturated solution of calcium chromate?

10 The solubility of carbon dioxide at 0° and one atmosphere pressure is 0.3346 g. per 100 g. water. (*a*) What volume of CO_2 does this represent at standard conditions? (*b*) What weight of CO_2 would be dissolved in 100 g. of water at 0° and 5 atmospheres pressure? (*c*) What volume would be dissolved at 0° and 5 atmospheres pressure?

Ans. (*a*) 170 ml. (*b*) 1.673 g. (*c*) 170 ml.

11 State the law which applies to the previous exercise.

12 A sulfuric acid solution has a density of 1.8 and is 90 per cent H_2SO_4. What weight of H_2SO_4 is present in 500 ml. of solution? Ans. 810 g.

13 What weight of glucose must be added to 100 g. of a 10 per cent solution of glucose to give a 25 per cent solution? Ans. 20 g.

14 Calculate the (*a*) molarity and (*b*) normality of solutions of each of the following containing 10 g. of the solute per liter of solution: (1) KOH, (2) H_3PO_4, (3) $MgCl_2$, (4) Na_2SO_4, (5) $Al_2(SO_4)_3$.

15 Calculate the percentage HCl in 12 *N* HCl which has a density of 1.2.

Ans. 36.5.

16 Calculate the normality of a solution of 55 per cent H_2SO_4 with a density of 1.45. Ans. 16.3.

17 Determine the normality of the following solutions which contain the indicated amount of dissolved substance per liter of solution:

(*a*) 100 g. NaOH
(*b*) 2.45 g. H_2SO_4
(*c*) 1.62 g. HBr
(*d*) 6.84 g. $Ba(OH)_2$
(*e*) 2.85 g. $Al_2(SO_4)_3$

Ans. (*a*) 2.5 (*b*) .05 (*e*) .05.

18 Calculate the weight of solute needed to prepare each of the following solutions:

(*a*) 250 ml. 0.1 *N* H_2SO_4
(*b*) 2 liters 0.25 *N* NaOH
(*c*) 100 ml. 0.01 *N* $Ba(OH)_2$
(*d*) 10 ml. 5 *N* H_3PO_4
(*e*) 1 liter 0.3 *N* KOH

Ans. (*a*) 1.23 g. (*b*) 20 g. (*c*) 16.8 g.

19 Calculate the normality of a solution of HBr, 35 ml. of which was required to neutralize 0.140 g. NaOH? Ans. 1.

20 250 ml. of 0.5 *N* HCl is diluted to one liter. What is the normality of the diluted solution?

21 To what volume must 50 ml. of 0.36 *N* H_2SO_4 be diluted to give 0.30 *N* acid?

Ans. 60 ml.

22 One gram of pure solid NaOH was dissolved in water and titrated to neutralization with HCl solution. 25 ml. of HCl solution was required. Calculate the normality of the acid.

23 A solution of HCl (called A) is titrated to neutralization with a solution of KOH (called B). 50 ml. of A neutralizes 20 ml. of B. Evaporation of the solution yields 0.149 g. of salt. What is the (*a*) normality of A, (*b*) normality of B, (*c*) molarity of A? (*d*) What volume of B would be required to neutralize 5 ml. of A? Ans. (*a*) 0.04.

24 40 ml. of an acid solution neutralized 0.212 g. of solid Na_2CO_3 according to the equation:

$$Na_2CO_3 + 2\ H^+ \rightarrow 2\ Na^+ + CO_2 + H_2O$$

What is the normality of the acid solution? Ans. 0.1.

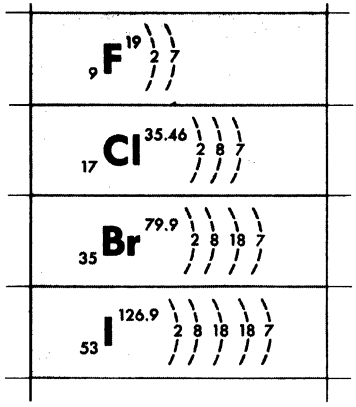
25 What would be the approximate freezing point of a solution which contains 250 g. of alcohol, C_2H_5OH, dissolved in one liter of water? Ans. $-10°$C.

26 A solution which contains 50 g. of solute in 500 g. of water freezes at a temperature of $-0.93°$ C. What is the molecular weight of the solute. Ans. 200.

27 7.29 g. of a certain nonelectrolyte was dissolved in 100 g. of water. The resulting solution was found to have a freezing point of $-0.396°$ C. What is the molecular weight of the nonelectrolyte?

28 Compound X has a molecular weight of 100. (*a*) How many grams of X dissolved in 1000 g. of water would lower the freezing point to $-9.3°$ C. if X is a nonelectrolyte? (*b*) What would be the boiling point of the solution at standard pressure if X is nonvolatile?

29 The molal freezing point constant for a certain liquid is 0.50° C. 26.4 g. of a solute dissolved in 250 g. of this liquid yields a solution which has a freezing point 0.275° below that of the pure liquid. Calculate the molecular weight of the solute. Ans. 192.



sixteen

THE HALOGENS

HALOGEN	SYMBOL	COLOR AND PHYSICAL STATE AT STANDARD CONDITIONS	MELTING POINT	BOILING POINT	FORMULA	COMMON OXIDATION STATE
Fluorine	F	pale-yellow gas	−223	−187	F_2	−1
Chlorine	Cl	yellowish-green gas	−101.6	−34.5	Cl_2	−1
Bromine	Br	deep red-brown liquid	−7.3	58.7	Br_2	−1
Iodine	I	gray solid	113	184	I_2	−1

Fluorine, chlorine, bromine, and iodine constitute a group or family of elements called the "halogens," a term which means "salt formers." The halogens are very active nonmetals and are very much alike in their chemical properties. The marked similarity in chemical properties of these elements is predicted from their atomic structure; each of the halogens has 7 valence electrons and thus exhibits a characteristic valence or oxidation state of −1.

Although these elements are markedly alike chemically, a gradual change in properties is shown as the atomic weight increases. Fluorine, with the lowest atomic weight, is the most active of the family, followed by chlorine of next higher atomic weight, then bromine, and finally iodine with the highest atomic weight. In physical properties, too, a gradual change may be noted; fluorine and chlorine are gases at ordinary temperatures, bromine is a liquid, and iodine is a solid.

Because of their extreme activity, the halogens are not found in the

free state but are widely distributed in nature as halide salts. All are found in sea water in the form of salts.

Chlorine, the most important of the halogens, will be studied in more detail than the others. Much of what we say about chlorine will apply also to the other halogens.

CHLORINE

History Scheele, a Swedish chemist, is credited with the discovery of chlorine in 1774. Scheele observed that a heavy, yellowish-green gas was obtained when manganese dioxide was allowed to act on hydrochloric acid. He believed the gas to be a compound, however, and it remained for Davy in 1810 to establish the substance as an element and to give it the name "chlorine" because of its color.

Occurrence Chlorine is found in combination with many of the metals as chlorides, by far the most abundant of which is NaCl. Sea water contains nearly 3 per cent NaCl. Evaporation of inland bodies of water has produced large and extensive deposits of it. The Great Salt Lake in Utah contains nearly 20 per cent. Large deposits of rock salt, which is impure NaCl, are found in New York, Michigan, Louisiana, Kansas, Oklahoma, and Texas.

In addition to sodium chloride, sea water contains smaller percentages of magnesium chloride, potassium chloride, and calcium chloride. Compounds of chlorine are found in the body—sodium chloride in the blood and hydrochloric acid in the gastric juices.

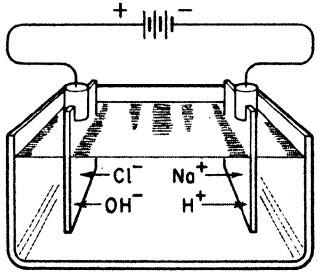


Figure 16–1 Electrolysis of an aqueous sodium chloride solution yields hydrogen at the cathode and chlorine at the anode.

Preparation (*a*) *Electrolysis of brine.* Chlorine is prepared commercially by the electrolysis of an aqueous sodium chloride solution. The processes taking place during electrolysis may be illustrated by means of a diagram (Figure 16–1). Sodium chloride is ionized in the solid and when the compound is dissolved in water, the sodium and chlorine ions are dispersed in the solution. Water itself ionizes slightly into hydrogen ions and hydroxyl ions. Thus, in the solution, four ions are present, two cations and two anions. When the electric current is passed through the solution, chlorine ions and hydroxyl ions migrate toward the anode (positive pole), while the sodium ions and hydrogen ions

move toward the cathode (negative pole). Since hydrogen ions accept electrons more readily than sodium ions, the former ions are discharged at the cathode and form hydrogen atoms. Two hydrogen atoms then combine to form a molecule of hydrogen which escapes from the solution as a gas. At the anode, chlorine ions are discharged in preference to hydroxyl ions, since chlorine ions give up electrons more readily than hydroxyl ions. As a result, free chlorine is formed at the anode. The solution contains an excess of sodium and hydroxyl ions which may be recovered in the form of solid sodium hydroxide by evaporation of the water present. The equation for the electrolysis process is

$$2\ NaCl + 2\ H_2O \xrightarrow[\text{current}]{\text{electric}} 2\ NaOH + H_2 + Cl_2$$

In the actual commercial process it is necessary to keep the chlorine separated from the aqueous sodium hydroxide solution, since chlorine reacts with the latter to form sodium hypochlorite. This may be accomplished by separating the anode and cathode compartments by means of a porous diaphragm.

(*b*) *Oxidation of chlorides.* Free chlorine may be obtained by the removal of an electron from the chloride ion:

$$Cl^- \rightarrow Cl + e \text{ (oxidation)}$$

The removal of electrons from a substance is termed *oxidation* (see page 266 for a further discussion); substances capable of removing electrons are termed *oxidizing agents.* A few substances which may oxidize chlorides will be discussed here.

Hydrogen chloride reacts slowly with oxygen at elevated temperatures and is the basis

$$4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2\ H_2O$$

for the Deacon process, used extensively at one time but now replaced by cheaper methods of production. In this process hydrogen chloride and oxygen gases are passed through a chamber heated to about 400° which contains pumice impregnated with a copper salt to act as a catalyst.

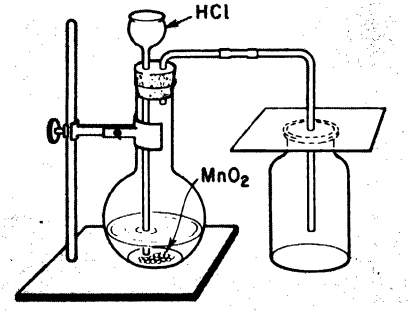


Figure 16–2 Laboratory preparation of chlorine.

In the laboratory, manganese dioxide is usually employed as the oxidizing agent. Chlorine is collected by displacement of air (Figure 16–2):

$$MnO_2 + 4\,HCl \rightarrow MnCl_2 + 2\,H_2O + Cl_2$$

Instead of hydrochloric acid, sodium chloride and sulfuric acid may be used with the manganese dioxide. This change is essentially the same as the one above since we may assume that the sulfuric acid first acts with the salt to form hydrogen chloride, which is then oxidized by the manganese dioxide:

$$2\,NaCl + 2\,H_2SO_4 + MnO_2 \rightarrow MnSO_4 + Na_2SO_4 + Cl_2 + 2\,H_2O$$

Other oxidizing agents may be employed with HCl:

$$2\,KMnO_4 + 16\,HCl \rightarrow 2\,KCl + 2\,MnCl_2 + 5\,Cl_2 + 8\,H_2O$$
$$K_2Cr_2O_7 + 14\,HCl \rightarrow 2\,KCl + 2\,CrCl_3 + 3\,Cl_2 + 7\,H_2O$$
$$HNO_3 + 3\,HCl \rightarrow NOCl + Cl_2 + 2\,H_2O$$
$$KClO_3 + 6\,HCl \rightarrow KCl + 3\,Cl_2 + 3\,H_2O$$
$$PbO_2 + 4\,HCl \rightarrow PbCl_2 + Cl_2 + 2\,H_2O$$

Physical properties Chlorine is a greenish-yellow gas at ordinary temperatures and has a sharp, disagreeable odor. It is very irritating to the mucous lining of the lungs, and its inhalation in large quantities may be fatal; for this reason, chlorine has been used as a war gas. The gas is moderately soluble in water; 2.26 volumes dissolve in 1 volume of water at 20°. The gas condenses to a liquid at a temperature of −34.5° at a pressure of one atmosphere and freezes to a solid at −101.6°. Chlorine is easily liquefied under pressure and is stored as a liquid in steel cylinders.

Chemical properties Because of its great activity, chlorine reacts with a great number of elements and compounds, some of the more important of which will be listed here.

(*a*) *Metals.* Chlorine combines directly with practically all of the metallic elements to form chlorides. The more active metals unite vigorously. Powdered antimony when sprinkled into a jar containing chlorine bursts into flame with the formation of a white cloud of antimony chloride. A few typical unions with metals are:

$$2\,Na + Cl_2 \rightarrow 2\,NaCl$$
$$Zn + Cl_2 \rightarrow ZnCl_2$$
$$2\,Sb + 3\,Cl_2 \rightarrow 2\,SbCl_3$$

(*b*) *Nonmetals.* Most of the nonmetals combine directly with chlorine. Phosphorus burns in chlorine forming phosphorus trichloride, PCl_3, a colorless liquid, and with an excess of chlorine forms PCl_5, a yellow solid:

$$2\,P + 3\,Cl_2 \rightarrow 2\,PCl_3$$
$$2\,P + 5\,Cl_2 \rightarrow 2\,PCl_5$$

Sulfur and chlorine combine at an elevated temperature to form sulfur monochloride, S_2Cl_2, a yellow liquid:

$$2\ S + Cl_2 \rightarrow S_2Cl_2$$

Chlorine and hydrogen combine slowly in the dark, but unite explosively in strong light with the formation of hydrogen chloride:

$$H_2 + Cl_2 \rightarrow 2\ HCl$$

(*c*) *Compounds of hydrogen.* Chlorine readily removes hydrogen from hydrocarbons (compounds of carbon and hydrogen) to form hydrogen chloride and carbon in each case. If a lighted jet of methane gas (this gas is the main constituent of natural gas) is introduced into an atmosphere of chlorine, combustion continues with the formation of a black sooty deposit of carbon:

$$CH_4 + 2\ Cl_2 \rightarrow C + 4\ HCl$$

A piece of filter paper which has been saturated with turpentine, $C_{10}H_{16}$, inserted into a jar of chlorine rapidly takes fire with the formation of a deposit of carbon on the sides of the vessel:

$$C_{10}H_{16} + 8\ Cl_2 \rightarrow 10\ C + 16\ HCl$$

Other hydrocarbons act similarly with free chlorine.

(*d*) *Water.* Chlorine with water forms a solution of hydrochloric and hypochlorous acids:[1]

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

Hypochlorous acid is quite unstable and breaks down on exposure to sunlight:

$$2\ HClO \rightarrow 2\ HCl + O_2$$

As a result, the equilibrium above is displaced to the right and eventually the reaction becomes complete to the right when the hypochlorous acid has completely decomposed.

(*e*) *Bases.* Since a solution of two acids is produced when chlorine is dissolved in water, we might suppose that the addition of a base to such a solution would result in the neutralization of the acids to form salts. This is the case with the formation of a chloride salt and a hypochlorite salt:

$$Cl_2 + 2\ NaOH \rightarrow NaCl + NaClO + H_2O$$

Uses Chlorine is used extensively as a bleaching agent. If a piece of

[1] The double arrows $\rightleftharpoons$ show an equilibrium reaction. See page 220.

colored calico is dipped into a water solution of chlorine, bleaching of the color takes place rapidly. The hypochlorous acid which is present in the solution seems to be the active bleaching agent, since dry chlorine is not very effective. Chlorine is too corrosive to be used with fibers of animal origin (wool, silk, etc.). Much of the chlorine produced commercially is used for bleaching wood pulp, which is used in the production of paper and rayon.

Pathogenic organisms are destroyed in water containing as little as one or two parts of chlorine per million; hence chlorine finds extensive use in the sterilization of drinking water.

Chlorine to be used for bleaching purposes is often transported in the form of bleaching powder, which is produced from lime and chlorine:

$$CaO + Cl_2 \rightarrow CaOCl_2$$

The chlorine is readily liberated from this compound by treatment with dilute acid:

$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$

Chlorine was the first of the war gases to be used in World War I. The gas was liberated when the wind was in the proper direction, and since the gas is nearly two and one-half times as heavy as air, it remained close to the ground where it was most effective. Most of the poisonous gases developed later in that war were chlorine compounds. Among the more effective gases were *mustard gas* $(CH_2ClCH_2)_2S$, *phosgene,* $COCl_2$, and *chlorpicrin,* CCl_3NO_2.

In addition to the preparation of chlorides of many of the elements, chlorine also finds use in the preparation of dyes and drugs.

A particularly effective new insecticide is a chlorine compound $(C_6H_4Cl)_2C_2HCl_3$, named dichloro-diphenyl-trichloro-ethane (DDT).

BROMINE

History and occurrence Balard in 1826 isolated a heavy dark brown liquid from sea salt. The liquid proved to be an element and was given the name "bromine," from the Greek word *bromos,* meaning stench. Bromides are found in natural salt brines and in deposits from such brines. The Stassfurt salt deposits in Germany, and brines from wells near Midland, Michigan, furnish small quantities of the element. Bromides are also found in sea water from which the element is extracted on a commercial scale.

Preparation Since chlorine is more active than bromine, the latter may be liberated from its salts by treatment with chlorine water:

$$2\ NaBr + Cl_2 \rightarrow 2\ NaCl + Br_2 \qquad (1)$$

Similar to chlorine, it may also be prepared by electrolysis of bromides or by the oxidation of hydrobromic acid.

It is frequently prepared in the laboratory by treating a bromide salt with an oxidizing agent and sulfuric acid; for example,

$$2\ NaBr + MnO_2 + 2\ H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + Br_2 + 2\ H_2O$$

Commercially, bromine is obtained from sea water by displacement of the bromide present with free chlorine according to equation (1) above. Sea water is pumped into large towers, where it is circulated in contact with chlorine. The liberated bromine is swept upward in the towers by an air stream and collected in a solution of sodium carbonate:

$$3\ Br_2 + 3\ Na_2CO_3 \rightarrow 5\ NaBr + NaBrO_3 + 3\ CO_2$$

Bromine is readily liberated from the solution by treatment with sulfuric acid:

$$5\ NaBr + NaBrO_3 + 3\ H_2SO_4 \rightarrow 3\ Na_2SO_4 + 3\ H_2O + 3\ Br_2$$

Properties and uses Bromine is a heavy, red-brown liquid at ordinary temperatures with a high vapor pressure evidenced by the brown vapor always present above a sample of the liquid. The vapors are particularly irritating to the eyes and to the respiratory system. Liquid bromine, if spilled on the skin, produces severe burns which are very slow to heal.

Bromine boils at 58.7°, and freezes to solid at −7.3°. Bromine water is produced by dissolving bromine in water, in which it is moderately soluble. Bromine dissolves readily in carbon disulfide, carbon tetrachloride, ether, and alcohol. In testing for the presence of bromine, one of these liquids is usually added, since the bromine is much more soluble in these liquids than in water; hence the element is concentrated in the added liquid and the color is intensified.

Bromine is used in the manufacture of dyes, drugs, and medicinals. Potassium bromide added to silver nitrate precipitates silver bromide, which, since it is very sensitive to light, is used extensively in the preparation of photographic films. The compound $C_2H_4Br_2$ is mixed with tetraethyl lead and added to gasoline for improved "antiknock" quality.

In chemical properties the element is very similar to chlorine. It is somewhat less active than chlorine, but nevertheless combines directly with most of the metals and nonmetals to form bromides.

IODINE

History and occurrence Iodine was discovered in 1812 by Courtois, who extracted crystals of the violet solid from the ashes of seaweed. Two

years later, Gay-Lussac proved this substance to be an element and named it "iodine" from the Greek, meaning violet.

The principal source of iodine is sodium iodate, $NaIO_3$, which occurs in small amounts in Chile saltpeter, $NaNO_3$. Free iodine is liberated from the former compound by reduction with $NaHSO_3$.

Iodine in the form of sodium iodide is found in very small amounts in sea water. Certain seaweeds called *kelp* also contain small quantities and have been employed as a commercial source of the element.

Preparation Iodine is prepared in the laboratory by the methods usually employed for the preparation of chlorine and bromine:

$$2\,NaI + MnO_2 + 2\,H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + I_2 + 2\,H_2O$$

Iodides are more easily oxidized than either chlorides or bromides.

Since iodine is less active than chlorine or bromine, both of these elements displace iodine from iodides:

$$2\,NaI + Br_2 \rightarrow 2\,NaBr + I_2$$
$$2\,NaI + Cl_2 \rightarrow 2\,NaCl + I_2$$

Properties and uses Iodine is a dark gray or black solid at ordinary temperatures. When heated below its melting point of 113°, iodine vaporizes rapidly. The vapor may be condensed as crystals on a cold surface, without apparent formation of liquid. The property of changing directly from solid to gas and from gas to solid without apparently liquefying is termed *sublimation*.

Iodine is only slightly soluble in water, but is readily soluble in a solution which contains potassium iodide because of the combination:

$$I_2 + KI \rightarrow KI \cdot I_2 \text{ or } KI_3$$

It is readily soluble in alcohol, carbon tetrachloride, and ether, and, as is the case with bromine, these solvents are often used in extracting the element from water solutions. Starch forms an unstable blue compound with iodine and is used as a test for the presence of free iodine.

Although less active than the other halogens, iodine nevertheless combines with most of the metals and many of the nonmetals to form iodides.

Everyone is familiar with the use of iodine as an antiseptic. A solution of iodine in alcohol is known as "tincture" of iodine. Silver iodide, like silver bromide, is sensitive to light and finds use in the photographic industry.

The presence of iodine in the body seems to be essential for good health. Iodine appears to perform a vital function in the thyroid gland, in which it is found in the compound, iodothyrin. If the body is not furnished

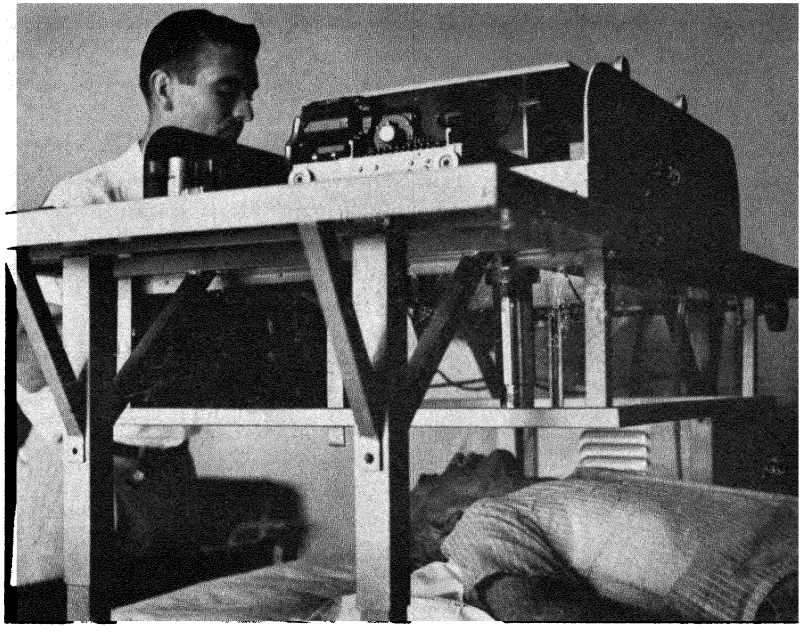


Figure 16–3 Radioactive iodine is an important tool in the diagnosis and treatment of malignant disease.

with iodine in some form, this vital gland does not function properly. Under normal circumstances, we derive sufficient iodine from foods such as butter, spinach, beans, and particularly sea foods.

FLUORINE

History and occurrence Although fluorine compounds are fairly common and have been known for several centuries, the element itself was not isolated until 1886 by Moissan, a French chemist. Among the more common minerals of fluorine are *fluorspar*, CaF_2; *cryolite*, Na_3AlF_6; and *apatite*, $CaF_2 \cdot 3\,Ca_3(PO_4)_2$. It was shown in the seventeenth century that fluorspar treated with acids yielded a substance capable of etching glass. This substance has since been proved to be hydrogen fluoride.

Preparation and properties The fact that fluorine was the last of the halogens to be prepared in the free state may be attributed to its extreme activity. Because of its activity, its compounds are very stable, and the methods used in the liberation of the other halogens from their compounds are not applicable.

Attempts to liberate fluorine from aqueous solutions by means of oxidizing agents or electrolysis fail since fluorine reacts vigorously with water according to the equation:[2]

$$2\,F_2 + 2\,H_2O \rightarrow 4\,HF + O_2$$

Moissan was finally able to isolate the element in 1886 by electrolyzing an anhydrous solution of potassium fluoride in liquid hydrofluoric acid. The mixture is a good conductor of the current and fluorine is liberated at the anode. The composition of the container and the electrodes to be used in the electrolysis process presents a problem, since fluorine is so extremely active. At the present time containers are made of Monel metal, an alloy of copper and nickel, which is resistant to the action of fluorine. The anode is composed of graphite.

In chemical properties the element is similar to the other halogens. It is the most active of the family and consequently will displace any of the others from their salts.

Fluorine is a pale yellow gas at ordinary conditions, very irritating and extremely poisonous. Its principal use is in the preparation of fluorine compounds, some of which are important commercially.

THE HYDROHALOGENS

The compounds HF, HCl, HBr, and HI are termed the *hydrohalogens* and their water solutions are known as *hydrofluoric, hydrochloric, hydrobromic,* and *hydriodic acids* respectively. All are colorless gases at ordinary temperatures and all are very soluble in water.

These compounds may be prepared by direct combination of the elements. The rate of reaction varies from an extremely rapid reaction with fluorine to a slow and incomplete reaction with iodine. In general this method of preparation is not applicable in the laboratory.

Preparation of hydrogen chloride and hydrogen fluoride The usual method employed for the preparation of any volatile acid is to *treat a salt of the desired acid with a less volatile acid and distil over the desired acid.* If NaCl is treated with concentrated sulfuric acid (a nonvolatile acid), hydrogen chloride, a gas at ordinary temperatures and therefore volatile, passes into the delivery tube and may be collected by displacement of air (Figure 16–4). The reaction may proceed in two steps:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$

If excess salt is present and the mixture is heated, a second reaction takes place:

[2] Ozone, O_3, is a product along with O_2.

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl \uparrow$$

Hydrogen fluoride is prepared from fluorspar, CaF_2, and concentrated sulfuric acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\,HF \uparrow$$

The reaction is usually carried out in a lead container which is resistant to the action of HF. Glass vessels cannot be used because the acid attacks the constituents in the glass, therefore, hydrofluoric acid is stored in wax containers

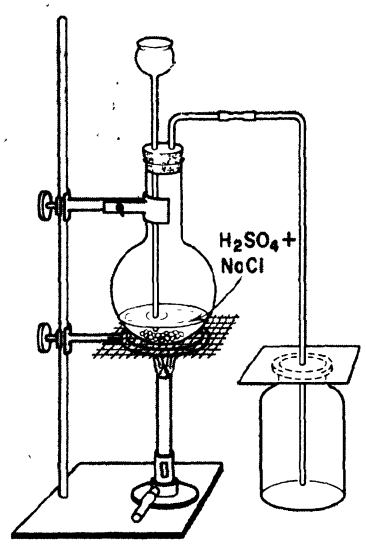


Figure 16–4 Hydrogen chloride generator.

Action of concentrated sulfuric acid on bromides and iodides We might expect that the reaction of concentrated sulfuric acid with bromides and iodides would be similar to its action with chlorides and fluorides:

$$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr \quad (1)$$
$$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI \quad (2)$$

The above reactions do take place, but the products are impure because of secondary reactions. Both HBr and HI are better reducing agents than HCl, and after their formation in reactions (1) and (2), they react with the excess sulfuric acid present. Some of the hydrogen bromide is oxidized to free bromine, and as a result the product of reaction (1) is somewhat brown in color.

$$2\,HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2\,H_2O \quad (3)$$

Hydrogen iodide is a still better reducing agent than hydrogen bromide and is almost completely oxidized to free iodine; the sulfuric acid is reduced to hydrogen sulfide:

$$8\,HI + H_2SO_4 \rightarrow 4\,I_2 + H_2S + 4\,H_2O \quad (4)$$

That HI is a better reducing agent than HBr is evident from reactions (3) and (4). While HBr reduces the oxidation number of sulfur from +6 in sulfuric acid to +4 in sulfur dioxide, HI reduces the oxidation number of sulfur from +6 to −2 in hydrogen sulfide.

Preparation of pure hydrogen bromide and hydrogen iodide Pure hydrogen bromide and hydrogen iodide are usually prepared by the action of water on phosphorus tribromide and phosphorus triiodide respectively:

$$PBr_3 + 3\,H_2O \rightarrow H_3PO_3 + 3\,HBr$$
$$PI_3 + 3\,H_2O \rightarrow H_3PO_3 + 3\,HI$$

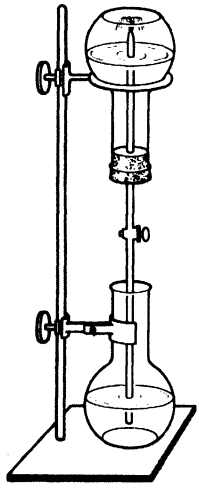


Figure 16–5 Hydrogen chloride fountain.

The phosphorus halides may be prepared by direct combination of the elements. Double decomposition reactions such as these in which water is one of the reactants are termed *hydrolysis* reactions.

Physical properties The hydrohalogens are colorless gases at ordinary temperatures and are extremely soluble in water.[1] All possess a sharp, irritating odor. For other physical properties, see Table 16–1.

At temperatures above 90°, determinations of densities of hydrogen fluoride indicate the formula to be HF, while at temperatures below 90° the molecules are associated to correspond with the formula H_2F_2. It is likely that an equilibrium between the two forms exists:

$$2\,HF \rightleftharpoons H_2F_2$$

Above 90° the equilibrium is displaced almost completely to the left while at ordinary temperatures the reverse is true. A still higher degree of association is indicated in liquid hydrogen fluoride.

TABLE 16–1 Physical Properties of Hydrohalogens

FORMULA	MOLECULAR WEIGHT	BOILING POINT	FREEZING POINT	SOLUBILITY IN WATER: VOLUMES OF GAS IN 1 VOLUME OF WATER
HF	20 (above 90°)	19.4	−92	
HCl	36.5	−84	−112	507 at 0°
HBr	81	−67	−89	610 at 0°
HI	128	−35	−51	425 at 10°

[1] The extreme solubility of the hydrohalogens in water may be demonstrated by the following experiment (Figure 16–5): The upper flask is filled with hydrogen chloride gas and the lower flask with water. When the stopcock is opened, hydrogen chloride begins dissolving in water. The solution process is slow at first because a small surface of water is exposed to the gas. As the gas dissolves a partial vacuum is produced in the upper flask and water flows up the vertical tube into the upper flask. The rate of solution increases until finally water sprays rapidly into the upper flask, and the gas seems to dissolve almost at once.

Chemical properties of hydrogen chloride Although pure HCl gas is relatively unreactive, its aqueous solution exhibits the characteristic properties of an acid—for example, it turns litmus red, reacts with metals above hydrogen in the activity series to form hydrogen, and reacts with bases to form salts:

$$Zn + 2\,HCl \rightarrow ZnCl_2 + H_2$$
$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$CuO + 2\,HCl \rightarrow CuCl_2 + H_2O$$
$$Na_2CO_3 + 2\,HCl \rightarrow 2\,NaCl + CO_2 + H_2O$$

Gaseous HCl reacts with gaseous ammonia to form a white cloud of solid ammonium chloride (enough water vapor is present to render the gas active):

$$NH_3 + HCl \rightarrow NH_4Cl$$

Uses of hydrochloric acid As an acid, hydrochloric acid is second only to sulfuric acid in importance. It finds extensive use in "pickling baths" for cleaning the layer of oxide from iron and steel objects before the latter are plated. Large quantities of HCl are used in the hydrolysis of starch to glucose in the manufacture of corn sirup. Other major uses are in the manufacture of textiles, dyes, and chemicals. Hydrochloric acid has an important role in the stomach, where it aids in digestion.

Hydrofluoric acid and fluorides Hydrofluoric acid possesses the unique property of reacting with silica, SiO_2, to form *silicon tetrafluoride*, SiF_4, a gas at ordinary temperatures:

$$SiO_2 + 4\,HF \rightarrow SiF_4\uparrow + 2\,H_2O$$

Glass, which is a mixture of sodium and calcium silicates, is readily attacked by the acid, the following reactions taking place:

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

Because of these reactions, hydrofluoric acid finds extensive use in the etching of glass. A glass object to be etched is coated with paraffin after which a design is cut into the paraffin. The object is then exposed to the action of hydrofluoric acid. Burets, pipets, graduated cylinders, and other pieces of chemical apparatus are thus etched.

Hydrofluoric acid is a weak acid, while the other hydrohalogen acids are very strong; as a result, its reactions with metals and bases are very slow. Salts of the acid are extremely poisonous and find limited use. Sodium fluoride and sodium aluminum fluoride are used as insecticides; sodium fluosilicate, Na_2SiF_6, is used as a germicide and deodorant. Several fluorine compounds are used as refrigerants: CCl_2F_2 (dichlorodi-

fluoromethane), with the trade name Freon, and $C_2Cl_3F_3$ (trichlorotrifluoroethane) are examples.

OXYGEN COMPOUNDS OF THE HALOGENS

Oxides Although the halogens do not combine directly with oxygen, several oxides have been prepared indirectly. Generally speaking, these compounds are unstable and difficult to preserve. Cl_2O, *chlorine monoxide*, a yellowish gas which may be condensed to a liquid at 4°, is the anhydride of HClO, and may be distilled from a solution of the acid under reduced pressure. The gas readily explodes when heated. ClO_2, *chlorine dioxide*, is a yellowish gas, liquefying at 10°. It may be produced by the action of a strong acid on a chlorate and since the ClO_2 is very unstable the reaction may occur with explosive violence:

$$6\,KClO_3 + 3\,H_2SO_4 \rightarrow 2\,HClO_4 + 4\,ClO_2 + 2\,H_2O + 3\,K_2SO_4$$

The oxide acts as a mixed anhydride since its solution in water produces both chlorous and chloric acids:

$$2\,ClO_2 + H_2O \rightarrow HClO_3 + HClO_2$$

Cl_2O_7, *chlorine heptoxide*, the anhydride of perchloric acid, is a colorless oily liquid with a boiling point of 82°. It readily explodes when struck or heated above its boiling point. It may be prepared by dehydration of $HClO_4$ with P_2O_5:

$$2\,HClO_4 + P_2O_5 \rightarrow Cl_2O_7 + 2\,HPO_3$$

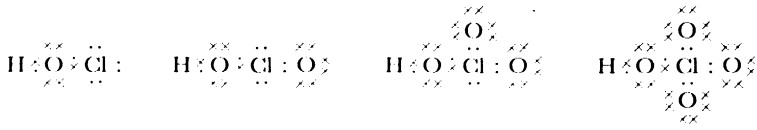
A few other oxides of the halogens—for example, F_2O, F_2O_2, and Br_3O_8—have been prepared.

Oxyacids of the halogens The halogens, with 7 electrons in the outer shell of their atoms, are capable of exhibiting several oxidation states by sharing of electrons with oxygen; as a consequence, they form a series of oxygen-containing acids with several acids in each series. The oxyacids are listed in Table 16–2.

TABLE 16–2 Halogen Oxyacids

NAME	OXIDATION NUMBER OF HALOGEN	FLUORINE	CHLORINE	BROMINE	IODINE
Per . . . ic	+7		$HClO_4$		HIO_4
. . . ic	+5	—	$HClO_3$	$HBrO_3$	HIO_3
. . . ous	+3	—	$HClO_2$		
Hypo . . . ous	+1	—	HClO	HBrO	HIO

The electronic configurations of the oxyacids of chlorine are given below:



Hypochlorous acid HClO is formed when chlorine is dissolved in water:

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

The bleaching action of chlorine, which is effective only in the presence of water, is due presumably to the oxidizing properties of hypochlorous acid produced.

Hypochlorous acid is a weak acid in contrast to hydrochloric acid, which is produced at the same time when chlorine is dissolved in water. Advantage is taken of this difference in acid strengths in separation of the two acids; the strong acid may be neutralized with $NaHCO_3$ or $CaCO_3$ leaving free hypochlorous acid in solution.

$$Cl_2 + NaHCO_3 \rightarrow NaCl + HClO + CO_2$$

A dilute solution of HClO may then be distilled from the mixture.

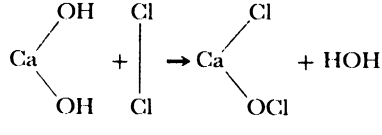
Treatment of chlorine water with a base like NaOH results in the formation of salts of two acids:

$$Cl_2 + 2\,NaOH \rightarrow NaCl + NaClO + H_2O$$

The resulting solution containing sodium chloride and sodium hypochlorite is widely used as a bleaching agent.

Bleaching powder Although liquid chlorine is now used extensively in bleaching operations, available chlorine as a solid powder of the composition $CaOCl_2$, called *bleaching powder*, or *chloride of lime*, has long been used. Easily made, transported, and convenient to use, its manufacture constitutes a large industry.

Bleaching powder is produced when chlorine gas is passed over layers of slaked lime, $Ca(OH)_2$:



Note that the compound is a mixed salt, containing both the chloride and hypochlorite acid radicals. It may be considered to be a mixture

of the two salts $CaCl_2$ and $Ca(ClO)_2$ present in equal molecular proportions. Chlorine is readily liberated by treatment with an acid:

$$\begin{array}{l} \text{Cl} \\ \text{Ca} \\ \text{OCl} \end{array} + H_2SO_4 \rightarrow CaSO_4 + \underline{HOCl + HCl} \qquad Cl_2 + H_2O$$

If lime is treated with HClO:

$$CaO + 2\,HClO \rightarrow Ca(ClO)_2 + H_2O$$

The $Ca(ClO)_2$, calcium hypochlorite, has twice the oxidizing capacity of $CaOCl_2$. It is called "high test" hypochlorite, "HTH."

Chlorates Sodium and potassium chlorates find extensive use as laboratory oxidizing agents and are widely used in production of matches, fireworks, and explosives. An oxidizable substance such as wood or charcoal burns brilliantly and rapidly when dropped into the molten salt. Potassium chlorate may be prepared by passing chlorine gas into a hot concentrated solution of KOH or by electrolysis of KCl solution. The reactions occurring in both cases may be summarized in the equation

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

Since potassium chlorate is much less soluble than the potassium chloride produced, it may be recovered by crystallization from the cooled solution.

Sodium chlorate is used as a weed killer, but it should be so used only in the absence of oxidizable dust, since combustion, once started, proceeds with great vigor.

Perchloric acid and perchlorates Perchloric acid is a colorless liquid which decomposes explosively if heated strongly. It is prepared by treatment of a perchlorate, preferably barium perchlorate, with dilute sulfuric acid followed by distillation under reduced pressure. It is one of the strongest acids, being comparable in strength to HCl and HNO_3. As a 60–70 per cent solution, it is used in the analytical separation of potassium, since potassium perchlorate is one of the few slightly soluble salts of potassium.

Magnesium perchlorate is an effective desiccant or drying agent, having the capacity to absorb up to 30 per cent of its own weight of water.

EXERCISES

1 From the standpoint of atomic structure, why would you expect the members of the halogen family to be very similar in chemical properties?

2 The halogens are never found in the uncombined or free state. Explain.

3 What products are always obtained upon the oxidation of hydrochloric acid?

4 Describe an experiment which you could carry out in the laboratory to show the relative activity of the halogens.

5 Why cannot fluorine be prepared in a similar manner to the other halogens? Show by diagram and equations what products would be formed during the electrolysis of an aqueous hydrofluoric acid solution.

6 List several similarities and several dissimilarities of members of the halogen group.

7 Explain clearly why concentrated sulfuric acid cannot be used in the preparation of pure hydrogen bromide and hydrogen iodide.

8 What is the general method for the preparation of a volatile acid? Write equations to illustrate for (*a*) nitric acid; (*b*) acetic acid.

9 Explain how you might test a sample of table salt for the presence of iodide.

10 A sample of chlorine water on exposure to the sunlight gradually loses its effectiveness as a bleaching agent. Explain.

11 Despite the fact that hydrogen chloride contains the element hydrogen in addition to chlorine, a liter of hydrogen chloride weighs less than a liter of chlorine. Explain.

12 Calculate the theoretical quantity of chlorine which is obtainable by the electrolysis of 200 pounds of a 20 per cent sodium chloride solution. What other products would be obtained and what weight of each?

13 Complete and balance:

(*a*) $Mg + HCl \rightarrow$
(*b*) $NH_4OH + HI \rightarrow$
(*c*) $F_2 + H_2O \rightarrow$
(*d*) $MnO_2 + HBr \rightarrow$
(*e*) $H_2 + F_2 \rightarrow$
(*f*) $Fe + Cl_2 \rightarrow$
(*g*) $I_2 + KOH \rightarrow$
(*h*) $AlBr_3 + H_3PO_4 \rightarrow$
(*i*) $CuO + HCl \rightarrow$
(*j*) $Al_2O_3 + HBr \rightarrow$
(*k*) $Cl_2 + NaOH \rightarrow$
(*l*) $K + Br_2 \rightarrow$

14 In those cases where a reaction occurs, write the equation. Indicate those cases in which no action takes place:

(*a*) Chlorine water is added to (i) potassium bromide, (ii) sodium fluoride, (iii) calcium iodide, (iv) a solution of potassium hydroxide, (v) hydriodic acid.

(*b*) Hydrochloric acid is added to (i) copper, (ii) ferric oxide, (iii) tin, (iv) SiO_2, (v) sodium hydroxide, (vi) manganese dioxide, (vii) mercury.

(*c*) Bromine water is added to (i) potassium chloride, (ii) magnesium, (iii) tin, (iv) sodium iodide, (v) calcium fluoride, (vi) hydrochloric acid, (vii) sodium hydroxide solution.

15 How many grams of bromine is necessary to liberate 50 grams of iodine from sodium iodide? Ans. 31.5.

16 500 grams of chlorine is mixed with 25 grams of hydrogen gas and the mixture exploded. What gases remained after the explosion, and how many grams of each?

17 How many liters of hydrogen chloride (measured at standard conditions) may be obtained by the action of concentrated sulfuric acid on 200 grams of sodium chloride? What would be the weight of this volume of HCl?

18 Calculate the volume of HCl necessary to exactly neutralize 100 liters of NH_3. (Gases measured at standard conditions.) Ans. 100 l.

19 Calculate the weight and volume of all gases at STP produced during the electrolysis of 500 grams of an aqueous solution of sodium chloride

20 A plant manufacturing phosgene, $COCl_2$, made its own CO gas but bought chlorine as a liquid under pressure in large cylinders. As 142 pounds of chlorine was used, what volume (at standard conditions) of CO was needed to make $COCl_2$? Ans. 717 cu ft

21 What weight of silver sulfate must be added to a solution of NaBr to prepare 82.4 pounds of AgBr?

22 Astatine (At), a member of the halogen family, was only recently discovered. From known properties of other members of the family, predict some of the properties of this element, such as melting point, boiling point, solubility in water, color, chemical activity, and stability of compounds.

23 Describe tests which you might use to differentiate between the four white salts NaF, NaCl, NaBr, NaI.

24 Complete and balance.

(*a*) $SiO_2 + HF$ (*b*) $CaF_2 + H_2SO_4$ (*c*) $C_{10}H_{16} + Cl_2$

25 How would you proceed in the laboratory to differentiate between aqueous solutions of HCl, HNO_3, and H_2SO_4?

26 Write equations to show the preparation of pure samples of HBr and HI.

27 Calculate the volume of HCl gas at standard conditions obtainable from 0.2 moles of $CaCl_2$. Ans. 8.96 l

28 The halogens show progressive differences in properties with increasing atomic weights. What change in the following properties occurs with increasing atomic weight (*a*) color of the element, (*b*) activity of the element, (*c*) stability of the hydrohalides, (*d*) color of hydrohalides, (*e*) ease of separation of the elements from compounds?

29 Chlorine may be prepared in the laboratory by the reaction

$$2\ KMnO_4 + 16\ HCl \rightarrow 2\ KCl + 2\ MnCl_2 + 5\ Cl_2 + 8\ H_2O$$

(*a*) What volume of chlorine gas (standard conditions) would be produced by using 0.04 moles of $KMnO_4$, with excess HCl? (*b*) What weight of $MnCl_2$ would be produced in (*a*)? Ans. (*a*) 2.24 l (*b*) 5.04 g

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seventeen

REACTION RATES AND CHEMICAL EQUILIBRIUM

In our discussions so far, we have learned that much information may be derived from a chemical equation—for example, the products which we can expect from a given set of reactants, and the weight relations between the substances involved in the reaction. The equation, however, does *not* tell us anything about the conditions under which the reaction will take place, nor does it give us any information about the rate or speed at which the reaction proceeds.

We have observed that some chemical changes—for example, the explosion of dynamite—take place very rapidly, while others—like the rusting of iron—take place very slowly over a period of days or even years. All chemical reactions require a certain amount of time, although in some cases it may be very difficult to measure the time interval. When we speak of reaction rate, we mean the amount of chemical change which takes place in a given interval of time. We might, for example, measure the volume of oxygen gas obtained in one minute by heating a given amount of potassium chlorate at a given temperature. This quantity of oxygen produced in a definite period of time would be a measure of the rate or speed of the reaction at that temperature. These reaction rates are of great importance to the chemist; often the feasibility of a chemical reaction, and particularly a commercial chemical process, depends upon the reaction rate—if the process is too slow, it may not be adaptable to commercial exploitation.

Factors which influence the speed of reactions Many factors are involved in reaction rates, but the more important ones which affect these rates may be summarized as follows:

(*a*) *Nature of the reacting substances.* Substances differ in activity and

hence in the speed with which they react with other substances. The active metals displace hydrogen vigorously and rapidly from acids, while the less active metals act slowly, if at all. Metals differ in their rates of corrosion because of differences in speed of combination with oxygen and other elements. Elements like nitrogen combine very slowly with other elements; in contrast to these, the halogens are a group of active nonmetals which combine with most of the other elements readily.

(*b*) *Temperature.* The speed of all chemical changes increases as the temperature rises. Hydrogen and oxygen combine very slowly at ordinary temperatures but do so rapidly at high temperatures. The same is true of a piece of coal which burns readily in air when the temperature is raised sufficiently. *In general, the speed of a chemical change is approximately doubled for each ten degrees rise in temperature.*

(*c*) *Catalysts.* Catalysts may alter the speed of chemical changes. The decomposition of potassium chlorate is speeded up by the addition of the catalyst, manganese dioxide. A catalyst may also reduce the speed; for example, acetanilide decreases the speed of decomposition of hydrogen peroxide. Catalysis is extremely important in the preparation of many industrial products. The success of many processes from a commercial standpoint depends upon the rate at which the desired products may be produced, which in turn may depend upon the speed of certain chemical changes. The addition of a catalyst may so speed up a slow chemical change as to make it commercially feasible.

(*d*) *Concentration.* From a kinetic standpoint, chemical change takes place as a result of collisions of molecules. The greater the number of collisions in unit time, the greater the conversion of initial substances into products in unit time—that is, the greater the speed of reaction. If the concentrations of reactants are high (a large number of molecules in a given volume), the chance for collision is much greater, just as the chance for collision between couples on a dance floor is much greater when the floor is crowded.

The student should not infer from the preceding discussion that all collisions of molecules necessarily result in chemical change. In some cases, a relatively large percentage of collisions may result in atomic rearrangements (chemical change), while in other cases only a small percentage of collisions will be effective. It is necessary, however, that actual contact be made between the interacting substances to produce chemical reaction.

The law of mass action Guldberg and Waage in 1867 expressed the relationship between mass or concentration and speed of reaction in the Law of Mass Action: *The speed of a chemical reaction is proportional to the*

product of the concentrations (or active masses) of the reacting molecules. Consider the reaction

$$A + B \rightarrow C + D$$

proceeding in a single step as shown by the equation. The rate at which A reacts with B will depend upon the number of collisions between A and B molecules. Suppose we have one molecule each of A and B in one liter of solution. We may say that the chance for collision is 1—that is, $1 \times 1 = 1$. If we double the number of molecules of A, then we have doubled the chance for collision between A and B molecules; hence the chance for collision is $2 \times 1 = 2$. If the number of B molecules is also doubled (the concentration of B is doubled), then the chance for collision becomes $2 \times 2 = 4$. The number of collisions, then, is proportional to the product of the concentrations of reacting substances. Since the speed at which A combines with B is dependent upon the number of collisions between A and B, it follows that the speed of reaction is also proportional to the product of the concentrations of A and B. If we denote the concentration of A molecules as $[A]$ and the concentration of B molecules as $[B]$, this may be expressed:

$$\text{Speed} \propto [A] \times [B] \quad (\propto \text{ means proportional})$$

or

$$\text{Speed} = k \times [A] \times [B]$$

where k is a constant. This k is termed a *velocity* or *rate constant*, and it includes the effects of temperature, pressure, catalyst, and nature of the reactants—all the factors other than concentration which influence the speed of reaction. It is customary to express the concentrations in terms of molarity—moles per liter.

If we apply the above relation to the reaction

$$H_2 + I_2 \rightarrow 2\,HI$$

then

$$\text{Speed} = k \times [H_2] \times [I_2]$$

where $[H_2]$ and $[I_2]$ represent the molar concentrations of H_2 and I_2, respectively.

The velocity or rate constant, k, for this reaction could be evaluated experimentally by measuring the amount of HI produced in unit time, let us say one minute, from known concentrations of H_2 and I_2, the latter expressed in moles per liter, that is,

$$k = \frac{\text{moles of HI produced per minute}}{[H_2] \times [I_2]}$$

Once the rate constant is evaluated, it could be used to determine the amount of HI produced in one minute from any given concentrations of H_2 and I_2.

Reversible and irreversible changes Under certain conditions, the products of a chemical change may react to re-form the original substances. Such chemical changes are said to be *reversible*. When mercuric oxide is heated to a temperature of 600°–700°, decomposition of the compound takes place, yielding mercury and oxygen as products:

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

This change is reversible, since at a temperature of 300°, mercury will combine with oxygen to form mercuric oxide:

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

Although most chemical changes are reversible, many must be classed as *irreversible*. When sugar ($C_{12}H_{22}O_{11}$) is heated, decomposition into carbon and water takes place:

$$C_{12}H_{22}O_{11} \rightarrow 12\ C + 11\ H_2O$$

Under no conditions known at present will carbon combine with water to form sugar. Hence the decomposition is irreversible; the products will not react to re-form the original substance. The following are other examples of irreversible reactions:

$$2\ Mg + O_2 \rightarrow 2\ MgO$$
$$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$$
$$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$$
$$\text{wood} + \text{oxygen} \rightarrow \text{ashes} + \text{gases}$$

CHEMICAL EQUILIBRIUM

We have encountered several examples of physical equilibrium in our study thus far; for example, saturated solutions. In such solutions, two processes are occurring in opposite directions with the same speed; namely, molecules or ions of solid are continually passing into solution, and at the same time molecules or ions from the solution are precipitating or depositing out as solid. Since these processes are taking place at the same speed, no apparent change in the solution is observed, and at a given temperature the solubility is a constant.

A liquid placed in a closed container soon comes to an equilibrium with its vapor. Molecules from the liquid are continually escaping from the surface of the liquid and passing into the vapor state; and at the same time molecules from the vapor state are passing into the liquid state. When equilibrium has been attained, these two processes are taking place with the same speed, and the rate of evaporation is equal to the rate of condensation.

A chemical equilibrium is like a physical equilibrium in that two opposing processes are occurring simultaneously with the same speed. However, there is this difference between physical equilibrium and chemical equilibrium: in a physical equilibrium, only a physical change occurs and there is no change in composition of the substances involved, whereas in a chemical equilibrium, a chemical change does occur -the reactants undergo a change in composition to form the products, which in turn are reconverted to the original reacting substances.

Equilibrium in reversible changes In discussing the action of steam on iron filings (page 96), it was shown that the following reaction takes place.

$$3\,Fe + 4\,H_2O\,(steam) \rightarrow Fe_3O_4 + 4\,H \qquad (1)$$

This reaction is reversible, since the passage of hydrogen gas over Fe_3O_4 results in the formation of iron and steam

$$Fe_3O_4 + 4\,H_2 \rightarrow 3\,Fe + 4\,H_2O \qquad (2)$$

In both of these cases, a gas has been passed over a solid; in the first, steam over iron, in the second, hydrogen over iron oxide. Let us now modify the conditions by enclosing iron filings and steam in a container so that no gaseous substance can escape. Reaction (1) above will proceed fairly rapidly at first, but reaction (2) cannot take place since no Fe_3O_4 and H_2 are initially present. However, as these two products are formed as a result of reaction (1), reaction (2) will start. At first, reaction (2) is slow as the concentration of reactants is small but gradually increases in speed until reactions (1) and (2) are taking place with the same speed. Under these conditions, the amounts of Fe, H_2O, Fe_3O_4, and H_2 remain unchanged, and the system is said to be in *equilibrium*.

To discuss the general case of equilibrium, consider the reaction:

$$A + B \rightarrow C + D$$

If the reaction is reversible, then C must react with D to re-form the reactants A and B.

$$C + D \rightarrow A + B$$

If the two reactions above occur at the same time and at the same speed, a chemical equilibrium results and may be represented thus.

$$A + B \rightleftharpoons C + D$$

When this condition results, no apparent change is taking place; analysis of the system would show that at all times constant amounts of reactants and products would be present. *Chemical equilibrium is an ap-*

parent state of rest in which two opposing chemical reactions are proceeding in opposite directions at the same speed

It should be pointed out that an equilibrium may be approached from either direction. In the reaction above, it would make no difference whether we started with A and B or C and D as reactants, the same final condition of equilibrium would result

Often the student has much difficulty in grasping the concepts of chemical equilibrium First of all, he must realize that all of the reactants and products are mixed together in the same reaction vessel The chemical equation for the equilibrium shows the mole ratio in which the substances react, but it does not show the relative amounts of substances which may actually be present in the equilibrium mixture For example, suppose we consider the equilibrium between NO, O_2, and NO_2 gases as shown by the equation

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2$$

At equilibrium, all three of these gases are present in the same reaction vessel, and the equation shows that when reaction occurs toward the right, 2 moles of NO will combine with 1 mole of O_2, or for the reverse reaction, 2 moles of NO_2 will produce 2 moles of NO and 1 mole of O_2 However, we might put NO and O_2 together in any proportion -for example, 10 moles of NO to 1 mole of O_2, or 50 moles of NO to 1 mole of O_2, or any other ratio Of course, analysis of the equilibrium mixtures would yield different concentrations of the component gases in each case, but equilibrium conditions would be established no matter what the ratio in which the gases were originally mixed together The equation tells us only in what ratio the substances actually *react*, but gives us no information about the relative amounts of substances actually present in an equilibrium mixture.

The equilibrium constant Again consider the reaction

$$A + B \rightleftharpoons C + D$$

in which an equilibrium exists between the four substances, A, B, C, and D. Two reactions are proceeding, one to the right (called the *forward reaction*) in which A and B react to form C and D, and the other to the left (called the *reverse reaction*) in which C and D react to form A and B. According to the law of mass action,

$$\text{Speed forward reaction} = k_1 \times [A] \times [B]$$

and

$$\text{Speed reverse reaction} = k_2 \times [C] \times [D]$$

At the beginning of the reaction, if we start with A and B, the concentrations of A and B will be high, and consequently the forward reaction

will proceed rapidly. At the start, no reverse reaction is possible, since C and D are not as yet present. But as C and D are formed, the reverse reaction will begin slowly and gradually increase in speed as C and D accumulate. Meanwhile, the forward reaction is slowing down as A and B are being used up. Equilibrium results when the speed in the two directions is equal, that is

$$\text{Speed of forward reaction} \longrightarrow = \longleftarrow \text{Speed of reverse reaction}$$

Consequently at equilibrium

$$k_1 \times [A] \times [B] = k_2 \times [C] \times [D]$$

or

$$\frac{k_1}{k_2} = \frac{[C]\,[D]}{[A]\,[B]}$$

or since the ratio of the two constants $\frac{k_1}{k_2}$ is also a constant, we may write

$$K = \frac{[C]\,[D]}{[A]\,[B]}$$

in which K is termed the *equilibrium constant.* We must keep in mind that equilibrium conditions may be approached from either direction. If we had started with C and D as reactants instead of A and B, the same final situation of equilibrium would result.

In the event that more than one molecule of a substance is used as a reactant or is formed as a product, such as

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

the expressions for the rates of reaction in the two directions are more complicated,[1] but it can be shown that the equilibrium constant is given by the expression:

$$K = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

in which each concentration is raised to that power which corresponds to the coefficient of that substance in the balanced equation. That this is so can be demonstrated in the laboratory by analyzing equilibrium systems of nitrogen, hydrogen and ammonia gases. For a general reaction:

$$mA + nB \rightleftharpoons rC + sD$$

[1] In general, the exact form of the rate expression for a reaction must be found by experiment. This is so because a reaction may proceed in several steps rather than in the single step shown by the equation. Many reactions have complicated rate expressions, but these cannot be considered here.

in which m, n, r, s represent the coefficients of A, B, C, D respectively in the balanced equation, the formulation for K becomes

$$K = \frac{[C]^r\,[D]^s}{[A]^m\,[B]^n}$$

Summarizing, we may say: *In a chemical equilibrium, the product of the concentrations of products divided by the product of concentrations of reactants—each concentration raised to that power whose exponent is the coefficient of the substance in the balanced chemical equation—is a constant.*

K has a constant numerical value for any given reaction at a given temperature Actual analysis of an equilibrium mixture will give the concentration of each of the substances and so will determine the value of K. If the concentration of one of the substances in the mixture is changed, the concentrations of other substances must change in such a way that the ratio

$$\frac{[C]\,[D]}{[A]\,[B]}$$

retains the same numerical value:

Suppose, for example, in the equilibrium

$$A + B \rightleftharpoons C + D$$

the concentration of A is increased. We should expect the speed of reaction between A and B to increase, since now there are more possible collisions between A and B molecules. As a result, the equilibrium is shifted to the right; the concentrations of C and D become larger. From an inspection of the formula for the equilibrium constant, it is evident that an increase of $[A]$ must result in an increase of $[C]$ and $[D]$ and a decrease in $[B]$, if K is to retain its value. In similar manner, changes in concentration of other reactants or products would result in concentration adjustments such that K would retain its constant value.

It should be evident from the expression for an equilibrium constant that if K has a large value, the numerator must be large as compared to the denominator; consequently, the concentrations of products are relatively high. This indicates that the reaction is more nearly complete to the right. On the other hand, a small value of K would show that the chemical change to the right has not proceeded very far.

The equilibrium constant is very important in chemistry, since it shows the extent to which a reaction may take place. In the commercial preparation of substances, it is desirable to choose a reaction in which K has a high value, since this would mean a high proportion of products.

The extent to which a reaction takes place is often roughly indicated by varying the length of the arrows appearing in the equilibrium equa-

tion. $\rightleftharpoons$ would indicate an equilibrium which is displaced far to the right and so has a high proportion of products; $\leftrightharpoons$ one far to the left, with a high proportion of reactants; intermediate stages may be represented by arrows of approximately the same length, $\rightleftharpoons$. A single arrow $\rightarrow$ indicates a complete reaction to the right; $\leftarrow$ indicates no reaction.

Chemical changes which go to completion Reactions which proceed in only one direction are *complete,* while those in which an equilibrium exists are *incomplete.* Irreversible reactions (page 220) are of necessity complete; also, every reaction becomes complete if one of the products is removed as fast as it is formed. There are three conditions under which a chemical change may proceed *practically* to completion.

(*a*) *Formation of a gas.* It is evident that removal of one of the products, as fast as it is formed, would preclude reaction in the reverse direction. Thus:

$$A + B \rightarrow C + D\uparrow$$

Suppose that D is a gas and escapes from the mixture. There is then no possibility of reaction between C and D, and the chemical change becomes complete to the right. In certain cases, the evolution of gas will depend upon the conditions under which the process is carried out. If solid NaCl is treated with concentrated H_2SO_4 and heated

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$

hydrogen chloride is evolved as a gas, and the change is complete to the right. This is the laboratory preparation of HCl. However, if a solution of NaCl in H_2O is used instead of solid salt, the reaction is incomplete, since the hydrogen chloride which may be formed remains in the solution (HCl is very soluble in water) and an equilibrium results:

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl$$

Now, if the mixture is heated, the hydrogen chloride distils off, and the change becomes complete to the right.

(*b*) *Formation of a precipitate.* A chemical change is essentially complete if one or more of the products precipitates from solution. When silver nitrate is added to a sodium chloride solution, insoluble silver chloride is produced which precipitates:

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3 \qquad (1)$$

In this case, one of the products is effectively removed from what we might term the "sphere of chemical action," and thus the change proceeds only to the right. It should be pointed out, however, that such reactions are not entirely complete, since all substances are soluble to some extent, and thus the soluble part would bring about a slight

reverse action. The more insoluble the product, the more nearly the reaction is complete.

In preparing a product in the laboratory, it is desirable to choose a chemical change which is essentially complete, since separation of the desired product is simplified. For example, a sample of $NaNO_3$ might be made according to the equation given in (1) above. If the proper amounts of reactants have been used, only AgCl and $NaNO_3$ remain. Since AgCl is insoluble, it may be filtered out, leaving $NaNO_3$ in solution. Solid $NaNO_3$ may then be obtained by evaporation of the water from the solution of the salt. This reaction would be preferable to the following

$$KNO_3 + NaCl \leftrightarrows KCl + NaNO_3$$

in which $NaNO_3$ is also a product. Since all four salts represented in the equation are soluble in water, the reaction proceeds only as the water solution is evaporated, and in accordance with the relative solubility of the component salts. (The least soluble salt would be the first to begin crystallizing from solution, and so on.) In any case, the reaction as represented is incomplete, and the separation of $NaNO_3$ from the other three would be a tedious and difficult procedure. The student should familiarize himself with the solubility of salts (see solubility rules on page 186). A knowledge of solubility rules enables us to predict whether or not a given reaction in which a salt is a product will proceed practically to completion.

(*c*) *Formation of water, an un-ionized substance.* Chemical changes between acids and bases in which water is a product are essentially complete. This may be attributed to the fact that water is a very slightly ionized substance. We shall elaborate on this particular type of reaction in the next chapter.

Le Chatelier's principle A principle of universal application to systems in equilibrium has been stated by Le Chatelier as follows: *If a stress is placed upon a system in equilibrium whereby the equilibrium is altered, that change will take place which tends to relieve or neutralize the effect of the added stress.* Consider the equilibrium reaction

$$A + B \rightleftharpoons C + D$$

We learned that an increase in concentration of any of the reactants or products would result in a shift in the equilibrium. An increase in concentration may be considered as an added stress or force. For example, if more A is added to the system, thereby increasing the concentration or stress of A, the equilibrium is shifted to the right, since by doing so A is used up in the reaction and consequently the stress (increase

in concentration of A) is relieved or diminished. On the other hand, if A is removed (the concentration of A decreased), the equilibrium will shift to the left, resulting in the formation of more A. The stress in this case is the removal of A, and the system tends to relieve or diminish this stress by forming more of A. Other stresses which may be imposed upon a system are the addition of heat (increase of temperature) and the application of pressure.

Effect of pressure upon a system in equilibrium Consider a reaction in which a relatively large change in volume occurs, for example,

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

The reactants N_2 and H_2 and the product NH_3 are all gaseous at ordinary temperatures. According to the equation, one volume of nitrogen reacts with three volumes of hydrogen to produce two volumes of ammonia. It is evident, then, that four volumes of reactants produce only two volumes of products, a decrease in volume as the reaction proceeds from left to right. We may readily predict the effect of increased pressure on this system from Le Chatelier's principle. If the pressure on the system is increased, the reaction will proceed to the right in the direction of smaller volume, because a decrease in volume will tend to relieve the added stress (pressure). If the added stress is a decrease of pressure, the reaction will be favored in which there is a volume increase, since an increase in volume will tend to offset or neutralize the decrease in pressure. This would result in a displacement of equilibrium to the left. A high pressure would be favorable in the production of ammonia by the above process, since the higher the pressure, the greater will be the displacement of the equilibrium to the right. A decrease in pressure would have the opposite effect, and the equilibrium would be displaced to the left.

Certain gaseous reactions involve no change in volume, for example,

$$H_2 + I_2\,(gas) \rightleftharpoons 2\,HI$$

A total of two volumes (one of hydrogen and one of iodine) of reactants produce two volumes of products (two volumes of hydrogen iodide). Pressure has no effect upon such a system as there is no volume change in the reaction.

The effect of temperature on an equilibrium All chemical changes are accompanied by changes in energy; certain reactions are exothermic—produce heat during the reaction; others are endothermic—absorb heat. In the reaction

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 + 24{,}000 \text{ calories}$$

nitrogen and hydrogen, in combining to form ammonia, produce heat which is arbitrarily designated by a + sign. When ammonia undergoes decomposition into nitrogen and hydrogen (the reverse of the reaction), an equivalent amount of heat must be taken up or absorbed. Heat absorbed will be designated by a − sign. When the system is at equilibrium, no heat change is taking place.

Let us apply Le Chatelier's principle to an equilibrium in which heat is added to the system (increase of temperature). To relieve the strain (increase of temperature) the system will absorb heat and in this way use up the added heat. Consider an equilibrium mixture of ice and water. A solid, in melting, absorbs heat. If an equilibrium mixture of ice and water is heated, the ice melts and absorbs heat, and the temperature does not rise above 0° until all of the ice is melted. The equilibrium proportions of ice and water shift so as to use up the newly applied heat.

In the reaction given above in which ammonia is produced, an increase of temperature would favor the reaction to the left—that is, the formation of nitrogen and hydrogen from ammonia, since that is the reaction which absorbs heat.

It should be realized that Le Chatelier's principle has considerable significance from a practical standpoint. If ammonia were being produced commercially by the method above, it would be desirable to have the equilibrium displaced as far to the right as possible, since this would mean a greater yield of ammonia. In order to accomplish this, a high pressure and a low temperature would be desirable. Ammonia is actually produced commercially (Haber process) by this reaction at a pressure of several hundred atmospheres and a temperature of 400°–500°. This temperature is rather high, but it is the minimum temperature which is feasible for the process, as the reaction between H_2 and N_2 to attain equilibrium takes place too slowly at lower temperatures.

If N_2 and H_2 gases are mixed at ordinary temperatures, reaction between them is so slow that thousands of years might elapse before equilibrium proportions of N_2, H_2, and NH_3 would be reached. However, at 400°–500°, equilibrium proportions are reached in a matter of minutes. Although the equilibrium proportions at the higher temperature are not quite so favorable as at ordinary temperature, time to attain equilibrium is very much reduced. It is economically feasible to obtain a 17.6 per cent yield of NH_3 by using 400°–500° temperature and 200 atmospheres pressure in a matter of minutes, then condense out the NH_3 and recycle the unused N_2 and H_2. It is not economically feasible to use room temperature and 200 atmospheres pressure to attain a much greater percentage of NH_3, for it would require ages of time.

Catalysts and equilibrium A catalyst cannot displace an equilibrium, but it may greatly reduce the time necessary for the establishment of equilibrium. This is extremely important from an industrial standpoint, since the speed at which a product can be produced is a primary consideration. Catalysts may be effectively used in many reactions which allow conversion of only a small percentage of reactants into products (equilibrium far to the left). From a production standpoint, it is more important to obtain a small yield in a few minutes than to obtain a larger yield if the latter required several days. A catalyst by its presence adds no energy to a system, and thus cannot alter equilibrium proportions.

EXERCISES

1 How does chemical equilibrium differ from physical equilibrium?

2 Differentiate between reversible and irreversible reactions.

3 What factors influence the speed of a reaction?

4 List the factors which may displace an equilibrium.

5 Under what conditions do reactions proceed to completion?

6 Write equations for four different methods of preparing KCl. Reactions must go to completion.

7 The following salts are soluble in water: $BaCl_2$, Na_3PO_4, $Al(NO_3)_3$, $CuSO_4$, KCl, $(NH_4)_2CO_3$, $ZnBr_2$, CaS, $Mg(C_2H_3O_2)_2$. (*a*) From this list select five pairs which brought together in solution form a precipitate. Write the equations. (*b*) Select five pairs which form no precipitate.

8 What is the effect of increased temperature and pressure on the following systems in equilibrium? All reactants and products are in the vapor state.

(*a*) $2\,X_2 + Y_2 \rightleftharpoons 2\,X_2Y_2 - 200$ calories

(*b*) $H_2 + I_2 \rightleftharpoons 2\,HI - 630$ calories

(*c*) $CO + Cl_2 \rightleftharpoons COCl_2 + 48{,}770$ calories

(*d*) $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 + 24{,}000$ calories

(*e*) $N_2 + O_2 \rightleftharpoons 2\,NO - 43{,}200$ calories

9 Given the following equilibrium mixture of gases at a temperature of 200° C., underline the right answer.

$$4\,NH_3 + 7\,O_2 \rightleftharpoons 6\,H_2O + 4\,NO_2 + \text{heat}$$

(*a*) Increased pressure will shift the equilibrium (left, right, not at all).

(*b*) Increased temperature will shift the equilibrium (left, right, not at all).

(*c*) Adding excess NH_3 will shift the equilibrium (left, right, not at all).

(*d*) Adding excess O_2 will shift the equilibrium (left, right, not at all).

(*e*) Adding a drying agent to absorb the water will shift the equilibrium (left, right, not at all).

10 Phosphorus pentachloride dissociates according to the equation:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

At a given temperature the dissociation is 20 per cent (to the right). (*a*) If we start with 0.5 mole PCl_5 in 1 liter, what will be the equilibrium concentrations

of the three constituents? (*b*) Calculate the value for the equilibrium constant.

Ans. (*a*) PCl_5 0.4 mole
PCl_3 0.1 mole
Cl_2 0.1 mole
(*b*) 0.025

11 $$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

An equilibrium mixture of the above gaseous mixture was analyzed and found to contain 0.4 mole of N_2, 0.2 mole of H_2, and 0.1 mole of NH_3 in 1 liter. Calculate the value for the equilibrium constant. Ans. 3.1.

12 If HI is 25 per cent dissociated according to the equation

$$2\,HI \rightleftharpoons H_2 + I_2$$

at a given temperature (*a*) calculate the equilibrium concentrations of HI, H_2, and I_2 if we start with 10 moles of HI in a one liter container, (*b*) calculate the value for the equilibrium constant.

13 $$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

At a given temperature this reaction is 20 per cent complete to the right. If 1000 molecules of nitrogen and 3000 molecules of hydrogen are mixed and heated to this given temperature, how many molecules of each of these gases will be present at equilibrium?

14 $$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$$

A reaction vessel with a capacity of one liter, in which the above reaction had reached a state of equilibrium, was found to contain 0.6 mole of SO_3, 0.2 mole of SO_2, and 0.3 mole of O_2. Calculate the equilibrium constant.

15 From the list of available starting materials select suitable compounds from which $MgCl_2$ may be prepared and show by balanced equations the reactions employed. Reactions must be complete. Available starting materials: $MgSO_4$; $FeCl_2$; HCl; $NaNO_3$; H_2SO_4; MgO; Mg; $BaCl_2$.

16 A liter reaction vessel containing the equilibrium mixture:

$$CO + Cl_2 \rightleftharpoons COCl_2$$

was found to contain 0.1 moles of $COCl_2$, 0.1 mole of CO and 0.5 moles of Cl_2. If 0.3 mole of CO is added at constant temperature, what will be the new concentrations of each component at equilibrium?

Ans. $COCl_2 = 0.577$; $CO = 0.223$; $Cl_2 = 0.323$.

17 At equilibrium in the system

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

concentrations are as follows; CO, 0.2 moles per liter; H_2O, 1.2 moles per liter; H_2, 0.8 moles per liter; CO_2, 0.8 moles per liter. (*a*) Calculate the equilibrium constant. (*b*) If the concentrations are changed such that CO is 0.5 moles per liter, H_2O is 1 mole per liter, and H_2 is 1 mole per liter, what must be the concentration of CO_2 at equilibrium, assuming no change in temperature?

18 At a given temperature, the equilibrium mixture

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

was analyzed and found to contain the following concentrations of gas measured in moles per liter: N_2, 0.4; H_2, 0.3; NH_3, 0.2. If hydrogen is introduced into the system at constant temperature so that its equilibrium concentration becomes 0.5 moles per liter, what must be the concentration of NH_3? Ans. 0.38.

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eighteen

THE THEORY OF IONIZATION

Introduction Modern theory of atomic structure (Chapter 3) has familiarized us with the nature of atoms, molecules, and ions. Ions are atoms or atomic groups which have either an excess or a deficiency of electrons.

The theory of ions originated with Faraday in 1832 and was extended by the Swedish chemist, Arrhenius, in 1887, many years prior to the modern concepts of atomic structure. The theory has undergone considerable modification since that time and is now successful in interpreting many hitherto inexplicable phenomena.

It will be recalled from Chapter 1 that theories are designed to explain facts obtained by experimentation. The modern scientist obtains experimental data and then seeks to explain the results obtained. These experimental facts may be explained by means of certain assumptions which are not subject to direct experimentation. This set of assumptions and its explanation of facts constitute the theory. As more data are obtained which are not readily explained by the assumptions, the theory will undergo modification.

In the sections to follow, we shall first outline the experimental evidence upon which the theory of ionization is based; second, the assumptions of the theory; and finally we shall be interested in the way the theory explains the experimental facts.

Facts leading to the ionization theory (1) *Aqueous solutions of acids, bases, and salts are conductors of the electric current.* With the aid of an apparatus as shown in Figure 18–1, the conductivity of solutions may be conveniently studied. The apparatus consists of two electrodes (copper wires may be used) connected in series with a 110-volt alternating-cur-

rent source and an ordinary electric light bulb. The electrodes are immersed in the solution whose conductivity is to be tested. If a current flows across the solution between the electrodes, the bulb will light, and the degree of conduction of the electric current is roughly indicated by the intensity of light shown in the bulb. If the solution is a good conductor (that is, if the resistance offered to the passage of the current is small), the bulb will show a bright light. But if resistance is high, the current cannot pass through the solution readily, resulting in a dim light or no light at all. In Table 18–1, the results obtained with various substances in aqueous solutions are summarized.

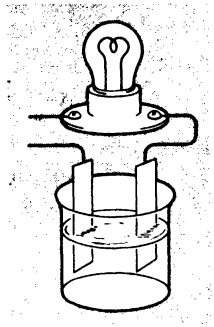


Figure 18–1 Apparatus for measuring electrical conductance of solutions.

Substances that conduct the electric current in aqueous solution are *electrolytes;* those showing no conduction are *nonelectrolytes.* From Table 18–1, we note: (1) acids, bases, and salts are electrolytes; (2) compounds differ in degree of conductivity—hydrochloric acid is a good conductor, acetic acid is only a fair conductor. Although acids, bases, and salts may show different degrees of conduction, in aqueous solution these classes of compounds all conduct the current to some extent. Even tap water shows some conduction because of dissolved mineral salts.

We may ask these questions: Why do acids, bases, and salts in aqueous solution conduct an electric current, while other substances in solution do not? Why are some electrolytes better conductors of current than others? We shall soon find the answers to these questions.

(2) *Aqueous solutions of acids, bases, and salts show abnormal boiling points and freezing points.* In the study of solutions it was pointed out that one mole of a substance (nonelectrolyte) dissolved in 1000 grams of water

TABLE 18–1 Conductivity of Aqueous Solutions

SUBSTANCE	LIGHT INTENSITY	CLASSIFICATION AS CONDUCTOR
HCl	bright	very good
NaOH	bright	very good
NH_3	dim	fair
$HC_2H_3O_2$	dim	fair
Sugar	none	nonconductor
HCl (in toluene)	none	nonconductor
Alcohol	none	nonconductor
Water (distilled)	none	nonconductor
Water (tap)	very dim	poor
NaCl	bright	very good
$CuSO_4$	bright	very good

(this would be a 1 molal solution) produced an elevation of the boiling point of 0.52° and a depression of the freezing point of 1.86°. One mole of any substance contains about 6×10^{23} molecules. It follows that the elevation of the boiling point 0.52° and the depression of the freezing point 1.86° are produced by this number of particles or molecules in 1000 grams of water. A solution containing twice this number of molecules (12×10^{23}) gives a boiling point elevation of $2 \times 0.52° = 1.04°$, and a freezing point depression of $2 \times 1.86° = 3.72°$. These properties, then, are dependent upon the number of dissolved particles. 0.52° is referred to as a normal elevation of the boiling point and 1.86° as a normal depression of the freezing point of water.

Table 18–2 reveals that electrolytes in aqueous solution exhibit abnormalities with respect to boiling point elevation and freezing point depression—sodium chloride produces almost double, and calcium chloride almost three times, the normal effect.

TABLE 18–2 Effect of Solutes on the Boiling and Freezing Points of Water

SUBSTANCE (1 mole in 1000 g. H_2O)	ELEVATION OF B.P.	DEPRESSION OF F.P.
$CO(NH_2)_2$ (urea)	.52° (normal)	1.86° (normal)
$C_{12}H_{22}O_{11}$	.52° (normal)	1.86° (normal)
NaCl	.97° (abnormal)	3.49° (abnormal)
$CaCl_2$	1.3° (abnormal)	4.83° (abnormal)
$AlCl_3$	1.73° (abnormal)	5.68° (abnormal)

Since the boiling point elevation is a function of the number of dissolved particles, it would seem that a mole of sodium chloride must furnish about twice as many particles in solution as a mole of a substance like sugar, which shows a normal effect on the boiling and freezing points of water. Since calcium chloride produces about three times the normal effect, about three times as many particles would be necessary. How can we account for the apparent increase in the number of particles present in aqueous solutions of acids, bases, and salts? We note that those substances which produce abnormal boiling and freezing points are the same substances which conduct the electric current in aqueous solution.

(3) *Reactions in solution.* Acids, bases, and salts in general show characteristic properties only in solution. For example, solid sodium chloride shows no tendency to react with solid silver nitrate when the two dry substances are mixed. However, if, to a solution of sodium chloride, is added a solution of silver nitrate, reaction takes place immediately according to the equation

$$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$$

Likewise, other substances which do not react in the pure state readily do so when dissolved in water.

Acids and bases exhibit their characteristic properties only in solution in water or certain other liquids. Pure HCl has little or no effect on litmus, but a water solution of hydrogen chloride turns blue litmus paper red. Similarly, pure sodium hydroxide has no effect on litmus, but a water solution shows the characteristics of a base—turns litmus blue and tastes bitter.

(4) *Molten salts are conductors.* Many molten salts are good conductors of the electric current—indeed the electrolysis of molten sodium chloride is a commercial means of producing metallic sodium.

Assumptions of the ionization theory To explain these facts, the following assumptions are made (the original assumptions of Arrhenius have been modified somewhat to explain adequately experimental evidence not known when the theory was proposed):

(*a*) *Electrolytes (acids, bases, salts) in aqueous solution produce two or more charged parts called ions.* A given electrolyte may yield one or more positive ions and one or more negative ions. The total positive charge on the ions is equal to the total negative charge on the ions.

Acids which are covalent compounds produce ions by the transfer of a proton from the acid molecule to a water molecule for example:

$$HCl + H_2O \rightarrow \underset{\text{hydronium ion}}{H_3O^+} + Cl^-$$

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

$$H_2SO_4 + 2\,H_2O \rightarrow 2\,H_3O^+ + SO_4^{--}$$

Although water plays an important role in the ionization of acids in producing the hydrated hydrogen ion (hydronium ion), the ionization of acids will ordinarily be shown as giving the simple hydrogen ion; for example,

$$HCl \rightarrow H^+ + Cl^-$$

This is justified since there is considerable uncertainty as to the degree of hydration of the hydrogen ion (the amount of water per hydrogen ion is probably more than one molecule). In simplifying the ionization process, we must remember that free hydrogen ions probably do not exist in aqueous solution but are hydrated to some degree.

Metallic hydroxides are termed *bases.* Those which are soluble in water—NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$—furnish hydroxide ions. NH_4OH also furnishes OH^- and is included as a base:

$$NaOH \rightarrow Na^+ + OH^-$$

$$Ca(OH)_2 \rightarrow Ca^{++} + 2\,OH^-$$

$$NH_4OH \rightarrow NH_4^+ + OH^-$$

Salts yield metallic ions (or complex positive ions) and acid radical ions:

$$NaCl \rightarrow Na^+ + Cl^-$$
$$CaCl_2 \rightarrow Ca^{++} + 2\,Cl^-$$
$$K_2SO_4 \rightarrow 2\,K^+ + SO_4^{--}$$
$$UO_2SO_4 \rightarrow UO_2^{++} + SO_4^{--}$$

Not all compounds in aqueous solution are ionized; for example, sugar and other solutes which do not give a conducting solution form no ions.

(*b*) *The number of charges on an ion is equal to its valence.*

(*c*) *Ionization of acids is not complete;* in all cases, undissociated molecules are in equilibrium with the ions; for example

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

or simply

$$HCl \rightleftharpoons H^+ + Cl^-$$

The extent of ionization (the degree of completeness of the above reaction to the right) is dependent upon both the solute and solvent.

An acid which can furnish more than one proton per molecule is termed a *polyprotic* (also called polybasic) acid. Thus H_2SO_4 is a *diprotic* acid; H_3PO_4 is a *triprotic* acid. When these acids are dissolved in water, ionization takes place in successive stages; for example, H_2SO_4 shows two stages of ionization:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^- \quad (1)$$
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{--} \quad (2)$$

or more simply

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \quad (1)$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{--} \quad (2)$$

The first reaction is much more complete than the second; that is, the equilibrium is displaced much farther to the right. Both H_2SO_4 and HSO_4^- are acting as acids in the reactions above, since each liberates or releases a proton to a water molecule. H_2SO_4 is said to be a stronger acid than HSO_4^- since reaction (1) is more complete than reaction (2). In general, if an acid ionizes in successive stages, each succeeding stage is less complete than the preceding one.

(*d*) *In general, salts and soluble metallic hydroxides are completely ionized, even in the solid state.*

Let us now interpret the facts which we have outlined by the assumptions we have made.

The conduction of the electric current The fact that electrolytes in water solution conduct the electric current is explained by assuming that

the ions act as carriers of the current across the solution between the electrodes Electrolysis consists in the discharge of ions at the electrodes of a cell through which a current is passing During the electrolysis of a copper chloride solution, for example (Figure 18–2), Cu^{++} ions move toward the negative pole of the cell (the cathode) and the Cl^- ions move toward the positive pole (the anode). Accordingly, positively charged ions are called *cations*, and negatively charged ions *anions* At the anode the Cl^- ion loses its charge and becomes a chlorine atom When two chlorine atoms are liberated, they unite to form a chlorine molecule (Cl_2) At the cathode each Cu^{++} ion is discharged and forms a copper atom Thus free chlorine is formed at the anode and metallic copper is produced at the cathode

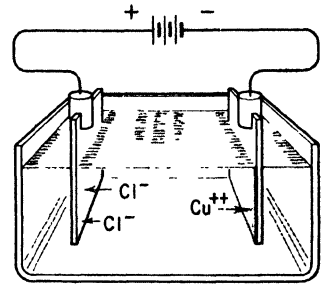


Figure 18–2 When an aqueous solution of cupric chloride is electrolyzed, metallic copper is plated out on the cathode, and chlorine gas is liberated at the anode.

The conductivity of a solution depends primarily upon two factors: (1) the number of ions present and (2) the speed at which the ions move through the solution The greater the number of ions and the greater the speed at which they travel, the better the conductivity of the solution

We noted that some electrolytes are better conductors than others, for example, hydrochloric acid is a very good conductor, while acetic acid is only fair We may explain the better conduction of hydrochloric acid by assuming that more ions are produced when mole quantities of hydrogen chloride are dissolved in water than when mole quantities of acetic acid are dissolved in water—that is, hydrochloric acid is more highly ionized than acetic acid.

The fraction of molecules which break up into ions is referred to as the *degree of ionization* Thus, if one half of the molecules dissolved in solution break up into ions, the electrolyte is said to be 50 per cent ionized, a degree of ionization of 0.5. The degree of ionization of a mole of solute appears to depend upon the extent of dilution. For example, pure liquid HCl is not ionized (0 per cent ionized). A mole of HCl in a small amount of water is only slightly ionized. However, a mole of HCl at infinite dilution would theoretically be completely ionized (100 per cent ionized). Similarly, a mole of salt appears to increase in degree of ionization with dilution.

Since the conductivity of a solution depends upon the number of ions, electrical conductivity measurements have been used to determine an apparent degree of ionization. The conductance by ions from a mole of electrolyte in dilute solution is greater than the conductance by ions from a mole of the same electrolyte in concentrated solution. Hence the molar conductance increases with dilution and would reach a maximum value in an infinitely dilute solution in which the ionization would presumably be 100 per cent. The degree of ionization at any concentration of electrolyte, then, may be calculated from the expression

$$\text{Apparent Degree of Ionization} = \frac{\text{Conductance at a Given Concentration}}{\text{Conductance at Infinite Dilution}}$$

A degree of ionization obtained by this method would be a true value only if no factors other than number of ions were responsible for conduction. As will be shown later, other factors are involved; therefore, the degrees of ionization obtained here are termed *apparent degrees of ionization*. Table 18–3 shows the apparent degree of ionization of several electrolytes as calculated from conductivity data.

TABLE 18–3 Degree of Ionization of Electrolytes in Aqueous Solution*

COMPOUND	IONIZATION	CONCENTRATION OF SOLUTION (normality)	APPARENT DEGREE OF IONIZATION
HCl	$H^+ + Cl^-$	1.0	0.78
HCl	$H^+ + Cl^-$	0.5	0.86
HBr	$H^+ + Br^-$	0.5	0.90
HNO_3	$H^+ + NO_3^-$	1.0	0.82
H_2SO_4	$2H^+ + SO_4^{--}$	1.0	0.51
H_3PO_4	$3H^+ + PO_4^{---}$	0.5	0.17
KOH	$K^+ + OH^-$	1.0	0.77
NaOH	$Na^+ + OH^-$	1.0	0.73
NH_4OH	$NH_4^+ + OH^-$	1.0	0.004
KCl	$K^+ + Cl^-$	0.1	0.86
$BaCl_2$	$Ba^{++} + 2Cl^-$	0.1	0.72
K_2SO_4	$2K^+ + SO_4^{--}$	0.1	0.72
$CuSO_4$	$Cu^{++} + SO_4^{--}$	0.1	0.45

* Data taken from Handbook of Chemistry and Physics, Chemical Rubber Publishing Co.

Abnormal boiling points and freezing points of aqueous solutions Table 18–2 (page 234) shows that NaCl produces about double the expected or normal effect in lowering the freezing point and raising the boiling point of water. Since these properties are dependent upon the number of dissolved particles, we must assume that almost twice as many particles are present. This is easily accounted for if we assume that most units of NaCl produce two ions:

$$NaCl \rightarrow Na^+ + Cl^-$$

Calcium chloride produces nearly three times the normal effect on the boiling and freezing points of water and this fact is likewise easily explained if we assume that each unit of $CaCl_2$ produces one calcium ion and two chloride ions, a total of three ions per unit:

$$CaCl_2 \rightarrow Ca^{++} + 2\,Cl^-$$

On this basis, we would expect an electrolyte which furnishes four ions to depress the freezing point of water four times the normal (1.86°); if five ions are produced, the effect would be five times the normal, and so on.

However, we may note from Table 18–2 that the effects are not quite twice, three, and four times the normal effect; for example, a molal solution of NaCl freezes at −3.49° which is not quite twice the expected effect, $2 \times -1.86° = -3.72°$. The logical explanation of this might seem to be that the ionization of NaCl is not complete—that is, not all NaCl units produce Na^+ and Cl^-. This was the explanation as originally given by Arrhenius. However, present-day evidence indicates that NaCl and other salts are 100 per cent ionized, and we must seek another explanation of the fact that boiling points and freezing points are not what might be expected.

Ionization of salts Debye and Hückel in 1922 extended the theory, earlier suggested by A. A. Noyes and others, that strong electrolytes are 100 per cent ionized. Recent studies have shown that many substances in the solid state consist of ions. Consequently, ions are present before the substance is dissolved in solution. Solution is not necessary for the ionization process; for example, X-rays have shown that sodium chloride in the solid state is composed of ions (Figure 18–3); each sodium atom has given up one electron and each chlorine atom has gained an electron. In the sodium chloride crystal, each sodium ion is surrounded by six chlorine ions (Figure 18–3). Similarly, each chlorine ion is surrounded by six sodium ions. This definite orientation or position of the ions in a salt crystal makes up a crystal lattice as shown in Figure 18–3.

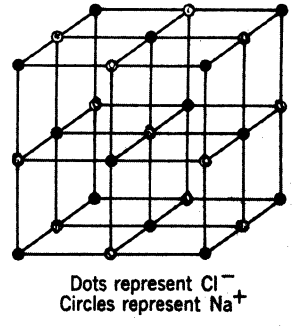


Figure 18–3 Structure of NaCl.

The existence of ions in the solid state is indicated by other facts; for example, many molten salts conduct the electric current.

Dissolving of electrovalent compounds in water When an electro-

valent compound such as NaCl is brought into contact with water, the forces of attraction between the ions in the crystal lattice are so weakened by the attraction of water dipoles (see Chapter 11) that the ions separate from the lattice and are dispersed in the solvent. Positive sodium ions are attracted by the negative ends of the water dipoles; likewise, the negative chloride ions are attracted to the positive ends of water dipoles so that each ion becomes surrounded with a shell of water molecules (see Figure 15–1). The *dielectric constant* is a measure of this ability of a solvent to weaken the forces of attraction between ions. Water has a dielectric constant of about 80 as compared to air as 1. This means that the force of attraction between ions in a water medium is only about $\frac{1}{80}$ as great as between ions in a medium of air. The high dielectric constant for water explains the relatively greater solubility of salts in water than in other solvents of lower dielectric constant.

Apparent and true degrees of ionization Arrhenius explained the conductivity of electrolytes on the basis of the number of ions produced in a solution. A solution of sodium chloride shows only about 90 per cent of the conduction that might be expected if it were completely dissociated into ions. Arrhenius explained this by assuming that the NaCl is 90 per cent ionized—that is, 90 out of every 100 molecules of NaCl are dissociated into ions and the remaining 10 molecules are undissociated and in equilibrium with the ions:

$$NaCl \rightleftharpoons Na^+ + Cl^- \text{ (Arrhenius)}$$

According to the modern theory NaCl is completely ionized:

$$NaCl \rightarrow Na^+ + Cl^- \text{ (Debye-Huckel)}$$

The latter theory explains the conductivity on the basis of the speed at which the ions move through the solution. When NaCl is dissolved, the sodium and chloride ions are further separated than in the crystal but tend to retain their position or orientation. In other words, each ion is surrounded by six ions of opposite charge. An ionic atmosphere of opposite charge is thus formed about each ion, and this results in a restricted movement of the ions; the ions cannot act independently of one another in the solution. The attractive force of the ions of opposite charge tends to exert a "drag" on the ion which is moving; consequently the mobility or speed of the ion is decreased. Therefore, NaCl acts as if it were 90 per cent ionized—that is, the salt gives the same conductance as would a solution in which 90 out of every 100 ions were unrestricted in their movement through a solution.

Likewise, freezing and boiling point studies may explain the apparent degree of ionization of a salt solution. NaCl does not produce quite

twice the effect on the boiling and freezing points of water (Table 18–2) since the ions are not entirely independent of their neighbors. If movement of the ions was unrestricted, then we should expect NaCl to produce exactly *twice* the normal depression of the freezing point of water; calcium chloride would produce three times the effect; aluminum chloride, four times; and so on.

The strength of electrolytes In aqueous solution, according to the ionic theory, all acids produce $H^+(H_3O^+)$, and this ion is responsible for the chief characteristics of an acid. In like manner, the similar properties of metallic hydroxides in aqueous solution are readily explained on the basis of OH^- ions, which are responsible for the bitter taste, soapy slippery feeling, and effect on litmus.

The strength of any electrolyte is measured by the concentration of ions produced in solution; thus, a strong acid would be one which furnishes a high concentration of H^+ ions. HCl is classed as a strong acid, since it is about 90 per cent ionized—that is, 90 out of every 100 molecules of HCl produce H^+ and Cl^- ions. Acetic acid is a weak acid, since it is only about 1 per cent ionized; only one molecule out of every 100 produces H^+ and $C_2H_3O_2^-$ ions.

A strong metallic hydroxide is one which gives a high concentration of OH^- ions in aqueous solution. The common strong bases are NaOH, KOH, $Ca(OH)_2$, and $Ba(OH)_2$; most others are weak.

In general, salts would be classed as strong electrolytes.

Neutralization reactions It was pointed out in Chapter 10 that an acid reacts with a metallic hydroxide (base) in aqueous solution to form a salt and water—a type of reaction called neutralization. Let us examine a few reactions of this type from an ionic standpoint:

$$NaOH + HCl \rightarrow NaCl + H_2O \text{ (molecular equation)}$$
$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O \text{ (ionic equation)}$$

NaOH, which is a strong base, gives Na^+ and OH^- ions in solution; HCl, a strong acid, furnishes H^+ ions as a result of its reaction with water. Water, since it is only slightly ionized, is written in the molecular form.

$$2\,KOH + H_2SO_4 \rightarrow K_2SO_4 + 2\,H_2O \text{ (molecular equation)}$$
$$2\,K^+ + 2\,OH^- + 2\,H^+ + SO_4^{--} \rightarrow 2\,K^+ + SO_4^{--} + 2\,H_2O \text{ (ionic equation)}$$

Note that in the two ionic equations above all ions except H^+ and OH^- may be canceled so that the essential change in the neutralization process is

$$H^+ + OH^- \rightarrow H_2O$$

Further evidence to show that this is the fundamental reaction of

neutralization is gained from thermal studies of the reactions of strong acids and bases; for example,

$$KOH + HCl \rightarrow KCl + H_2O + 13{,}700 \text{ calories}$$
$$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O + 13{,}700 \text{ calories}$$

Other reactions of strong acids and bases produce the same thermal change—13,700 calories per gram equivalent of acid or base neutralized. From an ionic standpoint all of these reactions involve simply the combination of H^+ and OH^- ions to form water; hence this thermal change must be the heat of the reaction:

$$H^+ + OH^- \rightarrow H_2O + 13{,}700 \text{ calories}$$

The neutralization of a strong base by a weak acid—for example, sodium hydroxide by acetic acid, might at first appear confusing to the student.

$$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$$

According to the equation, 1 mole of NaOH reacts with 1 mole of acetic acid. Since sodium hydroxide is highly ionized and acetic acid only weakly ionized, it might appear that a large excess of OH^- ions would be present in the solution, and reaction would stop after the relatively few hydrogen ions from acetic acid were neutralized. However, the neutralization is complete because as H^+ ions are used up in reaction with OH^- ions, more acetic acid ionizes, producing more H^+ ions. This process continues until the acetic acid has completely ionized. Likewise, in the neutralization of a weak base, OH^- ions would continue to be formed until neutralization was complete.

The Bronsted theory of acids and bases In aqueous solutions, the hydroxide ion, OH^-, is responsible for basic properties. The fundamental reaction of neutralization is

$$OH^- + H^+ \rightarrow H_2O$$

In this reaction, we may say that the hydroxide ion has accepted a proton. In order to extend the ideas of acid-base phenomena to solvents other than water, Bronsted, a Danish scientist, has proposed that anything which will accept a proton be termed a base, while anything which donates a proton be termed an acid. In other words, a base is a proton *acceptor*, an acid a proton *donor*. According to this concept, the reaction of HCl with liquid ammonia would be analogous to its reaction with water:

$$HCl + H_2O \rightleftharpoons \underset{(H_3O^+)}{H^+ \cdot H_2O} + Cl^- \qquad (1)$$

$$HCl + NH_3 \rightleftharpoons \underset{(NH_4^+)}{H^+ \cdot NH_3} + Cl^- \qquad (2)$$

In this case, NH_3 acts as the base since it accepts a proton from HCl to form ammonium ion, NH_4^+

In general, a proton donor reacts with a base according to the general reaction, where A is an anion

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{B} \rightleftharpoons \underset{\text{acid}}{H^+ \cdot B} + \underset{\text{base}}{A^-}$$

By far the most common usage of this concept of a base will be in water solutions where the base is OH^- ion

Other acid-base reactions Consider the reverse of equation (1) above

$$\underset{\text{acid}}{H^+ \cdot H_2O} + \underset{\text{base}}{Cl^-} \rightleftharpoons \underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O}$$

The hydronium ion $H^+ \cdot H_2O$ is giving up a proton to a Cl^- ion to form HCl Thus H_2O is acting as an acid, since it is here a proton donor Cl^- ion is a base, since it accepts a proton The reverse of equation (2) above is analogous

$$\underset{\text{acid}}{H^+ \cdot NH_3} + \underset{\text{base}}{Cl^-} \rightleftharpoons \underset{\text{acid}}{HCl} + \underset{\text{base}}{NH_3}$$

According to this concept, then, acids and bases may be either molecular or ionic From the two reactions above, we may tabulate the acids and bases

ACIDS	BASES
H_3O^+	Cl^-
HCl	H_2O
NH_4^+	NH_3

The Lewis theory A concept of acids and bases which is more general in its application is that introduced by G N Lewis According to the Lewis theory, any substance which has an unused pair of electrons (such as NH_3) may be considered as a base, while any substance which may attach itself to such an available pair of electrons would be classed as an acid For example, in the reaction of an acid anhydride with a basic anhydride to form a salt

$$SO_3 + CaO \rightarrow CaSO_4$$

$$\begin{matrix} O \\ S\ O \\ O \end{matrix} + O\ Ca \rightarrow \left[\begin{matrix} O \\ O\ S\ O \\ O \end{matrix}\right]^{--} Ca^{++}$$

CaO would be considered a base and SO_3 an acid In the Lewis theory, a base is an *electron pair donor* and an acid an *electron pair acceptor*

If we apply the Lewis theory to the ionization of acids, for example, to

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

we would classify H_2O as a base, since it donates a pair of electrons to H^+

Other reactions in aqueous solution The fact that certain reactions which do not take place between pure substances do proceed in aqueous

solution is explained by assuming that the reaction takes place between ions which are free to move about in the solution. Although solid NaCl and solid $AgNO_3$ do not react, when these are dissolved in water and the solutions mixed, a reaction takes place immediately with the formation of insoluble silver chloride From an ionic standpoint

$$Ag^+ + NO_3^- + Na^+ + Cl^- \rightarrow AgCl\downarrow + Na^+ + NO_3^-$$

In solution the ions are free to move about and collide with other ions In the above equation it is evident that the actual reaction is between Ag^+ and Cl^- ions to form AgCl. Na^+ and NO_3^- ions appear on both sides of the equation and may be canceled out. The Na^+ and NO_3^- ions are incidental to the primary reaction and may be replaced by other ions, for example, nitrate ion might be replaced with acetate or sulfate ion, and sodium ion might be replaced with any metal ion whose chloride is soluble. Hence the essential reaction of any soluble chloride salt and any soluble silver salt is

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

It will be recalled from the study of chlorides that Ag^+ ions constitute a test for their presence All chlorides act with Ag^+ ions to give insoluble AgCl as shown above.

The molecular formula is used to show the silver chloride, even though the solid is composed of ions. This convention will henceforth be used to differentiate between a solid electrolyte and a solution of its ions Sodium chloride, for example, in the solid state will be written as NaCl, but in solution will be shown as $Na^+ + Cl^-$

Many other precipitation reactions similar to the one described above will be encountered subsequently. From an ionic standpoint the fundamental reaction will always be a union of the ions of which the precipitate is composed

Double salts A number of naturally occurring crystalline minerals have formulas that correspond to a combination of two salts—for example, the minerals carnallite, $KCl \cdot MgCl_2 \cdot 6\,H_2O$, and schönite, $K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O$. As a solution of mixed salts crystallizes, there is frequently formed between the salts a crystalline compound of fixed composition. Some commonly prepared compounds of this nature are Mohr's salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\,H_2O$, and an alum, $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$. Salts of this kind which in solution give the individual metal ions and nonmetal (or negative radical) ions are called *double salts.* Such salts in solution exhibit chemical changes appropriate for each respective ion.

Complex salts Certain salts are termed complex because of the manner

of their ionization. For example, we might write the formula of potassium ferrocyanide as $Fe(CN)_2 \cdot 4\,KCN$ or as $K_4Fe(CN)_6$. The first formula implies a double salt, which, according to our discussion above, should give the ions of each salt in solution—that is Fe^{++}, CN^-, and K^+. Actually, very few Fe^{++} ions or CN^- ions are present in solution; the ions found are K^+ and $Fe(CN)_6^{----}$ (ferrocyanide). The second formula is preferable to the first for representing the composition of this salt, and the ionization would be shown as:

$$K_4Fe(CN)_6 \rightarrow 4\,K^+ + Fe(CN)_6^{----}$$

Other examples are

$$PbSiF_6 \rightarrow Pb^{++} + SiF_6^{--}$$
$$Na_3AlF_6 \rightarrow 3\,Na^+ + AlF_6^{---}$$
$$Na_2PtCl_6 \rightarrow 2\,Na^+ + PtCl_6^{--}$$
$$Na_3AsS_3 \rightarrow 3\,Na^+ + AsS_3^{---}$$

These compounds are called *complex salts* since in their ionization only two kinds of ions are formed, a single element ion and a complex ion. Since complex ions play an important role in chemistry in understanding many type reactions, some solubility phenomena, and certain metal ion separations, they will now be discussed briefly.

Complex ions Simple ions may sometimes combine with other ions or neutral molecules to form complex ions which in general have a high stability. Ordinarily the units in such a complex ion are held together by coordinate bonds of valence—that is, by a pair of electrons furnished by one of the ions or neutral molecules. The hydronium ion, H_3O^+, and the ammonium ion, NH_4^+, might be considered as complex ions, since a neutral molecule of water or ammonia furnishes a pair of electrons to combine with a proton (page 133).

More common examples of complex ion formation are those in which a metallic ion, such as Cu^{++}, Co^{+++}, or Ag^+, combines with a molecule or another ion to form a complex. Ammonia forms complex ions with a number of metallic ions; for example,

$$Cu^{++} + 4\,NH_3 \rightleftarrows Cu(NH_3)_4^{++}$$
$$Co^{+++} + 6\,NH_3 \rightleftarrows Co(NH_3)_6^{+++}$$
$$Ag^+ + 2\,NH_3 \rightleftarrows Ag(NH_3)_2^+$$

If NH_4OH is added to a solution of Cu^{++}, $Cu(OH)_2$ is first precipitated but redissolves as more NH_4OH is added because of the formation of $Cu(NH_3)_4^{++}$. The latter ion has a deep blue color. $Cu(OH)_2$, which is insoluble in water, is readily soluble in an aqueous solution containing free ammonia. Other hydroxides are soluble in NH_4OH if the metallic

ion forms a complex with NH_3. Consequently the formation of complex ions may be important in solubility considerations. In many cases, the number of molecules or ions combined with a simple ion is double the valence of the simple metallic ion. Thus Cu^{++} usually coordinates four such groups, Ag^+ two, and Co^{+++} six. The number of molecules or ions grouped about a central ion is referred to as the *coordination number*.

In qualitative chemical analysis, complex sulfide salts or ions are encountered in various separations. Although PbS will not dissolve in a Na_2S solution, HgS will. This is typical of a separation of metal compounds or ions; the reaction is written

$$HgS + Na_2S \rightarrow Na_2S \cdot HgS \quad \text{or} \quad Na_2HgS$$

or

$$HgS + S^{--} \rightarrow HgS_2^{--}$$

Similarly

$$As_2S_3 + 3\,Na_2S \rightarrow 3\,Na_2S \cdot As_2S_3 \quad \text{or} \quad 2\,Na_3AsS_3$$

or

$$As_2S_3 + 3\,S^{--} \rightarrow 2\,AsS_3^{---}$$

Cyanide ion, CN^-, readily forms complexes with several metallic ions

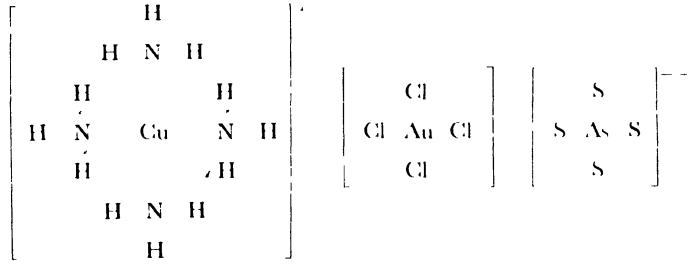
$$Ag^+ + 2\,CN^- \rightarrow Ag(CN)_2^-$$

$$Fe^{+++} + 6\,CN^- \rightarrow Fe(CN)_6^{---}$$

Silver cyanide, AgCN, which is insoluble in water, is readily soluble in excess CN^- because of the formation of the complex $Ag(CN)_2^-$ ion.

Halide ions frequently act similarly to form complex ions, such as $AuCl_4^-$, $CuCl_4^{--}$, SiF_6^{--}, $SbCl_6^{---}$, $PtCl_6^{--}$, and AlF_6^{---}.

The structures of the $Cu(NH_3)_4^{++}$, $AuCl_4^-$, and AsS_3^{---} complex ions are shown below.



Note the symmetry of these complex ions—each element (except H) has a ring of eight electrons. The charge of the complex ions can be determined by considering the charge of the central metallic ion and then the number of extra electrons added. The $Cu(NH_3)_4^{++}$ ion retains the charge of the Cu^{++} ion since the four added ammonia molecules are neutral. The $AuCl_4^-$ ion has a mono-negative charge because the Au^{+++} ion has had 4 Cl^- ions added.

The above examples represent a central metallic ion with a coordination number of 4. In many complex ions, the central ion exhibits a coordination number of 6. Spatially, these may be pictured as the coordinating groups occupying the corners of an octahedron with the metallic ion in the center. Examples are $Co(NH_3)_6^{+++}$, $PtCl_6^{--}$, and $Co(NH_3)_3(H_2O)_3^{+++}$.

EXERCISES

1 How do vapor pressure and boiling point effects show that there is a greater number of particles per mole in solutions of acids, bases, and salts than in solutions of nonelectrolytes such as sugar?

2 How may the nature of the charge borne by an ion be experimentally determined?

3 Why are solutions of certain acids and bases better conductors than others?

4 What would be the approximate freezing point of a solution which contains 234 grams of sodium chloride per 1000 grams of water? Ans. $-14°$.

5 How do the assumptions of the ionic theory explain the fact that some solutions are conductors of the electric current while others are not?

6 What is meant by "degree of ionization" or "extent of ionization"?

7 What is the difference between an ion and an atom? an ion and a molecule?

8 Although the compounds, chloroform, $CHCl_3$, and potassium chlorate contain chlorine, no precipitate is obtained with silver nitrate solution. Explain.

9 Of what unit particles are crystalline salts composed?

10 What are the essential differences between the Arrhenius and Debye-Hückel theories of ionization?

11 Write formulas of the ions present in aqueous solutions of the compounds: NaCl; Li_2SO_4; HBr; $Ca(OH)_2$; $Al(NO_3)_3$.

12 Write ionic equations for the following reactions in aqueous solution.

(*a*) $CaCl_2 + Ag_2SO_4$ (*c*) $PbCl_2 + K_2CrO_4$ (*e*) $HCl + KOH$

(*b*) $Ba(NO_3)_2 + H_2SO_4$ (*d*) $Ba(OH)_2 + HBr$

13 Discuss briefly why we believe that electrolytes exist in aqueous solution as ions. Include at least three lines of evidence to support this belief.

14 Give approximate boiling points at sea level for the following: molal H_2SO_4; suspension of 200 g. of powdered glass in a liter of water; 3.01×10^{23} glycerin molecules per liter; 0.5 molal NaCl solution.

15 Explain with the aid of an equation or equations how acids produce ions in a solution.

16 Write an ionic equation for:

(*a*) the neutralization of phosphoric acid with potassium hydroxide.

(*b*) the reaction of silver nitrate and ferric chloride solutions.

(*c*) the addition of hydrogen chloride gas to water.

(*d*) The reaction between zinc and hydrochloric acid.

17 Arrange the following solutions in order of increasing boiling point (assume almost complete ionization of the electrolytes): 18.06×10^{23} molecules of glycerin per 1000 g. H_2O; molal NaI; ten molal alcohol; 3.01×10^{23} molecules of sugar (mol. wt. 342) in 1000 g. H_2O; 0.1 molal HBr; molal K_2SO_4; normal H_2SO_4.

nineteen IONIC EQUILIBRIA

Most reactions of acids, bases, and salts are brought about in water solutions, and these necessarily involve the interaction of ions. Such processes are usually reversible, at least to some extent, and, as a result, equilibrium conditions are quickly established. To get a clear understanding of these reactions, it is necessary to know about the equilibria involved. In this chapter, we shall consider the ionic equilibria in aqueous solutions, the factors influencing these, and particularly the relationships of ionic concentrations in solutions of weak electrolytes. We shall find that ionic equilibria conform to the general principles of equilibrium processes and follow Le Chatelier's principle.

The concepts of ionic equilibria are particularly valuable in analytical chemistry, but they also find application in many other areas; for example, ion exchange in resins and gels (see water softening, page 391), biological processes involving body fluids; acidity or basicity of soils, and so on.

Ionization constants The law of mass action is applicable to ionic as well as to molecular reactions, and we may write an expression for the equilibrium constant for ionic reactions. In these cases, the equilibrium constant is usually written as K_i and termed the *ionization constant.* Thus, in the ionization of acetic acid, which is a weak electrolyte,

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

or

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

we may write

$$K_i = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

in which the bracket, [ ], represents the molar concentration of each ion or molecule. In other words, at a given temperature, the product of the concentrations of H^+ and $C_2H_3O_2^-$ ions divided by the concentration of

undissociated acetic acid must have a constant numerical value.[1] A small value for K_i means that the numerator is small as compared to the denominator, which, of course, means that the concentrations of H^+ ions and $C_2H_3O_2^-$ ions are relatively small as compared with the concentration of undissociated acetic acid. Thus the ionization constant is a measure of the extent of the dissociation and in the case of acids would be a measure of their strength, since the strength of an acid is determined by its ability to produce H^+ ions.

Obviously, if the concentrations of ions and undissociated molecules are known, K_i may be calculated. For example, in .1 molar acetic acid solution at 25° C., the acid ionizes to the extent of about 1.3 per cent. Since each molecule of acetic acid which ionizes produces one H^+ ion and one $C_2H_3O_2^-$ ion, the concentrations in the solution would be

$$[H^+] = 1 \times 013 = 0013 \text{ mole per liter}$$

and

$$[C_2H_3O_2^-] = 1 \times 013 = 0013 \text{ mole per liter}$$
$$[HC_2H_3O_2] = 1 - 0013 = 0987 \text{ mole per liter}$$

Substituting in the above formulation for K_i

$$K_i = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{0013 \times 0013}{0987} = 000018$$

usually written as 1.8×10^{-5}.

Below are given the ionization constants of a number of acids:

ACID	K_i
Acetic	1.86×10^{-5}
Benzoic	6.6×10^{-5}
Carbonic K_1	3×10^{-7}
Carbonic K_2	6×10^{-11}
Formic	2.1×10^{-4}
Iodic	1.9×10^{-1}
Phosphoric K_1	1.1×10^{-2}
Phosphoric K_2	2×10^{-7}
Phosphoric K_3	3.6×10^{-13}
Trichloracetic	2×10^{-1}

The larger the value of K_i, the stronger the acid; thus of the acids listed above, trichloracetic acid is the strongest and phosphoric acid the weakest.

[1] In the equilibrium

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

the concentration of H_2O in dilute solutions is essentially a constant, and this concentration term is embodied in the ionization constant, K_i, which is expressed as

$$K_i = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

It may be noted that two constants are given for carbonic acid and three for phosphoric acid. It will be recalled that acids with more than one replaceable hydrogen ionize in steps; therefore each successive step of the ionization is an equilibrium and would have a value for K. K_1 is for the first ionization step, K_2 for the second, etc. In the case of H_3PO_4

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_1 = 1.1 \times 10^{-2}$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--} \qquad K_2 = 2 \times 10^{-7}$$
$$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---} \qquad K_3 = 3.6 \times 10^{-13}$$

Thus H_3PO_4 is a stronger acid than $H_2PO_4^-$ which in turn is stronger than HPO_4^{--}.

The ionization of bases and their equilibrium constants would follow a similar pattern: the larger the value for the ionization constant, the stronger the base.

Common ion effect At a given temperature the relationship given for acetic acid

$$K_1 = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

must hold for all solutions of acetic acid. If the equilibrium is disturbed by changing the concentration of either H^+, $C_2H_3O_2^-$, or $HC_2H_3O_2$, the concentrations of the other two will adjust themselves in such a way that K retains its constant value. For example, if more acetate ion were added, the value for the concentration of H^+ would necessarily have to decrease, which in turn would cause an increase in the value of concentration of $HC_2H_3O_2$ in order that K remain constant.

The addition of an ion which is the same as one already present in the equilibrium is termed the *common ion effect.* Thus in the example above, the acetate is the common ion and its effect is to shift the equilibrium, resulting in a decrease of concentration of H^+ ions. Assuming that sodium acetate is the source of added acetate ion, the equations may be represented:

$$HC_2H_3O_2 \rightleftharpoons H^+ + \boxed{C_2H_3O_2^-}$$
$$NaC_2H_3O_2 \rightarrow Na^+ + \boxed{C_2H_3O_2^-}$$

The ionization of acetic acid is repressed and since the hydrogen ion concentration is decreased, the acidity of the solution is decreased. By regulating the amount of sodium acetate added to a solution of acetic acid, the acidity may readily be controlled. Careful control of acidity is extremely important in many chemical processes and often *common ion effect* is the basis for such control.

In a similar manner the addition of a common ion to a weak base reduces the alkalinity of the solution. For example, if NH_4Cl is added to a solution of NH_4OH, the concentration of OH^- is decreased:

$$\begin{array}{rcl} NH_4 + H_2O & \rightleftharpoons & NH_4^+ + OH^- \\ NH_4Cl & \rightleftharpoons & NH_4^+ + Cl^- \end{array}$$

Study the following sample calculations.

EXAMPLE 1 The ionization constant for acetic acid is 1.8×10^{-5}.

(*a*) Calculate the concentration of H^+ ions in a 0.1 molar solution of acetic acid.

$$K_i = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

Since each molecule of $HC_2H_3O_2$ which ionizes produces one H^+ ion and one $C_2H_3O_2^-$ ion,

$$[C_2H_3O_2^-] = [H^+]$$

Substituting in the above

$$K_i = \frac{[H^+] \times [H^+]}{0.1} = 1.8 \times 10^{-5}$$

$$[H^+]^2 = (1 \times 10^{-1})(1.8 \times 10^{-5}) = 1.8 \times 10^{-6}$$

$$[H^+] = \sqrt{1.8 \times 10^{-6}} = 1.34 \times 10^{-3}$$

(*b*) Calculate the concentration of H^+ ions in a 0.1 molar solution of acetic acid in which the concentration of acetate ions has been increased to 1 molar by addition of sodium acetate.

$$K_i = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

$$[H^+] = ?\quad [C_2H_3O_2^-] = 1\quad [HC_2H_3O_2] = 0.1$$

Substituting

$$\frac{[H^+] \times 1}{0.1} = 1.8 \times 10^{-5}$$

$$[H^+] = (1.8 \times 10^{-5})(1 \times 10^{-1}) = 1.8 \times 10^{-6}$$

The concentration of H^+ has been decreased from 1.34×10^{-3} to 1.8×10^{-6} mole per liter by the common ion effect.

EXAMPLE 2 The ionization constant for NH_4OH is 1.76×10^{-5}.

(*a*) Calculate the concentration of OH^- ions in a 1.0 molar solution of NH_4OH.

$$K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = 1.76 \times 10^{-5}$$

$$[NH_4^+] = [OH^-] \qquad [NH_4OH] = 1$$

Substituting

$$K_b = \frac{[OH^-] \times [OH^-]}{1} = 1.76 \times 10^{-5}$$

$$[OH^-]^2 = 1.76 \times 10^{-5} \text{ or } 17.6 \times 10^{-6}$$

$$[OH^-] = \sqrt{17.6 \times 10^{-6}} = 4.2 \times 10^{-3}$$

(*b*) Calculate the concentration of OH^- ions in a 1.0 molar solution of NH_4OH to which 0.1 mole of NH_4Cl is added to one liter of solution.

$$K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = 1.76 \times 10^{-5}$$

Since NH_4Cl is a salt and 100 per cent ionized, 0.1 mole of NH_4Cl would give 0.1 mole of NH_4^+

Then

$$[NH_4^+] = 0.1 \qquad [NH_4OH] = 1 \qquad [OH^-] = x$$

Substituting

$$K_b = \frac{0.1 \times [OH^-]}{1} = 1.76 \times 10^{-5}$$

$$[OH^-] = \frac{1.76 \times 10^{-5}}{1 \times 10^{-1}} = 1.76 \times 10^{-4}$$

The concentration of OH^- has been decreased from 4.2×10^{-3} to 1.76×10^{-4} moles per liter by the common ion effect.

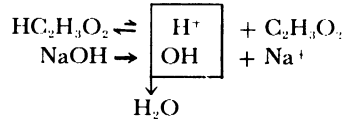
NOTE In the above reaction the relatively small concentration of NH_4^+ present from the ionization of NH_4OH is neglected, since it is small in comparison to the 0.1 mole of NH_4^+, added as NH_4Cl

Buffer solutions An important application of the common ion principle is the preparation of buffer solutions. They may be prepared from a combination of a weak acid and a salt of the weak acid—acetic acid and sodium acetate, for instance—or a weak base and a salt of the base—for example, NH_4OH and NH_4Cl. Such solutions are resistant to changes in acidity or basicity. Consider the addition of a strong acid like HCl to a solution of $HC_2H_3O_2$ and $NaC_2H_3O_2$.

$$\begin{array}{rl} NaC_2H_3O_2 \rightarrow Na^+ & + C_2H_3O_2^- \\ HCl \rightleftharpoons Cl^- & + \quad H^+ \end{array}$$

$$\downarrow \; HC_2H_3O_2$$

Even though a relatively high concentration of H^+ ions is added, the hydrogen ion concentration of the solution cannot be altered appreciably since the excess $C_2H_3O_2^-$ ions in the solution react with the added H^+ ions to form slightly ionized acetic acid. Thus the acidity remains essentially unchanged. In a somewhat similar way, the addition of OH^- ions to this same solution would not appreciably alter the acidity since the added OH^- ions would combine with H^+ ions to form undissociated H_2O molecules.



Although the number of H^+ ions in the solution is relatively small, they would be produced as needed by the dissociation of the acetic acid present.

The student should reason out for himself how a solution of a weak base and a salt of that base would act in resisting a change in alkalinity on addition of either H^+ or OH^- ions.

Buffers are important in many biological processes. Phosphates in the blood act as buffer salts since excess acid is neutralized by formation of relatively undissociated phosphoric acid. Thus the H^+ concentration of the blood is maintained at a nearly constant value.

Hydrogen ion concentration The hydrogen ion concentration is a measure of the acidity of a solution and is usually expressed in terms of moles per liter of solution.

In scientific work, the *p*H method[2] for expressing hydrogen ion concentration is employed. We may best illustrate this method with some actual examples. Let us consider the hydrogen ion concentration in solutions of hydrochloric acid. Hydrochloric acid is a strong acid and therefore nearly completely ionized. Assuming complete ionization, a solution of .01 *M* HCl will produce a 0.01 molar concentration of hydrogen ions; a solution of 0.001 *M* HCl gives a hydrogen ion concentration of 0.001 molar; and so on. These concentrations may be expressed as 10^{-2} and 10^{-3} ($.01 = 10^{-2}$ and $.001 = 10^{-3}$) respectively. The *p*H of the solution is taken as the exponent with its sign reversed.[3] Thus a solution of hydrogen ion concentration 10^{-2} would have a *p*H of 2; a solution of hydrogen ion concentration 10^{-3} has a *p*H of 3; and so

[2] *p*H was originally proposed as a measure of hydrogen ion concentration. Although the term "hydrogen ion concentration" is still in common usage, the ion which is actually responsible for acidity is the hydronium ion—that is, the hydrated H^+, H_3O^+.

[3] *p*H is defined as the negative logarithm of the hydrogen ion concentration—that is, $p\text{H} = -\log [H^+]$. Thus if $[H^+] = 10^{-2}$, $p\text{H} = -\log 10^{-2} = -(-2) = 2$.

on. Note that a change of one unit in *p*H corresponds to ten times the change in hydrogen ion concentration. The solution of *p*H 2 contains ten times the concentration of hydrogen ions as the solution *p*H 3. A study of Table 19–1 will further reveal the relationship between hydrogen

TABLE 19–1 Hydrogen Ion Concentration of Solutions of HCl

CONCENTRATION OF HCl IN MOLES PER LITER	CONCENTRATION OF HYDROGEN ION	pH
0.1	$0.1 = 10^{-1}$	1
0.01	$0.01 = 10^{-2}$	2
0.001	$0.001 = 10^{-3}$	3
0.0001	$0.0001 = 10^{-4}$	4
0.00001	$0.00001 = 10^{-5}$	5
0.000001	$0.000001 = 10^{-6}$	6
0.0000001	$0.0000001 = 10^{-7}$	7

ion concentration and *p*H. It may be noted from the table that the *p*H of the solution increases as the concentration of hydrogen ion decreases

The ionization of water Pure water is classed as a very poor conductor of electricity, liquid mercury, for example, is about 25,000,000 times as good a conductor as water The low conductivity of water may be attributed to its very slight ionization in accordance with the reaction:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Evidence indicates that but one molecule of water in 555,000,000 is ionized. This corresponds to 1 mole of H^+ and also 1 mole of OH^- per 10,000,000 liters of water Consequently in pure water

$$[H^+] = [OH^-] = \frac{1 \text{ mole}}{10{,}000{,}000 \text{ liters}} = \frac{1}{10^7} = 1 \times 10^{-7} \text{ mole per liter}$$

Hence the *p*H of pure water is 7, and since equal numbers of H^+ and OH^- ions are present, this *p*H represents a neutral solution.

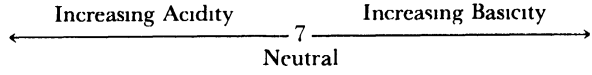
Applying the law of mass action to the above equilibrium equation,

$$K_1 = \frac{[H^+] \times [OH^-]}{[H_2O]}$$

The concentration of H_2O can usually be considered a constant in dilute solutions, hence $K_1 \times [H_2O]$ is a constant and may be represented by another constant K_w, called the "ion product" constant for water. The value of K_w at ordinary temperatures is 10^{-14}. This value is the product of the concentrations of hydrogen ion and hydroxyl ion in any water solution.

$$K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$$

Let us suppose that an acid is added to water until the hydrogen ion concentration is 10^{-3} (pH = 3). The increase in hydrogen ion concentration displaces the equilibrium above to the left and results in a decrease in the concentration of OH^-. The value of the concentration of OH^- in the solution must be 10^{-11}, since $10^{-3} \times 10^{-11} = 10^{-14}$. Students frequently think that an acid contains hydrogen ions but no hydroxyl ions, but it is evident from the above that any aqueous solution of an acid also contains hydroxyl ions. Likewise, any basic or alkaline solution contains not only hydroxyl ions but hydrogen ions as well. A solution in which the concentration of OH^- is 10^{-4} must have a hydrogen ion concentration of 10^{-10}. The pH of this latter solution would be 10, and since the $[OH^-]$ is greater than $[H^+]$, the solution is basic. Summarizing: a solution of pH 7 is neutral; a solution of pH less than 7 is acid; and one of pH greater than 7 is alkaline



A careful control of pH is important in many biological processes. Most of the body fluids in a healthy individual have a pH very near to 7. The gastric juice is an exception, having a pH of about 2 which means it is quite acid. pH is important in the growth of bacteria, and certain pH values represent optimum conditions for growth. The utility of soil for growing certain crops depends upon its acidity or alkalinity (its pH). Technicians use the so-called pH meter, which measures pH with an accuracy approaching 0.01 in the range 0–14 This device is essentially an electrolytic cell in which the voltage varies with H^+ concentration.

Indicators Certain organic substances undergo a change in color at rather definite pH values. For example, methyl orange has a red or orange color in solutions with a pH of 3 or less and a yellow color in solutions of pH more than 4. Phenolphthalein changes from colorless to red violet at a pH of 9 to 10. Such substances are called *indicators* and may be used to determine the approximate pH of a solution. Some of the more common indicators and color changes at various pH values are shown in Table 19–2.

To illustrate the use of indicators in determining approximate pH, suppose a given solution gives no color with p-nitrophenol and a red color with congo red indicator. Inspection of Table 19–2 shows that the pH of the solution must be approximately 5.

In order to choose the proper indicator to use in any given titration of acids and bases, we must know the pH of the solution when equivalent amounts of the acid and base are present. For example, the pH of the

TABLE 19-2 Color Change in Indicators at Various pH Values*

INDICATOR	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Methyl violet	Y	▒	BV	BV	BV	BV	V	V	V	V	V	V	V	V	V
Meta-cresol purple	R	R	▒	Y	Y	Y	Y	Y	▒	Pu	Pu	Pu	Pu	Pu	Pu
Thymol blue	R	R	▒	Y	Y	Y	Y	Y	Y	▒	B	B	B	B	B
Methyl orange	R	R	R	R	▒	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Congo red	B	B	B	B	▒	R	R	R	R	R	R	R	R	R	R
p-Nitrophenol	C	C	C	C	C	C	▒	Y	Y	Y	Y	Y	Y	Y	Y
Rosolic acid	A	A	A	A	A	A	A	P	P	P	P	P	P	P	P
Phenolphthalein	C	C	C	C	C	C	C	C	C	▒	V	V	V	V	V
Malachite green	BG	BG	BG	BG	BG	BG	BG	BG	BG	BG	BG	BG	▒	C	C

A amber
B blue
BG blue green
BV blue violet
C colorless
P pink
Pu purple
R red
V violet
Y yellow

* The shading in the squares signifies that the indicator is changing in color and shows the *p*H range over which the color change takes place.

solution resulting from neutralization of acetic acid with sodium hydroxide is 8.5, the same as would be obtained if pure sodium acetate were dissolved in water. Phenolphthalein changes color at a *p*H of about 9 and may be used satisfactorily in this titration. Actually, in the titration of strong acids and strong bases, any indicator which changes in a *p*H range of 5 to 9 may be used, but in the titration of weak acids and weak bases, the indicator must be carefully chosen to insure accuracy of a determination.

Solubility product principle If solid AgCl is shaken with water, Ag^+ and Cl^- ions from the crystal lattice of the solid pass into solution until the solution becomes saturated. In the saturated solution thus formed, an equilibrium exists between the ions in solution and the ions present in the solid crystal lattice:

$$\underset{\text{solid}}{AgCl} \rightleftharpoons Ag^+ + Cl^-$$

The amount of AgCl dissolved depends upon the temperature; at a given temperature the solubility of a substance is a constant.

Applying the law of mass action to the above equilibrium we may write:

$$K = \frac{[Ag^+] \times [Cl^-]}{[AgCl]}$$

The term in the denominator refers to the concentration of solid AgCl and as used here may be considered a measure of the tendency of the

solid to pass into solution. Since this tendency at a given temperature is independent of the amount of solid AgCl present, this term may be incorporated in the constant K to give a new constant $K_{s.p.}$

$$K_{s.p.} = [Ag^+] \times [Cl^-]$$

in which $K_{s.p.}$ is the *solubility product constant.* In other words, the product of the concentrations of ions in a saturated solution of a relatively insoluble salt, such as AgCl, at a given temperature is a constant. This is known as the *solubility product principle.*

The numerical value for $K_{s.p.}$ can readily be calculated if the concentrations of ions in the saturated solution are known. If a saturated solution of AgCl is prepared at 25°, the solubility by analysis is found to be 1.06×10^{-5} mole per liter. AgCl is completely ionized; hence each AgCl will give one Ag^+ and one Cl^- ion in solution. Consequently the concentration of Ag^+ ions will be 1.06×10^{-5} mole per liter, and the concentration of Cl^- ions will be 1.06×10^{-5} mole per liter. Substituting these concentrations in the solubility product formulation

$$K_{s.p.} = [Ag^+] \times [Cl^-]$$
$$K_{s.p.} = (1.06 \times 10^{-5})(1.06 \times 10^{-5}) = 1.1 \times 10^{-10}$$

The value for $K_{s.p.}$ is a measure of the solubility of a substance; the larger the value of $K_{s.p.}$, the greater must be the concentrations of ions and hence the greater the solubility of the substance. Likewise, the smaller the value of $K_{s.p.}$, the more insoluble the substance.

In the event that more than two ions of one kind are produced from an ionization, the concentration of that particular ion must be raised to that power which corresponds to the coefficient of the ion in the balanced equation as called for by the law of mass action. To illustrate

$$PbCl_2 \rightleftharpoons Pb^{++} + 2\,Cl^-$$
$$K_{s.p.} = [Pb^{++}] \times [Cl^-]^2$$

The solubility of $PbCl_2$ in water at 20° is 10.84 g. per liter. Since the molecular weight of $PbCl_2$ is 278

$$10.84 \text{ g.} = .039 \text{ mole}$$
$$[Pb^{++}] = 3.9 \times 10^{-2} \text{ mole per liter}$$

Since each $PbCl_2$ yields two Cl^-

$$[Cl^-] = 2 \times .039 = 7.8 \times 10^{-2} \text{ mole per liter}$$
$$K_{s.p.} = (3.9 \times 10^{-2})(7.8 \times 10^{-2})^2 = 2.4 \times 10^{-4}$$

A partial list of solubility product constants is given in Table 19–3.

TABLE 19–3 Solubility Product Constants

COMPOUND	$K_{s.p.}$	COMPOUND	$K_{s.p.}$
AgCl	1.1×10^{-10}	$BaSO_4$	1.0×10^{-10}
$PbCrO_4$	1.7×10^{-14}	HgS	4.0×10^{-54}
$Fe(OH)_3$	1.1×10^{-36}	CuS	8.5×10^{-45}
$BaCrO_4$	2.3×10^{-10}	CdS	3.6×10^{-29}
CaC_2O_4	3.9×10^{-9}	PbS	4.2×10^{-28}
$SrSO_4$	3.6×10^{-7}	ZnS	1.2×10^{-23}
$PbCl_2$	2.4×10^{-4}	FeS	1.5×10^{-19}
AgBr	4.0×10^{-13}	MnS	1.4×10^{-15}

Application of solubility product principle to formation of precipitates The formation of a precipitate depends first upon the formation of a saturated solution; only when the solubility of the substance is exceeded can a precipitate form. $K_{s.p.}$ is directly related to the solubility of a substance since it is equal to the product of ion concentrations in a saturated solution. Any solution in which the product of the ion concentrations exceeds $K_{s.p.}$ is supersaturated, and precipitation will occur until the solution is saturated, in which case the product of ion concentrations attains the value of $K_{s.p.}$ Any solution in which the ion product is less than $K_{s.p.}$ is unsaturated and is capable of dissolving more of the solute.

In the case of AgCl, when the product of the concentration of Ag^+ ions and the concentration of Cl^- ions exceeds 1.1×10^{-10}, the salt will precipitate. In a water solution of AgCl the concentrations of Ag^+ and Cl^- ions are the same, namely, 1.06×10^{-5} mole per liter. However, it is not necessary that the concentrations of the ions have equivalent values to bring about precipitation, so long as the product of these ion concentrations exceeds $K_{s.p.}$

Suppose we know the concentration of Ag^+ ions in a certain solution to be 1×10^{-7} mole per liter. We can calculate the concentration of Cl^- ions necessary to bring about precipitation. Substituting in the equation

$$K_{s.p.} = [Ag^+] \times [Cl^-] = 1.1 \times 10^{-10}$$

solving for $[Cl^-]$

$$[Cl^-] = \frac{1.1 \times 10^{-10}}{1 \times 10^{-7}} = 1.1 \times 10^{-3}$$

This concentration of Cl^- ions will just form a saturated solution, but any value of the concentration of Cl^- ions larger than 1.1×10^{-3} will cause a precipitate of AgCl to form.

It was shown above that the solubility of AgCl in water was 1.06×10^{-5} mole per liter, while the solubility in a solution in which the concentration of Cl^- ions is 1.1×10^{-3} is only 1×10^{-7} mole per liter; in other words, by using an excess of Cl^- the solubility of the salt has been decreased nearly a hundredfold. In the precipitation of ions from solution in qualitative and quantitative analysis, a large excess of the precipitating ion is used to reduce markedly the solubility of the substance and cause it to precipitate. Study the following illustrations:

EXAMPLE 1. With the aid of Table 19–3, calculate the minimum concentration of Br^- ion necessary to bring about precipitation of AgBr from a solution in which the concentration of Ag^+ ion is 1×10^{-5} mole per liter.

$$K_{s.p.} \text{ for AgBr} = [Ag^+] \times [Br^-] = 4 \times 10^{-13}$$

Substituting for $[Ag^+]$

$$(1 \times 10^{-5})[Br^-] = 4 \times 10^{-13}$$

$$[Br^-] = \frac{4 \times 10^{-13}}{1 \times 10^{-5}} = 4 \times 10^{-8}$$

This value for the concentration of Br^- would just form a saturated solution, but any value larger than this would cause precipitation of AgBr.

EXAMPLE 2. Will precipitation occur if .01 mole of Ba^{++} is added to a liter of solution containing .05 mole of SO_4^{--}?

$K_{s.p.}$ for $BaSO_4 = [Ba^{++}] \times [SO_4^{--}] = 1 \times 10^{-10}$

$[Ba^{++}] = .01$ mole per liter $= 1 \times 10^{-2}$ mole per liter

$[SO_4^{--}] = .05$ mole per liter $= 5 \times 10^{-2}$ mole per liter

Trial product $(1 \times 10^{-2})(5 \times 10^{-2}) = 5 \times 10^{-4}$

5×10^{-4} is larger than 1×10^{-10}; hence precipitation of $BaSO_4$ will take place.

EXAMPLE 3. After precipitation of $BaSO_4$ from a liter of solution which originally contained .01 mole of Ba^{++}, the concentration of SO_4^{--} was found to be .1 mole per liter. How much $BaSO_4$ was precipitated?

First calculate the concentration of Ba^{++} in the solution after precipitation:

$$K_{s.p.} = [Ba^{++}] \times [SO_4^{--}] = 1 \times 10^{-10}$$

$$|Ba^{++}| \text{ left in solution} = \frac{1 \times 10^{-10}}{.1} = 1 \times 10^{-9} \text{ mole per liter}$$

$$\text{Number of moles precipitated} = .01 - .000000001 = .009999999$$

The solubility product principle is applicable only to solutions of slightly soluble salts. Experimental studies show that it does not hold for soluble or moderately soluble salts.

The dissolving of precipitates Just as a precipitate is formed when the product of ion concentrations exceeds $K_{s.p.}$, so a precipitate must dissolve when the ion concentrations are decreased sufficiently to give an ion product less than $K_{s.p.}$ Anything which will lower the concentrations of ions in the solution will disturb the equilibrium with the undissolved solid. To re-establish equilibrium by replenishing the supply of ions, more solid will pass into solution. This process will continue until all the solid has dissolved, provided the concentrations of ions are continuously lowered. Decreasing the concentration of ions in solution may be accomplished in the following ways:

(*a*) Dilution—as a solution is diluted, the concentrations become less and more solid passes into solution.

(*b*) Addition of a reagent which forms an undissociated substance with one of the ions of the solid; for example, addition of HCl to a precipitate of calcium oxalate forms slightly dissociated oxalic acid:

$$\underset{\text{solid}}{CaC_2O_4} \rightleftharpoons Ca^{++} + \boxed{C_2O_4^{--}}$$
$$2\,HCl \rightarrow 2\,Cl^- + \boxed{2\,H^+} \rightarrow H_2C_2O_4$$

As $C_2O_4^{--}$ ions are removed by combination with H^+ ions, more CaC_2O_4 passes into solution to replenish the supply of $C_2O_4^{--}$ ions; if sufficient HCl is present, all of the precipitate will dissolve.

(*c*) Addition of a reagent which reacts with the solid to form a gas which is insoluble and escapes from solution; for example, ferrous sulfide is soluble in HCl:

$$\underset{\text{solid}}{FeS} \rightleftharpoons Fe^{++} + \boxed{S^{--}} \rightarrow H_2S$$
$$2\,HCl \rightarrow 2\,Cl^- + \boxed{2\,H^+}$$

Hydrolysis Although water is only slightly ionized according to the equation

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (1)$$

the few H^+ ions and OH^- ions produced may become of primary importance in aqueous solutions of certain salts. As long as the number of H^+ ions is equal to the number of OH^- ions, the solution is neutral. However, if something is added which furnishes either of the ions or which

uses up either of the ions, then one of the two ions is present in excess—if excess H^+ ions are present, the solution is acid; if excess OH^- ions are present, then the solution is basic.

Ions of salts may disturb the equilibrium in aqueous solution; as a result the solution is actually acidic or basic, depending on whether H^+ or OH^- ions are present in excess. This reaction of the ions of a salt with water is termed *hydrolysis*. We may illustrate hydrolysis with a few examples.

(*a*) *Sodium carbonate.* An aqueous solution of this salt tests basic toward litmus indicating an excess of OH^- ions present in the solution. This may readily be explained as follows. Sodium carbonate, a salt derived from the strong base, sodium hydroxide, and the weak acid, carbonic acid, is completely ionized into Na^+ and CO_3^{--}. CO_3^{--} ions have a great affinity for protons to form the weak (slightly ionized) acid, HCO_3^-, consequently, protons are removed from solution by the reaction

$$H^+ + CO_3^{--} \rightarrow HCO_3^-$$

As a result the equilibrium in (1) above is shifted in the direction of a higher concentration of OH^- ions to give the solution an alkaline reaction. Meanwhile, there has been no tendency for Na^+ and OH^- ions to combine since NaOH is a strong base. The equation for the reaction may be represented

$$2\ Na^+ + CO_3^{--} + H_2O \rightleftharpoons 2\ Na^+ + OH^- + HCO_3^- \qquad (2)$$

or

$$CO_3^{--} + H_2O \rightleftharpoons OH^- + HCO_3^-$$

since Na^+ ions may be canceled out. A solution of Na_2CO_3 is only weakly alkaline because the equilibrium in (2) above is far to the left. The extent of hydrolysis is said to be slight.

(*b*) *Ammonium chloride.* The ions present in the solution are H^+, OH^-, NH_4^+, Cl^-. There is very little tendency for H^+ to unite with Cl^- since HCl is a strong acid. However, NH_4^+ readily combines with OH^-, since NH_4OH (or $NH_3 + H_2O$) is a weak base. Accordingly an excess of H^+ ions are left in solution, which reacts acid to litmus. The reaction may be represented

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^- \qquad (3)$$

or

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

since Cl^- may be canceled out.

(*c*) *Sodium chloride.* Ions present in the solution are Na^+, Cl^-, H^+, OH^-. Since both NaOH and HCl are strong electrolytes, there is little

if any tendency for either to be formed. Hence the concentrations of H^+ and OH^- ions remain about equal, and the resulting solution is approximately neutral. The hydrolysis of a salt derived from a strong acid and strong base is negligible.

(*d*) *Ammonium acetate.* The aqueous solution contains NH_4^+, $C_2H_3O_2^-$, H^+, and OH^- ions. This salt is highly hydrolyzed (reaction far to the right) since both acetic acid and ammonium hydroxide are weak electrolytes:

$$NH_4^+ + C_2H_3O_2^- + H_2O \rightleftharpoons NH_4OH + HC_2H_3O_2 \qquad (4)$$

Both ammonium hydroxide and acetic acid are of about the same strength as electrolytes; consequently about the same number of H^+ and OH^- ions is left in solution, which is approximately neutral.

(*e*) *Copper sulfate.* Salts of most of the heavy metals contain hydrated ions and such ions may furnish protons to the solution and give it an acidic reaction. For example, copper sulfate in solution gives $Cu(H_2O)_4^{++}$ and SO_4^{--} ions. There would be little tendency for SO_4^{--} to combine with H^+ since H_2SO_4 is a strong acid. However, the hydrated cupric ions may react with water to form H^+ ions:

$$Cu(H_2O)_4^{++} + H_2O \rightleftharpoons Cu(H_2O)_3OH^+ + H_3O^+ \ (H^+ + H_2O) \qquad (5)$$

Thus a solution of this salt is slightly acidic because of the excess H^+ ions present.

It is evident from the above that whether or not the aqueous solution of a salt is acidic, basic, or neutral depends upon the strength of the acid and base from which the salt may be considered to be derived. A knowledge of the strength of acids and bases, therefore, is essential in predicting the effects of hydrolysis. Of the common acids, only HNO_3, H_2SO_4, and the hydrohalogen acids (except HF) are strong. Likewise, the strong bases in aqueous solution are KOH, NaOH, $Ca(OH)_2$, and $Ba(OH)_2$; others are weak. We may summarize the possible hydrolysis effects as follows:

1 Salt of strong acid and strong base. Solution is approximately neutral, *p*H about 7.
2 Salt of weak acid and weak base. Solution is approximately neutral, *p*H about 7. The *p*H will depend upon the relative strengths of the weak acid and the base.
3 Salt of weak acid and strong base. Alkaline solution, *p*H greater than 7.
4 Salt of strong acid and weak base. Acid solution, *p*H less than 7.

Conventions used in writing ionic equations Certain arbitrary conventions must be adopted in writing ionic equations, since both molecules and ions for a given substance may exist in the aqueous solution. It is customary to show the substance in its predominate form, unless it is desired to emphasize either the molecular or ionic form of the substance. Therefore, weak electrolytes which are only slightly ionized will be shown in the equation in molecular form unless the relatively few ions from these substances are to be emphasized. For example, H_2O, $HC_2H_3O_2$, NH_4OH, and H_3PO_4 will ordinarily be shown in molecular form. Of course, in the consideration of equilibrium constants such as were discussed earlier in this chapter, the relatively few ions in solution are of paramount importance, and the equilibrium in solution between molecules and ions must be shown.

It is also customary to represent a substance which is not in solution —a solid or gas, for example—in molecular form. Thus, sodium chloride in the solid state would be represented as NaCl, whereas in solution it would be shown as Na^+ and Cl^-. A substance precipitating from solution would be shown in molecular form and its insolubility would usually be designated by a downward arrow; for example, AgCl↓. Substances other than electrolytes, of course, are never shown in ionic form.

It is probable that all ions in aqueous solution are hydrated to some degree; in general, however, the exact amount of water of hydration is not known. Consequently we shall ordinarily show the ion in its anhydrous form. Particular attention has already been called to the hydrated hydrogen ion or hydronium ion.

In writing ionic equations, some instructors prefer to show in the equation all the ions present in the system, even though some of them may not actually take part in the reaction; others prefer to show only the ions which enter into the chemical change. The latter has advantages in that the equations are considerably simplified. Furthermore, a single equation may represent a number of chemical changes; for example, as already pointed out, the simple combination of H^+ and OH^- to form H_2O represents the actual change in neutralization reactions. A disadvantage of not showing all the ions present is that a subsequent treatment of the system might involve some ions not taking part in the primary reaction. Under such conditions, it would be desirable to have information on all ions or molecular species present in a system.

EXERCISES

1 Explain the effect of the addition of ammonium acetate to a solution containing acetic acid.

2 List five salts whose water solutions test acid to litmus; five whose water solutions test basic to litmus.

3 How would water solutions of the following salts test with litmus?

(*a*) $KC_2H_3O_2$	(*f*) KCl
(*b*) $(NH_4)_3PO_4$	(*g*) $BiCl_3$
(*c*) $CuBr_2$	(*h*) Na_2S
(*d*) NaCN	(*i*) $Al(C_2H_3O_2)_3$
(*e*) $ZnSO_4$	(*j*) $Zn(NO_3)_2$

4 Explain how indicators may be used to determine the approximate *p*H of a solution.

5 What would be the effect of adding each of the following to a solution of ammonium hydroxide: (*a*) solid NH_4Cl; (*b*) HCl; (*c*) solid KOH?

6 After copying (*a*)-(*j*), complete and balance the equations and by use of one of the following sets of arrows indicate comparative concentration of chemicals present at equilibrium:

$$\rightleftharpoons \; ; \; \rightleftharpoons \; ; \; \rightleftharpoons \; ; \; \rightarrow \; ; \; \leftarrow$$

(*a*) $AlBr_3 + Cl_2$	(*f*) $Br_2 + H_2O$
(*b*) $CuBr_2 + HOH$	(*g*) Step ionization of H_3PO_4
(*c*) $NaI + Ag_2SO_4$	(*h*) $Au + H^+ + Br^-$
(*d*) $K + F_2$	(*i*) $H^+ + NO_3^- + Ca^{++} + OH^-$
(*e*) $Na_2SiO_3 + HF$	(*j*) $CCl_4 + Ag^+ + NO_3^-$

7 From the following ionization constants, indicate the strongest acid and the weakest:

Nitrous acid: 4×10^{-4}	Butyric acid: 1.5×10^{-5}
Arsenious acid: 6×10^{-10}	Fumaric acid: 1×10^{-3}

8 Calculate the concentration of hydrogen ion in one liter of .3 molar acetic acid to which .1 mole of sodium acetate has been added. K_i for $HC_2H_3O_2 = 1.8 \times 10^{-5}$. Ans. 5.4×10^{-5}.

9 Calculate the hydrogen ion concentration of .1 molar lactic acid ($HC_3H_5O_3$) solution. K_i for lactic acid $= 1.4 \times 10^{-4}$. Ans. 3.7×10^{-3}.

10 Calculate the concentration of OH^- in .01 molar NH_4OH solution. K_i for $NH_4OH = 1.75 \times 10^{-5}$. Ans. 4.2×10^{-4}.

11 The ionization constant for an acid HX of concentration 0.01 *M* is 6.4×10^{-11} at 25°. Calculate the hydrogen ion concentration. What is the approximate *p*H of the solution? Ans. 6.

12 A hypothetical weak base ionizes according to the equation:

$$MOH \rightleftharpoons M^+ + OH^-$$

A salt, M_2SO_4, is added. The concentration of the base is 0.01 molar, and the salt 0.005 molar. Calculate (*a*) concentration of OH^- in the solution; (*b*) concentration of H^+; (*c*) *p*H of the solution. K_i for the base is 1×10^{-6}.

13 Assuming 100 per cent ionization, what would be the *p*H of .001 molar NaOH? Ans. 11.

14 Give approximate *p*H for: 0.0001 *N* KOH; $Cu(NO_3)_2$ solution; a dilute solution of sugar in water; CO_2 in water; Na_3PO_4 solution; 0.001 *N* H_2SO_4.

15 The ionization constant for formic acid (HCOOH) is 2×10^{-4}.
(*a*) What is the approximate *p*H of a 0.1 molar solution of formic acid?

(*b*) How much sodium formate (HCOONa) should be added to one liter of 0.1 molar formic acid solution to buffer the solution at a *p*H of 5?

Ans. (*b*) 2 moles.

16 HCN in a 0.01 *M* aqueous solution is 0.02% ionized. Calculate K_i for HCN. Ans. 4×10^{-10}.

17 Given $K_{s.p.}$ for the following compounds:

COMPOUND	$K_{s.p.}$
$PbCrO_4$	1.8×10^{-14}
MnS	1.4×10^{-15}
ZnS	1.2×10^{-23}
CuS	8.5×10^{-45}
$PbCO_3$	3.3×10^{-14}

List the compounds according to increasing solubility, placing the least soluble compound first.

18 $K_{s.p.}$ for $CaSO_4 = 6 \times 10^{-5}$. If .02 mole of Na_2SO_4 is added to a liter of solution containing 4×10^{-3} mole of calcium chloride, will $CaSO_4$ precipitate? Give reason for your answer.

19 Calculate the minimum concentration of Cl^- necessary to precipitate AgCl from a solution in which the concentration of Ag^+ is 5×10^{-2}. $K_{s.p.}$ for AgCl = 1.0×10^{-10}. Ans. 2×10^{-9}.

20 A solution of a hypothetical salt MX_2 contains an excess of M^{++} ions, and the solution is in equilibrium with solid MX_2. If the concentration of M^{++} is 2×10^{-3} gram ions per liter, and the concentration of X is 5×10^{-8} gram ions per liter, calculate the solubility product of the salt, MX_2.

Ans. 5×10^{-18}.

21 Calculate the solubility product constant for Ag_2SO_4 when the solubility is 1.4×10^{-2} mole/liter. Ans. 1.1×10^{-5}.

22 The solubility of PbS in water is 2×10^{-14} mole per liter. Assuming 100 per cent ionization, what is the solubility product constant for PbS?

Ans. 4×10^{-28}.

23 $K_{s.p.}$ for $BaSO_4$ is 1×10^{-10}. (*a*) Calculate the solubility of $BaSO_4$ in water. (*b*) What would be the solubility of $BaSO_4$ in a solution which is .01 molar with respect to sulfate ion? (*c*) By what factor is the solubility decreased from part (*a*) to part (*b*) above? Ans. (*a*) 1×10^{-5} (*b*) 1×10^{-8} (*c*) .001.

24 After precipitation of $Bi(OH)_3$ from a solution of $BiCl_3$ by the addition of NH_4OH, the concentration of OH^- in the solution is 5×10^{-4} mole/liter. (*a*) What is the concentration of Bi^{+++} remaining in the solution? $K_{s.p.}$ for $Bi(OH)_3 = 4 \times 10^{-30}$. (*b*) What is the approximate *p*H of the solution?

Ans. (*a*) 3×10^{-20} (*b*) 11.

25 $K_{s.p.}$ for $CaC_2O_4 = 2.6 \times 10^{-9}$. If 0.001 mole of $CaCl_2$ and 0.001 mole of $(NH_4)_2C_2O_4$ are mixed in one liter of solution, what weight of CaC_2O_4 in grams will precipitate? Ans. 0.122 g.

26 $K_{s.p.}$ for $PbSO_4 = 2.3 \times 10^{-8}$. Calculate the solubility of $PbSO_4$ in a 0.1 molar solution of $(NH_4)_2SO_4$.

REFERENCES

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Moeller, T., *Inorganic Chemistry,* New York, John Wiley & Son, Inc. (1952).

twenty OXIDATION-REDUCTION

Chemical changes may be classified in two large groups: (1) those involving no change in oxidation number of the elements; and (2) those in which a change of oxidation numbers occurs. The latter are termed *oxidation-reduction* or simply *redox* reactions.

Double decomposition chemical changes, which are among the most common of reactions, involve no change in oxidation number of any of the elements. Usually these involve reactions of acids with bases; acids with salts; salts with salts; and so on. In these, there is simply an exchange of partners, so to speak, between the ions of which these compounds are composed. Most other types of chemical changes fall into the category of oxidation-reduction.

Review the oxidation number concept as discussed in Chapter 9. Recall that the electrovalence of a positive or negative ion is also its oxidation number. For example, the oxidation number of Na^+ is $+1$, and the oxidation number of SO_4^{--} is -2. Uncombined elements have a zero oxidation number; hydrogen and oxygen in compounds have oxidation numbers of $+1$ and -2, respectively. The oxidation number of a given element in a compound which involves electron sharing is the apparent charge on the atom which will give the compound a neutral character when positive and negative oxidation numbers are assigned to all other elements in the compound. Thus, the oxidation number of sulfur in Na_2SO_4 would be $+6$, and for each sulfur in $K_2S_2O_3$ it would be $+2$. In dealing with radical ions, the algebraic sum of the oxidation numbers must be the same as the charge on the ion. For example, in the phosphate ion, PO_4^{---}, an oxidation number of $+5$ must be assigned to the phosphorus atom.

An example of oxidation-reduction *Oxidation* is defined simply as a change in which the oxidation number of an element increases. Such a change can take place only at the expense of a decrease in the oxidation number of some other element. The latter is termed *reduction*. For

example, consider the following reaction:

$$\overset{0}{2\,Al} + \overset{0}{3\,S} \rightarrow \overset{+3\ -2}{Al_2S_3}$$

in which the oxidation number of each element is written above the symbol. Aluminum and sulfur in the free state have, in accordance with our rules (page 128), an oxidation number of 0; whereas in the compound, aluminum sulfide, the oxidation number of aluminum is $+3$ and that of sulfur is -2. In this reaction, aluminum gains in oxidation number from 0 to $+3$ and hence is *oxidized;* whereas sulfur loses in oxidation number from 0 to -2 and is *reduced.*

Let us examine this reaction in another way. As it proceeds, each atom of aluminum gives up 3 electrons and each atom of sulfur takes up 2 electrons. In the reaction as a whole, 6 electrons given up by the 2 aluminum atoms are taken up by the 3 sulfur atoms. A transfer of electrons has taken place, and the resultant compound Al_2S_3 is electrovalent; it is composed of Al^{+++} and S^{--} ions. In this particular case, Al gains in oxidation number or loses electrons; likewise, sulfur loses in oxidation number or gains electrons. It is often convenient when dealing with electrovalent substances to discuss these changes in terms of a gain or loss in electrons as well as in terms of changes in oxidation number. To summarize: for reactions involving a transfer of electrons,

Oxidation is *gain* in oxidation number or *loss* of electrons.
Reduction is *loss* in oxidation number or *gain* of electrons.

Oxidation and reduction are mutually dependent processes; if electrons are taken up by one substance, they must be given up by another. There can be no oxidation without reduction, nor reduction without oxidation.

The union of aluminum and sulfur may be written as taking place in two steps with e representing an electron:

$$2\,Al \rightarrow 2\,Al^{+++} + 6\,e \text{ (oxidation)} \quad (1)$$
$$6\,e + 3\,S \rightarrow 3\,S^{--} \text{ (reduction)} \quad (2)$$

By adding the two steps and cancelling the electrons, we obtain the net equation which was written above.

Oxidizing and reducing agents Oxygen, sulfur, or other nonmetals, as they combine with metals, are recognized as *oxidizing agents*; therefore, the metals must be the *reducing agents.* In all oxidation-reduction chemical changes, the following relationship exists:

Oxidizing agent = electron receiver = loser in oxidation number
Reducing agent = electron giver = gainer in oxidation number

The receiver-loser and giver-gainer relationship is somewhat confusing, but it is helpful to consider that a particle giving away negative charge must itself become more positive. If it receives a negative charge, it becomes less positive In the combination

$$2\ Fe + 3\ Cl_2 \rightarrow 2\ FeCl_3\ (2\ Fe^{+++},\ 6\ Cl^-)$$

Cl_2 is the oxidizing agent, each Cl receives 1 electron and loses 1 in oxidation number. Fe is the reducing agent· each Fe gives 3 electrons and gains 3 in oxidation number In the replacement

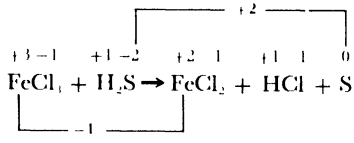
$$Zn + CuSO_4\ (\text{solution}) \rightarrow ZnSO_4\ (\text{solution}) + Cu$$

or

$$Zn + Cu^{++} + SO_4 \rightarrow Zn^{++} + SO_4 + Cu$$

Cu^{++} is the oxidizing agent it receives 2 electrons and loses 2 in oxidation number Zn is the reducing agent· it gives 2 electrons and gains 2 in oxidation number

Balancing oxidation-reduction equations To balance these equations, we make use of the rule that the *total gain in oxidation numbers must equal the total loss in oxidation numbers of the elements* Consider the reaction



in which the oxidation number of each element is placed above the symbol Two of the elements undergo a change in oxidation number; each iron atom loses 1 (from +3 to +2) and each sulfur atom gains 2 (from −2 to 0) in oxidation number The loss of 1 in oxidation number of Fe is indicated by −1, and the gain of 2 in oxidation number of S is indicated by +2. To balance the gain and loss, 2 iron atoms will be required for each sulfur atom, and this will call for a ratio of 2 $FeCl_3$ to 1 H_2S. This must be the ratio in which these two substances react.

$$2\ FeCl_3 + 1\ H_2S \rightarrow 2\ FeCl_2 + 2\ HCl + S$$

Having obtained the ratio of the oxidizing agent, $FeCl_3$, to the reducing agent H_2S, it is easy to complete the balancing of the equation on the right side. In this equation, the change in oxidation number of sulfur (2) is made the coefficient of $FeCl_3$, while the change in oxidation number of iron (1) is the coefficient of H_2S

In general, we may employ the following steps in balancing oxidation-reduction equations.

1 Write the oxidation number of each of the elements in each compound above the symbol of the element in the equation.

2 Determine which elements have changed in oxidation number and the amount of change. Usually two elements only will have changed; one gains in oxidation number while the other loses.

3 Balance the gain and loss in oxidation numbers. This may be accomplished automatically by placing the number representing the change in the oxidizing agent in front of the formula for the reducing agent, and vice versa.

4 Complete the balancing of the two elements which have changed oxidation number on the right side of the equation, keeping in mind that the ratio of oxidizing agent to reducing agent as determined from the change in oxidation numbers must be maintained. Balance hydrogen and oxygen atoms after all other elements have been balanced.

Let us illustrate the outlined steps by balancing an equation:

(1) $\overset{0}{P} + \overset{+1\,+5\,-2}{HNO_3} \rightarrow \overset{+1\,+5\,-2}{HPO_3} + \overset{+2\,-2}{NO} + \overset{+1\,-2}{H_2O}$

(2) $\overset{0}{P} + \overset{+5}{HNO_3} \rightarrow \overset{+5}{HPO_3} + \overset{+2}{NO} + H_2O$ (3 and 5 indicate the gain and loss)

(3) $3\,P + 5\,HNO_3 \rightarrow HPO_3 + NO + H_2O$

(4) $3\,P + 5\,HNO_3 \rightarrow 3\,HPO_3 + 5\,NO + H_2O$ (balanced)

Oxidation-reduction equations are more difficult to balance by ordinary trial and error methods than those which involve no change in oxidation number. The "change in oxidation number" method for balancing oxidation-reduction equations, however, is rapid and accurate. Note these examples:

EXAMPLE 1:

$$\overset{+1\,-2}{H_2S} + \overset{+1\,+7\,-2}{KMnO_4} + \overset{+1\,-1}{HCl} \rightarrow \overset{0}{S} + KCl + \overset{+2\,-1}{MnCl_2} + \overset{+1\,-2}{H_2O}$$

(+2 and 5 indicate the gain and loss)

Mn in $KMnO_4$ undergoes a change in oxidation number of 5, while the sulfur atom in H_2S changes by 2 units in oxidation number. Thus the number 5 is made the coefficient of H_2S, and the number 2 is made the coefficient of $KMnO_4$:

$$5\,H_2S + 2\,KMnO_4 + HCl \rightarrow S + KCl + MnCl_2 + H_2O$$

The ratio of H_2S to $KMnO_4$ must be 5 to 2 as determined by the rule

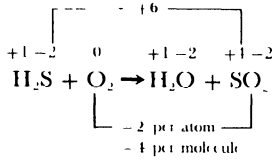
of change in oxidation numbers. Since this ratio fixes the number of sulfur, potassium, and manganese atoms in the equation, those elements should be balanced immediately on the right side of the equation,

$$5\ H_2S + 2\ KMnO_4 + HCl \rightarrow 5\ S + 2\ KCl + 2\ MnCl_2 + H_2O$$

Note that so far we have done nothing about the HCl, since there has been no change in oxidation number in this compound. However, at this point we see that the number of chlorine atoms on the right side is now fixed at 6 (2 chlorine atoms in 2 KCl and 4 more in 2 $MnCl_2$). Six molecules of HCl will be necessary to furnish these 6 chlorine atoms; hence we arrive at the coefficient 6 for HCl. Now the hydrogen and oxygen atoms are balanced last

$$5\ H_2S + 2\ KMnO_4 + 6\ HCl \rightarrow 5\ S + 2\ KCl + 2\ MnCl_2 + 8\ H_2O \text{ (balanced)}$$

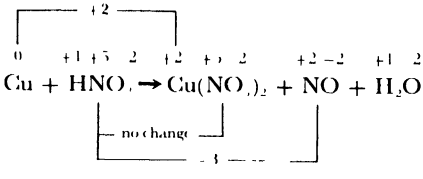
EXAMPLE 2.



Since 2 atoms of oxygen are present per molecule, the change per molecule is 4 (2 for each atom), and the ratio of H_2S to O_2 becomes 4 to 6 or 2 to 3.

$$2\ H_2S + 3\ O_2 \rightarrow 2\ H_2O + 2\ SO_2$$

EXAMPLE 3.



From change in oxidation numbers, the ratio of the reducing agent Cu, to the oxidizing agent, HNO_3, must be 3 to 2:

$$3\ Cu + 2\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + H_2O$$

We note that part of the HNO_3 undergoes no change in oxidation number in forming the salt, cupric nitrate; however, 3 $Cu(NO_3)_2$ calls for 6 more atoms of nitrogen which must be furnished by the nitric acid (this is the only source of nitrogen atoms). This requires 6 additional molecules of HNO_3 to be added to the 2 molecules which have been reduced to nitric oxide. The complete equation becomes:

$$3\ Cu + 2\ HNO_3 + 6\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$

or

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$

The change in oxidation numbers gives us information only about the parts which undergo oxidation and reduction. No information about the amount of a reagent used in some capacity other than oxidation-reduction is indicated. Thus, in the above, the ratio of reducing agent to oxidizing agent is 3 to 2, but because part of the nitric acid is used in another capacity, the number of molecules of HNO_3 used in this other capacity must be added to those used for oxidation purposes. It is evident from the equation that only ¼ of the HNO_3 (2 molecules of 8) act in an oxidizing capacity; the other ¾ act as a salt former (to form copper nitrate).

After a little practice, the student may determine the oxidation number changes by inspection and place the correct coefficients in the equation. Occasionally it may be necessary to double the numbers corresponding to the changes; however, the ratio must be maintained and if one number is doubled, the second must also be doubled. For example, in the reaction:

$$KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + Fe_2(SO_4)_3 + H_2O$$

(−5 over $KMnO_4$ → $MnSO_4$; +1 over $FeSO_4$ → $Fe_2(SO_4)_3$)

an even number of atoms of Fe are necessary on the right side, so the numbers used in the final balancing must be 10 to 2 (which is the same ratio as 5:1); thus:

$$2\ KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 \rightarrow K_2SO_4 + Fe_2(SO_4)_3 + 2\ MnSO_4 + 8\ H_2O$$

Ionic oxidation-reduction equations Having balanced the above molecular equation by changes in oxidation numbers, we may then write in ionic form:

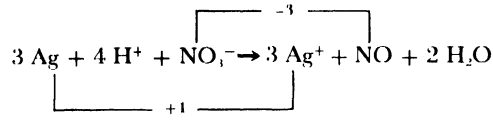
$$2\ MnO_4^- + 10\ Fe^{++} + 16\ H^+ \rightarrow 2\ Mn^{++} + 10\ Fe^{+++} + 8\ H_2O \qquad (1)$$

Note that the ions not taking part in the chemical change have been omitted; they would merely cancel each other on either side of the equation if written. Other molecular equations in ionic form are:

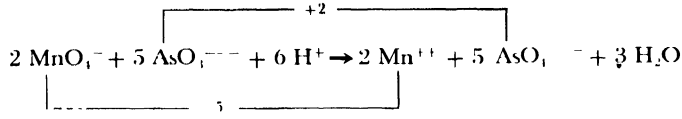
$$3\ Cu + 2\ NO_3^- + 8\ H^+ \rightarrow 3\ Cu^{++} + 2\ NO + 4\ H_2O$$
$$2\ Fe^{+++} + H_2S \rightarrow 2\ Fe^{++} + 2\ H^+ + S$$
$$5\ H_2S + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ S + 2\ Mn^{++} + 8\ H_2O$$

It is often preferable to write and balance a chemical change involving ions without first writing the molecular equation. The equation is bal-

anced by a consideration of change in oxidation numbers as explained above for molecular equations For example:



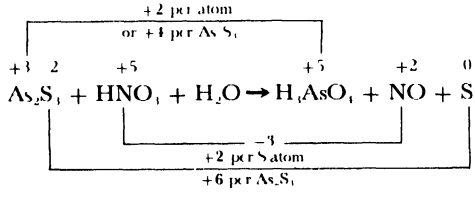
or



It is to be noted in all of these balanced ionic equations that the net positive or negative charge on one side of an equation balances that on the other side; for example, in equation (1) above, the net charge on the left is (2−) + (20+) + (16+) = 34+, and on the right side is (4+) + (30+) = 34+. The equation is said to be balanced *electrically* as well as atomically.

More difficult oxidation-reduction equations Occasionally an equation is encountered in which more than two elements change in oxidation numbers.

EXAMPLE 1:

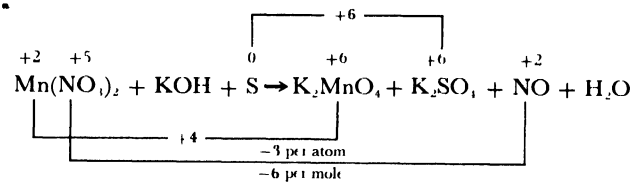


Note that both As and S atoms in As_2S_3 are oxidized; each As atom from +3 to +5 and each S atom from −2 to 0. Since there are 2 As atoms per As_2S_3 molecule, the total change in As is $2 \times +2 = +4$. Likewise, the total change in S in As_2S_3 is $3 \times +2 = +6$. The net total change in As_2S_3 is $(+4) + (+6) = +10$ The change in N in HNO_3 is simply +5 to +2, a loss in oxidation number of 3 Hence the ratio of As_2S_3 to HNO_3 is 3 to 10. On balancing the hydrogen and oxygen atoms, the equation becomes:

$$3\ As_2S_3 + 10\ HNO_3 + 4\ H_2O \rightarrow 6\ H_3AsO_4 + 10\ NO + 9\ S$$

To arrive at the proper coefficients for equations of this type, it is necessary only to determine the total net change of oxidation numbers in each molecule of reacting substances.

EXAMPLE 2:



Net change in $Mn(NO_3)_2 = +4 + (-6) = -2$
Net change in S $= +6$

This gives a ratio of 6 to 2, or 3 to 1; therefore

$$3\ Mn(NO_3)_2 + 8\ KOH + S \rightarrow 3\ K_2MnO_4 + K_2SO_4 + 6\ NO + 4\ H_2O$$

The step ion-electron method of balancing equations This method is applicable only to ionic reactions; however, since most reactions in solution are between ions, the method proves convenient and useful. The method takes into account only those ions in solution which actually enter into reaction; in other words, only the net reaction in shown. Those ions which remain unaltered in the solution do not appear in the equation. The oxidation-reduction equation is broken down into two partial equations or steps called *half-reactions;* one equation represents the oxidation step, the other the reduction step. The number of electrons transferred in each step is indicated, and each equation is balanced both atomically and electrically. The gain and loss of electrons is then balanced by multiplying each step by the appropriate number.

EXAMPLE 1:

$$FeCl_3 + SnCl_2 \rightarrow FeCl_2 + SnCl_4 \text{ (not balanced)}$$

From an ionic standpoint, we should write down only the ions which enter into the chemical change—namely Fe^{+++}, which is reduced to Fe^{++}, and Sn^{++}, which is oxidized to Sn^{++++}. The two half-reactions would be

$$Sn^{++} \rightarrow Sn^{++++} + 2\ e \text{ (oxidation)}$$
$$Fe^{+++} + e \rightarrow Fe^{++} \text{ (reduction)}$$

Each step is now balanced electrically as well as atomically. Since 2 electrons appear in the first step, we may balance electrons by multiplying the second equation by 2

$$2\ Fe^{+++} + 2\ e \rightarrow 2\ Fe^{++}$$

Now the two steps may be added (electrons are cancelled), and we obtain the net ionic reaction

$$\begin{array}{r} Sn^{++} \rightarrow Sn^{++++} + 2e \\ 2\ Fe^{+++} + 2e \rightarrow 2\ Fe^{++} \\ \hline Sn^{++} + 2\ Fe^{+++} \rightarrow Sn^{++++} + 2\ Fe^{++} \end{array}$$

Note that the final step is also balanced electrically; the net charge on each side of the equation is +8.

EXAMPLE 2: Copper reacts with dilute nitric acid to form cupric ions, water, and nitric oxide. Applying the ion-electron method to this reaction, copper is oxidized from the free state to cupric ion:

$$Cu \rightarrow Cu^{++} + 2\ e \text{ (oxidation)} \qquad (1)$$

Meanwhile, nitric acid is reduced to NO and H_2O, the latter two substances being un-ionized:

$$H^+ + NO_3^- \rightarrow NO + H_2O$$

The latter equation is balanced atomically as follows:

$$4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O$$

This equation is now balanced atomically but not electrically, since the net charge on the left is +3, and the net charge on the right side is 0. The addition of 3 e to the left side will balance the step electrically:

$$3\ e + 4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O \qquad (2)$$

To balance the gain and loss of electrons, equation (1) may be multiplied by 3 and equation (2) by 2, then:

$$\begin{array}{r} 3\ Cu \rightarrow 3\ Cu^{++} + 6e \\ 6e + 8\ H^+ + 2\ NO_3^- \rightarrow 2\ NO + 4\ H_2O \\ \hline 3\ Cu + 8\ H^+ + 2\ NO_3^- \rightarrow 3\ Cu^{++} + 2\ NO + 4\ H_2O \end{array}$$

EXAMPLE 3: It is further assumed in the ion-electron method that H^+ ions and H_2O molecules may be used to balance each half-reaction atomically if the reaction is being carried out in acid solution, or OH^- ions and H_2O molecules may be used if the reaction is in basic solution. To illustrate, permanganate ion will oxidize sulfide ion to free sulfur in acid solution

$$S^{--} \rightarrow S + 2\ e \qquad (1)$$

and the permanganate ion is reduced to manganous ion

$$MnO_4^- \rightarrow Mn^{++}$$

To balance the latter step atomically, we may add 8 hydrogen ions to the left side, in which case 4 molecules of water will appear on the right side:

$$8\ H^+ + MnO_4^- \rightarrow Mn^{++} + 4\ H_2O$$

5 electrons are then necessary on the left side to balance electrically:

$$5\ e + 8\ H^+ + MnO_4^- \rightarrow Mn^{++} + 4\ H_2O \qquad (2)$$

Combining steps (1) and (2) and balancing gain and loss of electrons,

$$\begin{array}{r} 5\ S^{--} \rightarrow 5\ S + 10\ e \\ 10\ e + 16\ H^+ + 2\ MnO_4^- \rightarrow 2\ Mn^{++} + 8\ H_2O \\ \hline 5\ S^{--} + 16\ H^+ + 2\ MnO_4^- \rightarrow 5\ S + 2\ Mn^{++} + 8\ H_2O \end{array}$$

Predicting products of oxidation-reduction reactions An important objective of the chemist is to learn how to predict the probable results of chemical changes. We cannot summarize here all the information needed to predict chemical behavior over the broad field of inorganic chemistry; however, certain basic patterns of behavior may be outlined from which some reasonable predictions may be made.

Oxidizing and reducing agents usually behave in fairly definite ways, and if we learn these patterns of behavior for the common oxidizing and reducing agents, we should be able to predict many reactions with better than a fair degree of success. Thus, concentrated nitric acid, in acting as an oxidizing agent, is usually reduced to NO_2 and H_2O, whereas dilute nitric acid usually yields NO and H_2O. Likewise, permanganate ion, MnO_4^-, which is a common laboratory oxidizing agent ($KMnO_4$), yields Mn^{++} and H_2O when the oxidation-reduction reaction is carried out in acid solution, or MnO_2 and H_2O in neutral or basic solution. Some of the common oxidizing agents and their usual reduction products are tabulated below:

OXIDIZING AGENT	PRODUCTS
HNO_3 (conc)	$NO_2 + H_2O$
HNO_3 (dilute)	$NO + H_2O$
MnO_4^- (acid soln)	$Mn^{++} + H_2O$
MnO_4^- (basic soln)	MnO_2
$Cr_2O_7^{--}$ or CrO_4^{--}	$Cr^{+++} + H_2O$
F_2, Cl_2, Br_2 or I_2	F^-, Cl^-, Br^-, I^-
Fe^{+++}	Fe^{++}
MnO_2	Mn^{++}
$KClO_3$	KCl

Similarly, reducing agents follow fairly definite patterns. The elements, particularly the metals, constitute the largest single group of reducing agents. Nearly all may be converted into oxides, and these changes would all represent reducing properties of the elements. If an element like Na, K, Ca, Mg, or Al exhibits a single valence, the element can form only a compound in which that particular valence is shown; that

is, these elements may exhibit only one oxidation state. If more than one oxidation state is possible, the element will generally acquire the higher oxidation state whenever it undergoes oxidation; thus, iron is most likely to be oxidized to Fe^{+++} rather than Fe^{++}. Some of the more common reducing agents and their oxidation products are tabulated below:

REDUCING AGENTS	PRODUCTS
Metals	Metallic ions (cations)
H_2S	S, or possibly SO_2 or SO_4^{--}
S	SO_2 or SO_4^{--}
HCl, HBr, HI	Free halogen
Fe^{++}	Fe^{+++}
Sn^{++}	Sn^{++++}
$C_2O_4^{--}$ (oxalate)	$CO_2 + H_2O$

To illustrate the use of this summarized data on oxidizing and reducing agents, consider a reaction in acid solution between oxalate ion, $C_2O_4^{--}$ and permanganate ion, MnO_4^-. From the tables above, we note the products are CO_2, Mn^{++}, and H_2O; hence

$$5\ C_2O_4^{--} + 2\ MnO_4^- + 16\ H^+ \rightarrow 10\ CO_2 + 2\ Mn^{++} + 8\ H_2O$$

or consider the reaction of H_2S with concentrated HNO_3. We may represent the reaction as producing S, SO_2, or H_2SO_4.

$$H_2S + 2\ HNO_3 \rightarrow S + 2\ NO_2 + 2\ H_2O$$

With excess HNO_3 and heat, sulfur perhaps would be oxidized further, and we might reasonably expect something like this:

$$H_2S + 8\ HNO_3 \rightarrow H_2SO_4 + 8\ NO_2 + 4\ H_2O$$

Whether or not a reaction will proceed between a given oxidizing agent and a given reducing agent depends primarily on what we call *oxidation potentials,* a subject which we shall develop in some detail in Chapter 32. Meanwhile, the general information which is recorded above will allow us to make some reasonable predictions regarding oxidation-reduction processes.

EXERCISES

1 From the standpoint of oxidation numbers, define the following terms: (*a*) oxidation; (*b*) reduction; (*c*) oxidizing agent; (*d*) reducing agent.

2 From a consideration of change of oxidation number or electron transfer, balance the following equations and indicate the oxidizing agent and reducing agent:

(*a*) $FeCl_3 + H_2S \rightarrow FeCl_2 + HCl + S$

(*b*) $Bi(OH)_3 + Na_2SnO_2 \rightarrow Bi + Na_2SnO_3 + H_2O$
(*c*) $SnCl_2 + H_2SO_3 + HCl \rightarrow SnCl_4 + H_2S + H_2O$
(*d*) $H_2S + HNO_3 \rightarrow H_2SO_4 + NO_2 + H_2O$
(*e*) $KIO_3 + KI + HC_2H_3O_2 \rightarrow KC_2H_3O_2 + H_2O + I_2$
(*f*) $Fe + HNO_3 \rightarrow Fe(NO_3)_3 + NO + H_2O$
(*g*) $HMnO_4 + AsH_3 + H_2SO_4 \rightarrow H_3AsO_4 + MnSO_4 + H_2O$
(*h*) $As_4 + HNO_3 \rightarrow HAsO_3 + NO + H_2O$
(*i*) $Sb_2S_5 + HNO_3 \rightarrow Sb_2O_5 + H_2SO_4 + NO + H_2O$
(*j*) $KMnO_4 + H_2C_2O_4 + H_2SO_4 \rightarrow K_2SO_4 + CO_2 + MnSO_4 + H_2O$

3 Balance the equations given below. Note that three elements change in oxidation number.

(*a*) $MnBr_2 + HNO_3 + PbO_2 \rightarrow HMnO_4 + Br_2 + Pb(NO_3)_2 + H_2O$
(*b*) $CrI_3 + KOH + Cl_2 \rightarrow K_2CrO_4 + KIO_4 + KCl + H_2O$

4 Write balanced ionic equations for:

(*a*) Bismuth trisulfide plus nitric acid yielding trivalent bismuth ion, sulfur, nitric oxide, and water.

(*b*) Sulfite ion plus permanganate ion yielding sulfate ion, divalent manganese ion, and water.

5 Complete and balance the following equations in the steps indicated, using the ion-electron method; then add the two half-reactions to obtain the complete single step equation. Make cancellations wherever possible.

(*a*) $Zn \rightarrow Zn^{++}$
$Cl_2 \rightarrow Cl^-$

(*b*) $CuS \rightarrow Cu^{++} + S$
$H^+ + NO_3^- \rightarrow H_2O + NO$

(*c*) $Fe^{+++} \rightarrow Fe^{++}$
$Sn^{++} \rightarrow Sn^{++++}$

(*d*) $Mn^{++} + H_2O \rightarrow MnO_4^- + H^+$
$H^+ + PbO_2 \rightarrow Pb^{++} + H_2O$

(*e*) $Bi(OH)_3 \rightarrow Bi + OH^-$
$OH^- + SnO_2^{--} \rightarrow SnO_3^{--} + H_2O$

(*f*) $Sb^{+++} \rightarrow Sb$
$Fe \rightarrow Fe^{++}$

(*g*) $Fe^{++} \rightarrow Fe^{+++}$
$Cr_2O_7^{--} + H^+ \rightarrow Cr^{+++} + H_2O$

(*h*) $Zn \rightarrow Zn^{++}$
$HAsO_2 + H^+ \rightarrow AsH_3 + H_2O$

(*i*) $Pt + Cl^- \rightarrow PtCl_6^{--}$
$H^+ + Cl^- + NO_3^- \rightarrow NOCl + H_2O$

(*j*) $Bi_2O_5 + H^+ \rightarrow Bi^{+++} + H_2O$
$Cl^- \rightarrow Cl_2$

(*k*) $Fe^{++} \rightarrow Fe^{+++}$
$H_2O_2 + H^+ \rightarrow H_2O$

6 The following ionic equations are to be balanced. Where necessary, add H^+, OH^-, or H_2O. Break the reaction down into its two half-reactions, the oxidation part and the reduction part, and balance each part by the ion-electron method. Then add the two parts to get the single step equation.

(*a*) $Fe + H^+ + NO_3^- \rightarrow Fe^{+++} + NO + H_2O$
(*b*) $Co(OH)_2 + O_2^{--} \rightarrow Co(OH)_3 + OH^-$
(*c*) $NiS + Cl^- + NO_3^- \rightarrow NiCl_4^{--} + S + NO$
(*d*) $H_2O_2 + MnO_4^- + H^+ \rightarrow O_2 + Mn^{++} + H_2O$
(*e*) $Mn^{++} + ClO_3^- \rightarrow MnO_2 + ClO_2$
(*f*) $MnO_4^- + NO_2 + H^+ \rightarrow Mn^{++} + NO_3^- + H_2O$
(*g*) $I_2 + H_2O + Cl_2 \rightarrow IO_3^- + H^+ + Cl^-$

(*h*) $H_2SO_3 + MnO_4^- + H^+ \rightarrow HSO_4^- + Mn^{++}$
(*i*) $Zn + CNS^- \rightarrow Zn^{++} + H_2S + HCN$

7 Complete and balance:

(*a*) $Na_2C_2O_4 + KMnO_4 + H_2SO_4 \rightarrow$
(*b*) $FeSO_4 + HNO_3 + H_2SO_4 \rightarrow$

8 Write the two preceding equations ionically.

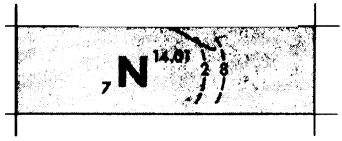
9 Balance the following equations by any method:

(*a*) $Sb + HNO_3 \rightarrow Sb_2O_5 + NO_2 + H_2O$
(*b*) $MnO_2 + BiO_3^- + H^+ \rightarrow HMnO_4 + Bi^{+++} + H_2O$
(*c*) $NiS + H^+ + Cl^- + NO_3^- \rightarrow Ni^{++} + S + NOCl + H_2O$
(*d*) $Fe^{++} + Cr_2O_7^{--} + H^+ \rightarrow Fe^{+++} + Cr^{+++} + H_2O$
(*e*) $F_2 + H_2O \rightarrow HF + O_3$
(*f*) $Sn^{++} + ClO_4^- + H^+ \rightarrow Sn^{++++} + Cl^- + H_2O$
(*g*) $H_2SO_3 + IO_3^- \rightarrow SO_4^{--} + I^- + H_2O$

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Eblin, Lawrence P., "Oxidation Number in Auto-Redox Reactions," *J. Chem. Ed.* 28:221 (1951).



twenty-one

NITROGEN AND THE ATMOSPHERE

History In 1772, Rutherford, a Scottish botanist, showed that an inert substance incapable of sustaining life remained after the combustion of various substances in air. The nature of this inert substance remained obscure until Lavoisier recognized it as an elementary substance. Because of its inertness, it was given the name "azote," which means "lifeless." Later the name was changed to nitrogen, since the element is a constituent of "niter," now known as potassium nitrate.

Importance of nitrogen Nitrogen is characterized by its tendency to remain in the uncombined state. Because of its inactivity, we might think of it as being a relatively unimportant component of the atmosphere. However, a careful study of the ways in which nitrogen and its compounds influence our lives will convince us of the vital importance of this element. The air we breathe is approximately 80 per cent nitrogen, 20 per cent oxygen, and 0.04 per cent carbon dioxide. Exhaled air also contains about 80 per cent nitrogen; the oxygen content is about 16 per cent and carbon dioxide content 4 per cent. We use, then, only about 4 per cent of the air we breathe in; our lungs pump a large amount of inert nitrogen in and out.

Combustion of fuel would be extremely rapid were it not for the nitrogen present in the air. A glowing cigarette placed into pure oxygen bursts into flame and quickly burns up. Smoking would be out of the question if the atmosphere were pure oxygen. Corrosion of metals would proceed at a rapid rate, so rapid as to make many metals impractical for use. All oxidation processes in which air is the oxidizing agent would be difficult to control were it not for the fact that inert nitrogen is present.

Certain nitrogen compounds are essential for the growth of plants and animals. Proteins—complex organic compounds containing nitrogen—are present in every living cell. A study of the element, then, is impor-

tant to the biologist. Since very few plants have the ability to utilize nitrogen from the atmosphere, we must replenish the supply in soil with nitrogen-containing fertilizer. Hence nitrogen is important to those engaged in agriculture.

Nitrogen is a constituent of many of our foods and as such plays an important part in processes of animal metabolism. Nitrogen compounds are used extensively in the production of drugs and dyestuffs and are present in practically all explosives.

The occurrence of nitrogen Tremendous quantities of free nitrogen are found in the atmosphere; it has been estimated that there are more than 20 million tons over each square mile of the earth's surface. Certain natural gases contain a small percentage of the free element. Relatively little nitrogen is found as compounds; the main concentrated source of combined nitrogen is sodium nitrate (Chile saltpeter), fairly large deposits of which are found in Chile. Small deposits of potassium nitrate (saltpeter) are also known. Proteins constitute another source of combined nitrogen. Small quantities of nitrate or ammonium salts are naturally present in all soils.

Laboratory preparation (*a*) *From the air* This involves separating the two main constituents of air—nitrogen and oxygen, either by physical means (see page 84) or by removing the oxygen by chemical means. Since oxygen is quite an active substance and nitrogen is much less active chemically, the difference in activity may be used as a basis for separation. Phosphorus readily combines with oxygen in the air to form phosphorus pentoxide. Since nitrogen does not combine with phosphorus, an effective means of separation is as follows: A piece of phosphorus is burned in air which is enclosed in a bottle inverted over water. The oxygen is removed by combination with the phosphorus. The phosphorus pentoxide dissolves in the water, forming phosphoric acid. The reactions are:

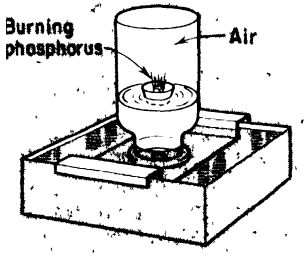


Figure 21–1 Obtaining nitrogen from air.

$$4\,P + 5\,O_2 \rightarrow 2\,P_2O_5$$
$$P_2O_5 + 3\,H_2O \rightarrow 2\,H_3PO_4$$

Nitrogen prepared by this method is not pure, as it contains a small amount of water vapor and the rare gases present in the atmosphere. Certain metals, such as heated copper, may also be used to remove the oxygen from the air in much the same manner as phosphorus.

(*b*) *From certain compounds of nitrogen.* Chemically pure nitrogen is conveniently prepared by heating together solutions of sodium nitrite and ammonium chloride:

$$NaNO_2 + NH_4Cl \rightarrow NaCl + \underbrace{NH_4NO_2}_{\rightarrow N_2 + 2\,H_2O}$$

This is a double decomposition reaction between two salts; the ammonium nitrite formed, since it is unstable toward heat, breaks down to yield nitrogen and water. A combination of any nitrite salt and any ammonium salt would give a reaction similar to that above.

If ammonia is passed over hot copper oxide, the following reaction takes place:

$$3\,CuO + 2\,NH_3 \rightarrow 3\,Cu + 3\,H_2O + N_2$$

Cupric oxide acts as an oxidizing agent, ammonia as a reducing agent.

Commercial preparation Commercial nitrogen is prepared by liquefaction of air and subsequent fractional distillation (see page 84). The nitrogen obtained by this process contains about one per cent of other substances, mainly argon. Argon is also inactive chemically, so its presence does not interfere in the use of the nitrogen.

Properties of nitrogen Nitrogen is an odorless, colorless, and tasteless gas at ordinary temperatures. The boiling point under atmospheric pressure is $-195.8°$, and its freezing point, $-209.9°$. Because of its low boiling point, nitrogen is difficult to liquefy. 22.4 liters of the gas at standard conditions weigh 28 grams; hence its formula is N_2. The two atoms of nitrogen are held together in each molecule by covalent linkages. The gas is relatively insoluble in water; a little more than 2 ml. dissolves in 100 ml. of water at standard conditions.

Chemically, nitrogen is an inert substance; it combines with few elements and then only with difficulty. We shall refer to these reactions later in discussing the compounds of nitrogen.

NITROGEN FIXATION

Nitrogen in the combined state—that is, in compounds—is far more useful and important than in the free state. Animals and plants (with few exceptions) cannot use free nitrogen but must depend on nitrogen compounds for this essential element. It is the problem of the chemist to convert free nitrogen into compounds that can be utilized. Any process by which elementary nitrogen is converted into nitrogen compounds is termed *nitrogen fixation.*

Nitrogen compounds are essential to plant and animal life in building up proteins, complex organic substances containing the elements carbon, hydrogen, oxygen, nitrogen, and sometimes phosphorus and sulfur. Animals must eat protein directly, as the body is incapable of building up proteins from other nitrogen compounds. Beans, peas and meat contain considerable protein. The plant, on the other hand, can synthesize plant protein from ammonium salts or nitrate salts which it derives from the soil. The soil may get some nitrogen compounds from the decay of plants, leaves, and other organic matter. Farm soil must be frequently replenished with fertilizer in the form of animal refuse matter, manure, or compounds of nitrogen such as ammonium sulfate or calcium nitrate.

Methods for the fixation of nitrogen can be divided into two groups: (1) natural fixation and (2) artificial fixation

Natural fixation (*a*) Certain plants such as peas, beans, alfalfa, and clover, called *legumes,* are equipped with nodules which contain nitrogen-fixing organisms. These organisms are able to assimilate nitrogen directly from the atmosphere, converting free nitrogen into nitrogen compounds. To replenish the soil with nitrogen, legumes may be grown on the depleted soil and plowed under, in which case decomposition occurs, furnishing fixed nitrogen to the soil. A system of crop rotation, using leguminous plants for maintaining soil fertility, is now an approved practice.

(*b*) One of nature's principal methods of replenishing the supply of nitrogen compounds in the soil occurs as a result of electrical discharges in air and subsequent rainfall. At the high temperature associated with lightning bolts or other arc discharges, nitrogen and oxygen gases combine to form nitrogen oxides. These oxides with air moisture form nitrous and nitric acids which come to the earth in rainfall. A person out in a thunder shower is being subjected to a shower of very dilute nitric and nitrous acids. As these acids act on soil minerals, soluble nitrogen-containing salts are formed in soil waters. For example, as the very dilute nitric acid acts on limestone, $CaCO_3$, calcium nitrate is formed; this salt is a common soil mineral. Considering the bulk of the atmosphere as a factory for HNO_3 production, and the geologic time of operation, we can account for millions of tons of nitrate compound formation.

Artificial fixation Man's methods of nitrogen fixation will be discussed in detail in the next chapter. The important processes are: (1) the Haber; (2) the Birkeland-Eyde; (3) the cyanamide.

The nitrogen cycle It might occur to us that since nitrogen is continually being fixed from the air by natural and artificial methods, the

supply of nitrogen in the atmosphere would decrease. Careful analysis of the air, however, shows that this is not the case; the percentage of nitrogen in the air remains nearly constant because a balance between free and combined nitrogen is maintained as a result of decomposition of nitrogen compounds, yielding elementary nitrogen. The cycle of changes which nitrogen undergoes—the *nitrogen cycle* of nature—can best be shown by a diagram (Figure 21–2). Although the process involves more steps than indicated, the diagram represents the essential changes taking place.

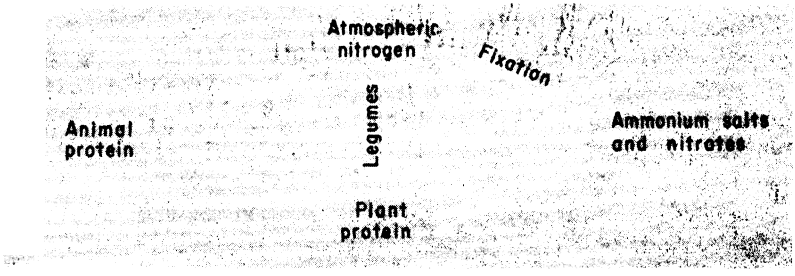


Figure 21–2 The nitrogen cycle.

We may start with elementary nitrogen and trace some of the possible changes. A nitrogen atom in the free state may be fixed by (1) legumes into plant protein, (2) lightning discharges into nitrate salts, or (3) artificial processes into ammonium or nitrate salts. A plant may then utilize the salts for production of plant protein. The plant may serve as a food for animals in which case the original nitrogen atom may become a part of animal protein; or degradation of the plant may again produce ammonium salts. Animal protein, in undergoing decay or degradation, may be converted either into ammonium salts or into free nitrogen which finds its way back into the atmosphere where it is again ready to start another cycle of changes.

OTHER GASES OF THE ATMOSPHERE

Although nitrogen and oxygen are the most abundant constituents of the atmosphere, small quantities of water vapor, carbon dioxide, dust particles, argon, and other inert gases are present. The average composition of dry air by volume is shown in Table 21–1.

Carbon dioxide in the air Analysis of air shows an average carbon dioxide content of about 0.035 per cent (Table 21–1). This carbon

TABLE 21-1 Composition of Dry Air

COMPONENT	PERCENTAGE BY VOLUME	COMPONENT	PERCENTAGE BY VOLUME
Nitrogen	78.0	Hydrogen	.01 or less
Oxygen	21.0	Neon	.0015
Argon	.94	Helium	.0005
Carbon dioxide	.03–.04	Krypton	.00005
		Xenon	.000006

dioxide is produced as a result of the respiration processes of man and animals, decay and rotting, and the combustion of coal, wood, gasoline, and other fuels. The content of carbon dioxide is usually appreciably higher in urban centers than in the country because of the concentration of population and industrial activity. In poorly ventilated rooms the content may run as high as 3 per cent. About one-fifth of the oxygen taken into the lungs from the air is exhaled as carbon dioxide.

We might ask why the content of carbon dioxide in the air does not increase because of the continued processes mentioned above. Actually, a nearly constant balance is maintained between the carbon dioxide and the other constituents of the atmosphere, since plants utilize carbon dioxide of the atmosphere in building up sugars, starches, cellulose, and plant tissue. In plant tissue, water and carbon dioxide somehow combine to form complex compounds—a process called *photosynthesis*. The reactions are catalyzed by chlorophyll, the green coloring matter of plants. The reaction producing starch may be represented as

$$6\,CO_2 + 5\,H_2O \rightarrow C_6H_{10}O_5 + 6\,O_2$$

Note that oxygen is also produced in the reaction and is released to the atmosphere. Energy for the above reaction is derived from the sun. While animals use oxygen and liberate carbon dioxide in respiratory processes, plants do just the opposite in photosynthesis—they use carbon dioxide and liberate oxygen.

Millions of years ago in the Carboniferous era, vegetation was abundant and tropical over most of the land surface. Coal beds of arctic

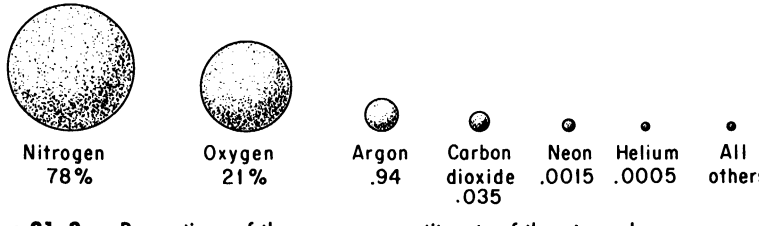


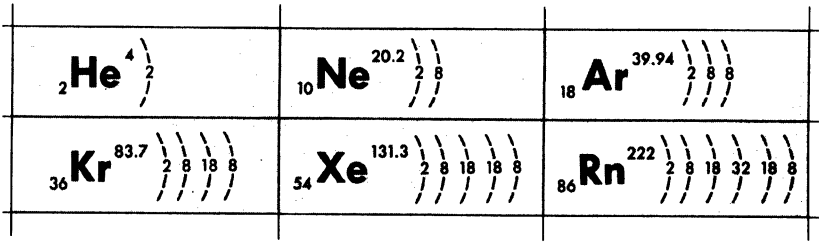
Figure 21-3 Proportions of the gaseous constituents of the atmosphere.

regions are remnants of marked plant growth of long, long ago. Such luxurious plant growth is explained by the possibility that the CO_2 content of the air was much higher—perhaps 2 or 3 per cent rather than the .035 per cent of today—and also by the fact that the temperature of the earth's surface was higher.

Water vapor in the atmosphere Water in the atmosphere is present as a result of evaporation from oceans, lakes, and streams over the earth's crust. For every temperature there is a saturation pressure of water vapor in the air, and this saturation pressure is the vapor pressure of water at the temperature in question. Thus at 20° the air is saturated with water when the pressure of water vapor in the air is 17.5 mm. (Table 11–3, page 148.) Usually the pressure of water vapor in the air is less than this saturation pressure. The ratio of the pressure of the water vapor in the air to the saturation pressure at any given temperature is called the *humidity*. If the pressure of water vapor in the air is 10 mm. at 20°, the humidity is $\frac{10}{17.5} = 57.1$ per cent. Of course, if the pressure of water vapor were 17.5 mm., the humidity would be 100 per cent.

When the atmosphere is cooled during the night, the cooling may progress to the point where the pressure of water vapor in the air becomes greater than the saturation pressure. When this occurs, dew or fog is formed as a result of condensation of water vapor from the air. Clouds result from the rising and subsequent cooling of moist warm air, and the formation of large droplets may result in precipitation of rain.

THE INERT GASES



GAS	SYMBOL	BOILING POINT	FREEZING POINT	CRITICAL TEMP.	QUANTITY IN AIR: PARTS PER MILLION
Helium	He	−269	———	−268	4
Neon	Ne	−246	−249	−229	12
Argon	Ar	−186	−189	−122	9400
Krypton	Kr	−152	−169	− 63	.5
Xenon	Xe	−109	−140	− 17	.06
Radon	Rn	− 62	− 71		

Lord Rayleigh and William Ramsey in 1894 discovered an inert gas in the atmosphere which they called *argon*, meaning "inert." The

discovery came as a result of studies of the atomic weight of nitrogen. Nitrogen derived from the atmosphere invariably gave a higher atomic weight than nitrogen derived by chemical means. These studies led to the conclusion that air contained, besides nitrogen, some inert substance more dense than nitrogen. Further investigation resulted in the isolation of argon from the atmosphere. Argon is present in the air to the extent of nearly one per cent. Since the discovery of argon, other rare gases have been isolated from the atmosphere, including helium, neon, krypton, xenon, and radon.

The inactivity of these elements (Group VIII*A* of the periodic table) may be explained on the basis of their atomic structure. Helium has two electrons in the first orbit (its outer orbit), which represents a stable configuration. The other elements have eight electrons in the outermost orbit, which represents a stable state. The atom of each of these elements is completely satisfied in its electronic configuration and so has no tendency to give up, take up, or share electrons. As a result, we would not expect these elements to form compounds or undergo chemical change. The molecules of these gases are monatomic, since the atoms of the elements have no tendency to combine with one another.

Helium is unique among the chemical elements, as it was discovered in the atmosphere around the sun before being found on the earth. As much as two per cent of helium is found in certain natural gas wells in Kansas and Texas. Its source is the radioactive decay of certain elements found in minerals. Helium has the lowest boiling point of any substance known; consequently it may be separated from the other constituents of natural gas by lowering the temperature sufficiently to liquefy or freeze the other components. The boiling point of helium is $-268.5°$; its freezing point, $-272°$ at 26 atmospheres pressure, is just a degree above the absolute zero temperature.

Helium is used mainly in balloons and other lighter-than-air craft. While helium is somewhat heavier[1] than hydrogen, it has the important advantage of being noncombustible and having a lower rate of diffusibility. Helium is also used in diving bells to lessen the danger of caisson disease or the *bends,* which results from a too rapid escape of nitrogen from the blood stream of divers coming to the surface. At the high

[1] Although helium is twice as heavy as hydrogen, its lifting power is almost as good. The lifting power of a gas in a balloon depends upon the difference between the density of the gas on the inside and the air on the outside.

22.4 cu. ft. H_2 = 2 oz.
22.4 cu. ft. He = 4 oz.
22.4 cu. ft. air = 29 oz.

Lifting power:
22.4 cu. ft. H_2 = 29 − 2 = 27 oz.
22.4 cu. ft. He = 29 − 4 = 25 oz.

Thus helium is $\frac{25}{27}$ or about 93 per cent as effective as hydrogen in lifting power.

pressures in diving bells, the solubility of nitrogen of the air in the blood increases, and if the pressure is decreased too rapidly, gas bubbles may develop in the blood stream as a result of escape of the nitrogen gas. Since the solubility of helium in blood is much less than that of nitrogen, it may advantageously be mixed with oxygen for use under high pressures.

One of the important uses of the inert gases, particularly neon, is to produce colored light in discharge tubes. Although these gases do not form ions in ordinary chemical changes, ions may be produced by removal of electrons in a discharge tube under a high alternating current potential. The gas is enclosed in a tube at a low pressure (5–10 mm.) where the application of several thousand volts produces ions and renders the gas a conductor of the current. Light of a characteristic color is emitted because of the "activation" of the atoms through a displacement of electrons. Neon produces the familiar orange-red color of neon signs, argon gives a purple color, krypton and xenon produce a blue light. By mixing the gases and using different colored glasses, various shades of color may be obtained.

Argon is used in filling electric light bulbs; it seems to have certain advantages over nitrogen in prolonging the life of the filaments.

Radon will be considered in Chapter 31. Its only uses depend upon its radioactivity.

Air pollution Pollution of air by industrial activity, trash burning and automotive exhaust gases has become a serious problem in heavily populated areas. It is particularly acute in places where topographical features and climatic conditions are such that a given air mass remains stagnant over the area without air-cleaning precipitation. Pollutants that cause major difficulties are oxides of sulfur and nitrogen, ozone, hydrocarbons, smoke and other forms of particulate matter. Reactions between these materials in strong sunlight undoubtedly form more complex compounds that contribute to the problem. These pollutants may cause unsavory odors; health injuries, particularly through eye and lung irritation; damage by deterioration, corrosion, and soiling; and damage to crops and vegetation. Government agencies and industrial groups are giving the problem intensive study with a view toward establishment of standards for maximum allowable concentrations of various pollutants, and modification or curtailment of activities that contribute to air pollution.

EXERCISES

1 What is meant by "nitrogen fixation"?

2 If a liquid mixture of the constituents of the atmosphere is warmed, in what order would the various constituents distil off?

3 List four plants which have the ability to fix nitrogen from the atmosphere.

4 Calculate the weight of 100 liters of nitrogen gas at standard conditions.

5 Devise a means of determining the molecular weight of nitrogen.

6 Calculate the weight of nitrogen obtainable by the action of ammonium chloride on 100 g. of sodium nitrite. What volume would this weight of nitrogen occupy at standard conditions? Ans. 40.6 g.; 32.5 l.

7 Of what importance is the "nitrogen cycle"? Trace the chemical changes which a nitrogen atom might undergo in progressing through the nitrogen cycle.

8 Give one important use of each of the following rare gases: helium, neon, argon.

9 Calculate the weight of 50 liters of nitrogen enclosed in a steel cylinder under a pressure of 100 atmospheres and a temperature of 0°. Ans. 6.25 kg.

10 Diagram the nitrogen atom. Show how three atoms of hydrogen may combine with one atom of nitrogen to form NH_3. Is the linkage covalent or electrovalent?

11 Calculate the weight of nitrogen produced by passing 100 liters of ammonia gas at standard conditions over cupric oxide, according to the equation:

$$3\ CuO + 2\ NH_3 \rightarrow 3\ Cu + N_2 + 3\ H_2O$$ Ans. 62.5 g.

12 Diagram the structure of the elements He, Ne, and Ar. On the basis of atomic structure, why would you expect these three elements to show similarities in chemical behavior?

13 What weight can be supported by a balloon containing 10,000 liters of helium gas? Assume standard conditions for both air and helium, and consider the volume of air displaced to be equal to the volume of helium.

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twenty-two

COMPOUNDS OF NITROGEN

Although nitrogen is a relatively inert substance in the elementary state, it forms a number of compounds in which it exhibits oxidation states from -3 to $+5$. The most common oxidation states are -3, as in ammonia and ammonium salts, $+3$ as in nitrites and $+5$ as in nitric acid and nitrates. These compounds will be considered in some detail.

Nitrogen forms the N^{---} ion in crystalline nitrides. This ion is unstable in aqueous solution, since it reacts with water to form ammonia and hydroxide ion. In its other compounds, nitrogen is covalently bonded.

AMMONIA AND AMMONIUM SALTS

Decay of nitrogenous matter in the absence of air produces ammonia. The decomposition may be brought about with the aid of heat or in the presence of putrefying bacteria. Ammonia at one time was produced by distilling animal horns and hoofs; hence the name "spirits of hartshorn." As a result of the action of bacteria on nitrogen compounds, small quantities of ammonia gas may be present in air. Because of the great solubility of ammonia in water, however, it rapidly finds its way by the action of rain and snow to the soil where it may be converted into other compounds.

Laboratory preparation of ammonia. (*a*) *From ammonium salts.* Ammonia is most conveniently prepared in the laboratory by the action of a strong base on an ammonium salt; for example:

$$NH_4Cl + NaOH \rightarrow NH_4OH^1 + NaCl$$
$$NH_4OH \rightarrow NH_3 \uparrow + H_2O$$

[1] NH_4OH has never been isolated as a compound. This formula, however, is widely used to represent a solution of NH_3 in H_2O in which some NH_4^+ and OH^- exist.

The reaction is caused to go to completion by the use of heat, since ammonium hydroxide is unstable and breaks down to give water and ammonia which escapes as a gas and is collected by the displacement of air. (See Figure 22-1.) Since the gas is extremely soluble in water, it cannot be collected by water displacement. The reaction given above is a typical one for the preparation of ammonia Any ammonium salt and strong base may be employed. $Ca(OH)_2$ is usually used instead of sodium hydroxide because it is cheaper:

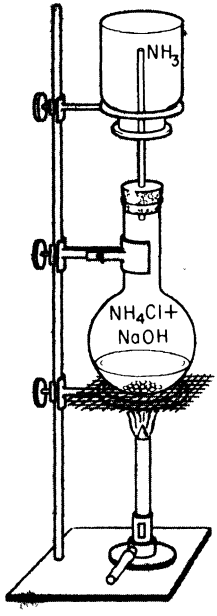


Figure 22-1 Ammonia may be collected by upward displacement of air.

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\ NH_4OH$$
$$\downarrow$$
$$2\ NH_3 \uparrow + 2\ H_2O$$

(*b*) *From nitrides.* The action of water on a nitride produces ammonia:

$$Mg_3N_2 + 6\ H_2O \rightarrow 3\ Mg(OH)_2 + 2\ NH_3 \uparrow$$

These reactions of nitrides are of theoretical interest only.

Commercial preparation of ammonia (*a*) *From coal.* Coal, a product of decomposition of vegetation, contains a small percentage of combined nitrogen. When coal is heated in the absence of air in the production of coke, an ammoniacal liquor is produced as a by-product Ammonia is recovered from this liquor by distillation and subsequent absorption in water. The ammonium hydroxide solution thus produced may be converted into ammonium salts by the addition of acids. Most of the ammonium sulfate used as a fertilizer is prepared in this manner.

(*b*) *Haber process.* When nitrogen and hydrogen gases are heated together in the presence of certain catalysts, some ammonia is formed according to the reaction:

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3 + 24{,}000\ \text{cal.}$$

The reaction is very incomplete at ordinary conditions, with equilibrium established when the ammonia content is less than one per cent. Since the reaction is exothermic, it is evident from a consideration of Le Chatelier's principle (page 227) that a low temperature is favorable to the formation of ammonia. However, if the temperature is below

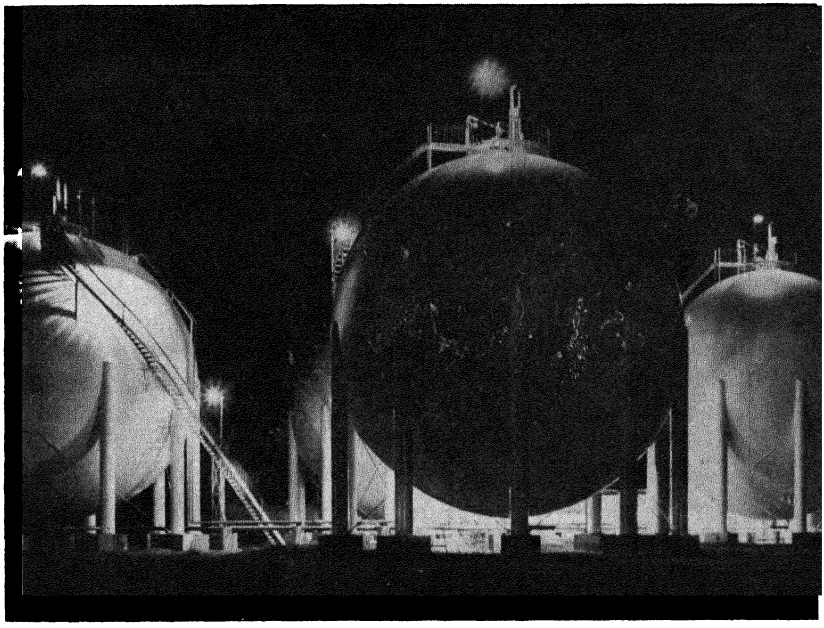


Figure 22–2 Spherical tanks for storing ammonia.

about 500°, the combination of nitrogen and hydrogen occurs too slowly to be practical as a commercial means of preparation. Applying Le Chatelier's principle, we note that an increase of pressure will shift the equilibrium to the right—that is, toward the formation of ammonia. An increase of pressure from 1 atmosphere at 500° to 200 atmospheres at 500° increases the equilibrium yield of ammonia in the above reaction from 0.13 per cent to 17.6 per cent. The process is ordinarily carried out at a temperature of approximately 500° and at a pressure of 200 atmospheres in the presence of a catalyst mixture such as Fe_3O_4 and $K_2O \cdot Al_2O_3$. Ammonia is liquefied from the equilibrium mixture by rapid refrigeration of the gas mix, and the residual N_2 and H_2 is counterpassed back to the high-pressure catalyst chamber. Since large supplies of nitrogen compounds are essential in making explosives, this process was vital to Germany during World War I. Germany's access to the Chilean nitrates was cut off by the British blockade, and had Germany been unable to utilize nitrogen from the air to produce explosives, the war would have lasted only a few months. Haber, a German chemist, perfected the process just before World War I began. In World War II, Germany again had to rely on synthetic nitrogen compounds.

A flow sheet for ammonia synthesis is given on page 564.

(*c*) *The cyanamide process.* During the war years of 1914–1918, the United States built several plants—the largest at Muscle Shoals, Alabama—for the production of synthetic ammonia by the cyanamide process. This process depends for its success upon the development of cheap electric power. The first step in the preparation of ammonia consists in heating lime, CaO, and carbon together in an electric furnace to a temperature of approximately 3000°. Calcium carbide is formed:

$$CaO + 3\,C \rightarrow CaC_2 + CO$$

Nitrogen obtained from the liquefaction of air is passed over the crushed calcium carbide at a temperature of about 1000°. *Calcium cyanamide,* $CaCN_2$, is produced:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

The cyanamide is then treated with steam under pressure, forming ammonia and calcium carbonate:

$$CaCN_2 + 3\,H_2O \rightarrow CaCO_3 \downarrow + 2\,NH_3$$

Cyanamide itself may be used directly as a fertilizer, since this last reaction proceeds slowly in soil.

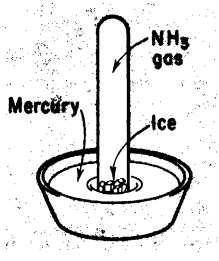


Figure 22–3 Solubility of NH_3 in water.

Properties of ammonia Ammonia is a colorless gas with a sharp, irritating odor at ordinary temperatures. It is easily liquefied, forming a colorless liquid, the boiling point of which is −33°. The gas is extremely soluble in water; 1 liter of water dissolves more than 1000 liters of the gas at 0°. Its extreme solubility in water may be demonstrated by placing a small piece of ice on the surface of mercury in a tube filled with ammonia gas, as shown in Figure 22–3. As the ice melts, the ammonia dissolves and the mercury rapidly rises and almost fills the tube.

When ammonia is dissolved in water, it reacts with the water to form a basic solution:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

This is an equilibrium reaction; the change to the right takes place to only a slight extent. Consequently ammonium hydroxide is referred to as a weak base. Concentrated ammonium hydroxide contains about 28 per cent of ammonia at ordinary conditions of temperature and

pressure. Since it has basic properties, ammonium hydroxide reacts with acids to form ammonium salts:

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$
$$2\ NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2\ H_2O$$

Ammonia acts like a basic anhydride, reacting with acids to form ammonium salts:

$$NH_3 + HCl \rightarrow NH_4Cl$$
$$2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

Reaction of ammonia with acid gases in the laboratory causes the familiar white salt deposits on laboratory glassware and windows.

Ammonium salts have one characteristic generally not possessed by other salts. If an ammonium salt such as NH_4Cl is heated, it is dissociated according to the reaction:

$$NH_4Cl \rightarrow NH_3 + HCl$$

The gases, ammonia and hydrogen chloride, recombine on cooling, forming solid ammonium chloride.

Ammonia readily burns in pure oxygen in the presence of a catalyst, forming nitric oxide and water:

$$4\ NH_3 + 5\ O_2 \rightarrow 6\ H_2O + 4\ NO$$

This reaction represents one step in the preparation of nitric acid from the air by the Ostwald process (page 295).

Uses of ammonia and ammonium salts Ammonia is used extensively as a refrigerant. If liquid ammonia is allowed to evaporate, it absorbs much heat from the surroundings. The gas may then be compressed and liquefied again, after which it once more goes through the cycle of evaporation and liquefaction. See page 149.

Large quantities of ammonia are converted into ammonium salts, which are used as fertilizers. A solution of ammonia in water is used as a cleansing agent and as a water softener. Ammonia is also used in the Solvay process (Chapter 29) for producing soda.

Application of ammonia gas directly to the soil has had spectacular results on irrigated farmlands in the West. The equipment consists essentially of tractor-mounted tanks of liquid ammonia and a battery of several steel tubes welded to the backs of cultivator shovels for injecting the gas into the soil. These tubes are connected with hoses to the ammonia tanks from which the flow of ammonia gas can be controlled with a meter. Very little loss occurs if the gas is placed about six inches below the surface. The practice of feeding the ammonia gas directly into irrigation streams is also successful.

Other compounds of nitrogen and hydrogen Two additional nitrogen-hydrogen compounds merit mention. A compound, $H_2N–NH_2$ or N_2H_4, is a liquid called *hydrazine.* Its water solution acts as a weak base and on neutralization forms salts such as N_2H_5Cl and $N_2H_6Cl_2$. A compound HN_3 (note formula difference from NH_3) is called *hydrazoic acid.* The water insoluble salts of this acid, silver azide, AgN_3, and lead azide, PbN_6, are very sensitive explosives; consequently they are used as detonators to initiate the explosion of less sensitive explosives.

NITRIC ACID AND NITRATES

Nitric acid was prepared by the alchemists from saltpeter (KNO_3) and concentrated H_2SO_4. It was used for separating gold and silver, the silver being soluble and the gold insoluble. The acid was called *aqua fortis* from the Latin meaning "strong water."

Laboratory preparation A general method of preparing a volatile acid (see Chapter 16) is to treat a salt of the desired acid with concentrated sulfuric acid and distil. Since pure HNO_3, hydrogen nitrate, is volatile (b.p. 86° C.) and can be distilled easily, we may use this method for its preparation. Sodium nitrate (Chile saltpeter) is the salt employed:

$$2\ NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HNO_3 \uparrow$$

Since the pure gaseous or liquid hydrogen nitrate is active and attacks rubber, an all-glass apparatus is essential in the distillation (Figure 22–4). The nitric acid distils over and may be condensed in a beaker

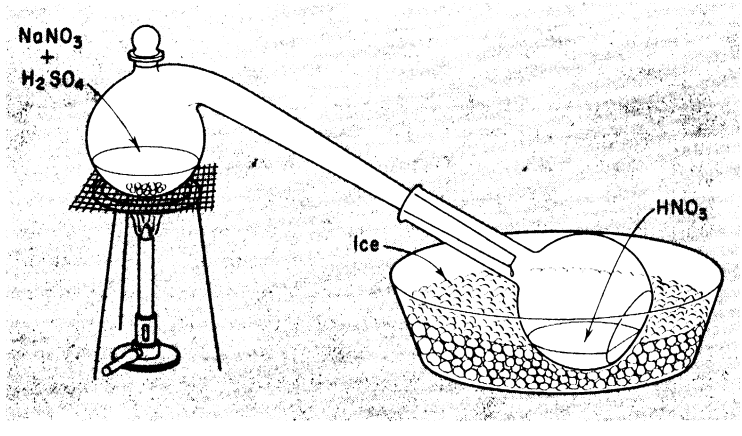


Figure 22–4 Preparation of nitric acid.

or flask cooled by ice water. This reaction is used for the preparation of some nitric acid on a commercial scale, but large iron retorts are used. Because nitric acid is slightly decomposed by impurities to form nitrogen dioxide, the acid produced by this method is not pure. The nitrogen dioxide may be removed, however, by bubbling air through the acid.

Commercial preparation (*a*) *Same as laboratory preparation.*

(*b*) *Haber-Ostwald process* This is the process which enabled Germany, during 1914–1918, to fix nitrogen from the atmosphere and convert it into nitric acid for use in the manufacture of explosives. Nitrogen is first converted into ammonia by the Haber process (see page 290). Ammonia and air in the proportions of one volume of ammonia to about ten volumes of air are passed over a platinum catalyst at a temperature of about 700°. The ammonia is oxidized to nitric oxide (a colorless gas):

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$$

NO readily combines with excess oxygen to form nitrogen dioxide, NO_2 (a brownish-red gas):

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

Nitrogen dioxide is then dissolved in water to produce nitric acid and nitric oxide:

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO$$

The NO produced is again mixed with air and converted to NO_2. The acid produced by this method is about 50 per cent by weight and may be concentrated by distillation. This method of preparing nitric acid is widely used in the world today.

(*c*) *Birkeland-Eyde process.* Many years ago, man learned how to hasten artificially one of nature's methods of nitrogen fixation. Cavendish discovered that nitrogen and oxygen would combine if air was passed through an electric discharge:

$$N_2 + O_2 \rightarrow 2\,NO - 43{,}200 \text{ calories}$$

Since this reaction is endothermic, it is favored by high temperatures (Le Chatelier's principle). Thus, air passed through an electric arc or through a highly heated checkerwork of bricks is converted in small percentage to oxides of nitrogen. These oxides of nitrogen are converted into nitric acid by the same reactions as those in the Ostwald process. Birkeland and Eyde of Norway perfected the arc process, successful commercial use of which depends upon the production of cheap electricity.

Properties of nitric acid Nitric acid is a colorless liquid when pure, with a density of 1.5 and a boiling point of 86°. Commercial nitric acid is about 68 per cent HNO_3 by weight and has a density of about 1.4.

Chemically, nitric acid is characterized by its acid, oxidizing, and nitrating properties. As an acid, it is highly ionized in dilute aqueous solution. It exhibits typical acid reactions, reacting with metallic oxides and bases to form salts. In addition to its acid properties, nitric acid acts as a powerful oxidizing agent:

(*a*) *Action with metals* Nitric acid reacts with practically all of the metals, even those below hydrogen in the activity series. This would seem to be contradictory to the rule that only metals above hydrogen react with acids; however, nitric acid reacts with metals below hydrogen, *not* because of its acid properties, but because of its oxidizing action.

$$3\,Cu + 8\,HNO_3 \rightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$$

or

$$3\,Cu + 8\,H^+ + 2\,NO_3^- \rightarrow 3\,Cu^{++} + 2\,NO + 4\,H_2O$$

Other metals react similarly. Platinum and gold resist the oxidizing action. The reduction product of nitric acid depends somewhat on the concentration of the acid Thus dilute acid produces nitric oxide, while concentrated acid produces nitrogen dioxide:

$$Cu + 4\,HNO_3 \rightarrow Cu(NO_3)_2 + 2\,NO_2 + 2\,H_2O$$

or

$$Cu + 4\,H^+ + 2\,NO_3^- \rightarrow Cu^{++} + 2\,NO_2 + 2\,H_2O$$

Metals above hydrogen in the activity series react with nitric acid to produce hydrogen *only* if the acid is very dilute and cold.

(*b*) *Action with nonmetals* Hot concentrated nitric acid oxidizes several of the nonmetals, as shown by the equations:

$$S + 4\,HNO_3 \rightarrow SO_2 + 4\,NO_2 + 2\,H_2O$$
$$P + 5\,HNO_3 \rightarrow H_3PO_4 + 5\,NO_2 + H_2O$$
$$C + 4\,HNO_3 \rightarrow CO_2 + 4\,NO_2 + 2\,H_2O$$

(*c*) *Action with hydrochloric acid.* A mixture of three moles of hydrochloric acid to one mole of nitric acid is called *aqua regia* from the Latin "royal water." Aqua regia dissolves gold and platinum, metals inactive in either of the acids alone. The nitric acid oxidizes the hydrochloric acid to free chlorine, which is probably the active oxidizing agent in reactions with gold and platinum:

$$6\,HCl + 2\,HNO_3 \rightarrow 3\,Cl_2 + 2\,NO + 4\,H_2O$$
$$2\,Au + 3\,Cl_2 \rightarrow 2\,AuCl_3$$

(*d*) *Explosives manufacture* (*nitration reactions*). Nitroglycerin is prepared by the action of a concentrated nitric acid-sulfuric acid mix on glycerin. The concentrated sulfuric acid acts as a dehydrating agent (page 323).

$$\underset{\text{glycerin}}{C_3H_5(OH)_3} + 3\ HNO_3 \rightarrow \underset{\text{nitroglycerin}}{C_3H_5(NO_3)_3} + 3\ H_2O$$

Trinitrotoluene (TNT) is produced by a similar reaction:

$$C_6H_5CH_3 + 3\ HNO_3 \rightarrow C_6H_2CH_3(NO_2)_3 + 3\ H_2O$$

Most of the compounds formed by the action of nitric acid on organic substances are explosive in character. Dynamite consists of nitroglycerin absorbed in a mixture such as sawdust and nitre. "Smokeless powder" is essentially cellulose nitrate or *guncotton*, which is produced by reaction of cellulose with nitric acid.

An explosion occurs as a result of a rapid chemical reaction attended by the formation of a large volume of gas. When nitroglycerin explodes, the volume of gas produced is many times the volume of the liquid nitroglycerin.

We may arrive at the approximate change in volume during the explosion of nitroglycerin from the following calculations:

$$4\ C_3H_5(NO_3)_3 \rightarrow 12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2$$

908 oz. of liquid nitroglycerin (about 1 cu. ft.) produces about $(12 + 10 + 6 + 1) \times 22.4 = 650$ cubic feet of gaseous products measured at standard conditions. Furthermore, the heat of explosion will expand the product gases to a much larger volume. If the explosive products tend to be confined, as in an artillery projectile or in a hole in rock, a disruptive pressure results as the small volume of initial explosive material, on detonation, forms so much gaseous product.

The crystalline substance NH_4NO_3 may be termed an explosive, and it is mixed in high percentage with other explosive materials. As the other materials explode, the shock brings about the instant decomposition of NH_4NO_3 into gaseous nitrogen, water, and oxygen.

Nitric acid is also used in the manufacture of certain dyes and drugs. Nitrates are used as fertilizers.

Action of heat on nitrates All nitrates decompose when heated. Sodium and potassium nitrates yield oxygen and the nitrite of the metal:

$$2\ NaNO_3 \rightarrow 2\ NaNO_2 + O_2$$

The nitrates of the heavy metals produce oxygen, nitrogen dioxide, and the oxide of the metal:

$$2\ Pb(NO_3)_2 \rightarrow 2\ PbO + 4\ NO_2 + O_2$$

Test for the nitrate ion If concentrated sulfuric acid is slowly added to a test tube containing a solution of nitric acid or a nitrate with ferrous sulfate, a brown ring is formed at the junction of the two liquids (Figure 22–5).

$$2\ NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HNO_3$$

$$2\ HNO_3 + 6\ FeSO_4 + 3\ H_2SO_4 \rightarrow 3\ Fe_2(SO_4)_3 + 2\ NO + 4\ H_2O$$

$$NO + FeSO_4 \rightarrow \underset{\substack{\text{nitrosyl ferrous}\\ \text{sulfate (brown)}}}{FeSO_4 \cdot NO}$$

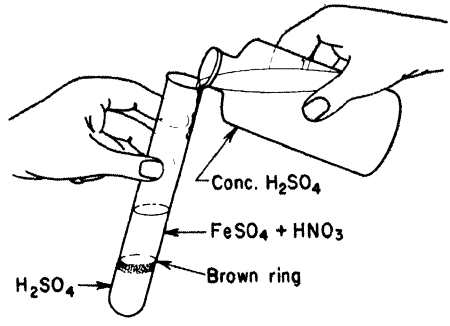


Figure 22–5 Test for nitrate ion.

OXIDES OF NITROGEN

Five oxides of nitrogen are well known

Nitrous oxide, N_2O, a colorless gas
Nitric oxide, NO, a colorless gas
Nitrogen dioxide, NO_2, a reddish brown gas
Nitrogen trioxide, N_2O_3, a blue liquid boiling at 3°
Nitrogen pentoxide, N_2O_5, a white solid

Nitrous oxide The gas is produced by cautiously heating ammonium nitrate:

$$NH_4NO_3 \rightarrow N_2O + 2\ H_2O$$

For laboratory study, it may be collected by displacement of hot water, since the gas is moderately soluble in cold water (61 ml. dissolves in 100 ml. water at 24° C.). Like oxygen, nitrous oxide supports combustion; a glowing splint burns vigorously when thrust into a bottle of the gas, and phosphorus or sulfur also burn vigorously in the gas.

Nitrous oxide has a sweet, pleasant odor and because of the exhilarating effect when inhaled is often referred to as "laughing gas." It is widely used as an anesthetic in dentistry and in minor surgical operations.

Nitric oxide As pointed out earlier, nitric oxide is a reduction product of dilute nitric acid and is conveniently prepared by the action of dilute acid on a metal; for example

$$3\,Cu + 8\,HNO_3 \rightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$$

The gas is colorless and relatively insoluble in water and is the most stable of the oxides of nitrogen. A glowing splint thrust into the gas will go out; however, if vigorously burning phosphorus is placed in nitric oxide, it will continue to burn, leaving free nitrogen.

Nitrogen dioxide When colorless nitric oxide is brought into contact with air or oxygen, reddish brown nitrogen dioxide is rapidly formed:

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

It may also be obtained by the action of concentrated nitric acid on metals; for example,

$$Cu + 4\,HNO_3 \rightarrow Cu(NO_3)_2 + 2\,NO_2 + 2\,H_2O$$
$$Cu + 4\,H^+ + 2\,NO_3^- \rightarrow Cu^{++} + 2\,NO_2 + 2\,H_2O$$

When heated, the reddish brown color becomes more intense; when cooled, the color fades to a pale yellow. Density studies show that an equilibrium exists in the gas between colorless N_2O_4 and brown NO_2:

$$\underset{\text{colorless}}{N_2O_4} \rightleftharpoons \underset{\text{red-brown}}{2\,NO_2} - x \text{ calories}$$

Since the reaction to the right is endothermic, an increase of temperature will shift the equilibrium to form more NO_2. When cooled, the reaction to the left forming N_2O_4 is favored. Thus the gradations of color with temperature change are explained on the basis of a shift in the equilibrium.

Nitrogen dioxide is an intermediate compound formed in the preparation of nitric acid by the Haber-Ostwald process (page 295). When dissolved in water, oxidation and reduction take place within the molecules of NO_2 (called *auto-oxidation*) to form nitric acid and nitric oxide:

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO$$

It is evident from the equation that two-thirds of the compound is oxidized to nitric acid while simultaneously one-third is reduced to nitric oxide. Thus two molecules are oxidized at the expense of the reduction of one molecule.

A product called "fuming nitric acid" is formed when nitrogen dioxide is dissolved in nitric acid. Nitrogen dioxide also plays an important role in the preparation of sulfuric acid by the lead chamber process (page 322).

Nitrogen trioxide N_2O_3 is the anhydride of nitrous acid, and may be produced by the action of sulfuric acid on a nitrite salt.

$$2\,NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HNO_2$$
$$2\,HNO_2 \rightarrow N_2O_3 + H_2O$$

The gas obtained in this reaction appears to be a mixture of equimolecular proportions of NO and NO_2, but when cooled to 3° it becomes a liquid which has a composition as represented by the formula N_2O_3.

Nitrogen pentoxide N_2O_5, the anhydride of nitric acid, may be produced by dehydration of HNO_3 with phosphorus pentoxide.

$$2\,HNO_3 + P_2O_5 \rightarrow 2\,HPO_3 + N_2O_5$$

The product, a white solid melting at 30°, may be separated from the reaction mixture by low temperature distillation. The anhydride reacts vigorously with water to form nitric acid.

EXERCISES

1 List the various processes for the fixation of atmospheric nitrogen
2 What is the general method for preparation of ammonia in the laboratory?
3 Ammonium carbonate, used as smelling salt, gives a strong odor of ammonia, while other ammonium salts do not. Explain
4 Complete and balance

(*a*) $NH_3 + H_2O \rightarrow$
(*b*) $NH_3 + H_2SO_4 \rightarrow$
(*c*) NH_4NO_2 (heat) $\rightarrow$
(*d*) $(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow$
(*e*) $SO_2 + NH_4OH \rightarrow$
(*f*) $HNO_3 + Ag \rightarrow$
(*g*) $HNO_3 + C_2H_4(OH)_2 \rightarrow$
(*h*) $S + HNO_3$(conc.) $\rightarrow$
(*i*) $MgO + HNO_3 \rightarrow$
(*j*) $N_2O_5 + H_2O \rightarrow$

5 Write equation or equations for the preparation of NH_4NO_3 from NH_4Cl and other needed chemicals
6 Calculate the weight of ammonia obtainable from 100 g of $(NH_4)_3PO_4$. Ans. 31.2 g
7 Suggest a method for the determination of the molecular weight of NH_3
8 Why cannot HNO_3 be prepared by the reaction

$$NaNO_3 + HCl \rightarrow NaCl + HNO_3$$

9 Calculate the weight of 100 liters of ammonia at STP. Ans. 76 g
10 Why was the Haber process of vital importance to Germany during the two world wars?
11 By means of equations, show that

(*a*) HNO_3 may act as an acid
(*c*) NH_3 may act as a reducing agent
(*b*) HNO_3 may act as an oxidizing agent
(*d*) NH_3 neutralizes acids

12 From the equations for the cyanamide process, calculate the quantities of lime (CaO), coke (C), and nitrogen necessary to produce one pound of ammonia

13 Describe how you would proceed to test a sample of fertilizer for the presence of ammonium salts.

14 What volume of NH_3 measured at standard conditions must bubble into and react with H_3PO_4 to prepare 4 moles of $(NH_4)_3PO_4$?

15 "Rain during a thunderstorm is very dilute nitric acid." Write equations to explain this phenomenon.

16 Ammonium nitrate, which is used as a fertilizer, may be prepared by absorbing ammonia in a solution of nitric acid.

(*a*) How much ammonia at STP by volume would be necessary to neutralize the nitric acid obtained from one ton of $NaNO_3$ (Chile saltpeter) of 70% purity?

(*b*) What weight of NH_4NO_3 would be obtained in (*a*)?

Ans. (*a*) 5900 cu. ft. (*b*) 1318 lb.

17 Nitric acid may be prepared in the laboratory by heating a mixture of Chile saltpeter and concentrated sulfuric acid, according to the equation:

$$2\,NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HNO_3$$

Calculate the weights of reactants necessary to prepare 252 lb. of HNO_3.

18 Given a bottle of 60% HNO_3 of specific gravity 1.4, calculate and explain how you would make up one liter of 1.0 *N* HNO_3.

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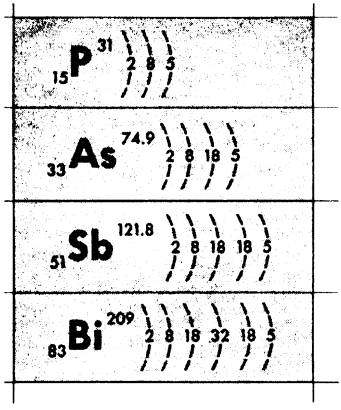
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twenty-three OTHER GROUP V-A ELEMENTS

ELEMENT	SYMBOL	COLOR AND PHYSICAL STATE	SP. GR.	MELTING POINT, °C.	BOILING POINT, °C.	OXIDATION STATES
Phosphorus	P	yellow solid	1.8	44	280	−3, +3, +5
Arsenic	As	gray solid	5.7	sublimes	....	−3, +3, +5
Antimony	Sb	silvery solid	6.7	631	1440	−3, +3, +5
Bismuth	Bi	silvery solid	9.8	271	1450	−3, +3, +5

In addition to nitrogen, the elements phosphorus, arsenic, antimony, and bismuth appear in Group V*A* of the periodic table. Although these elements show some similarities to nitrogen, there are many marked differences in chemical properties. As the atomic weight increases, a gradual change from distinct nonmetallic properties to metallic properties is observed. Nitrogen and phosphorus are distinctly nonmetallic in character; antimony and arsenic exhibit properties of both a metal and a nonmetal, and bismuth exhibits characteristic metallic properties.

Compounds of the elements are usually covalent—that is, the atoms are held together by a sharing of electrons. The elements form many similar compounds:

HYDRIDES	CHLORIDES	OXIDES	ACIDS
NH_3	NCl_3	N_2O_3; N_2O_5	HNO_2; HNO_3
PH_3	PCl_3	P_2O_3; P_2O_5	H_3PO_3; H_3PO_4
AsH_3	$AsCl_3$	As_2O_3; As_2O_5	H_3AsO_3; H_3AsO_4
SbH_3	$SbCl_3$	Sb_2O_3; Sb_2O_5	$HSbO_2$; H_3SbO_4
BiH_3	$BiCl_3$	Bi_2O_3	$HBiO_3$

PHOSPHORUS

History and occurrence Brand, a German alchemist in quest of the philosopher's stone, accidentally prepared the element in 1669 while experimenting with urine. On distilling a mixture of urine, sand, and charcoal and heating the residue, he obtained a substance which glowed in the dark. The substance was subsequently shown to be an element and was given the name *phosphorus*, which means "light bearer."

The element is never found in the free state, but its compounds are widely distributed. The most abundant mineral is *phosphate rock* or *phosphorite*, which is largely $Ca_3(PO_4)_2$. Deposits are found in Montana, Idaho, and several of the southern states. Bones of man and animals have a high percentage of calcium phosphate; many body proteins contain phosphorus, particularly nerve tissues and brain cells. In all, the human body contains about one per cent of the element.

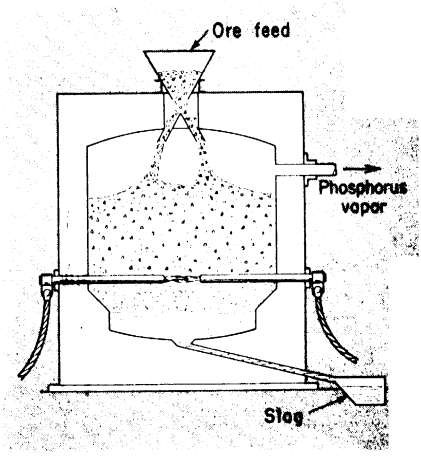


Figure 23–1 Phosphorus furnace.

Preparation Phosphorus is prepared by heating a mixture of phosphate rock, sand, and coke to a high temperature in an electric furnace (Figure 23–1). Heat is produced by the resistance to the passage of current between the electrodes near the bottom of the furnace. The reaction probably takes place in two steps:

$$2\,Ca_3(PO_4)_2 + 6\,SiO_2 \rightarrow 6\,CaSiO_3 + P_4O_{10}$$
$$P_4O_{10} + 10\,C \rightarrow P_4\uparrow + 10\,CO$$

Molten calcium silicate (slag) collects at the bottom and may be drawn off. Phosphorus leaves the furnace as a vapor; the vapor is condensed to a liquid which is further cooled and cast into sticks.

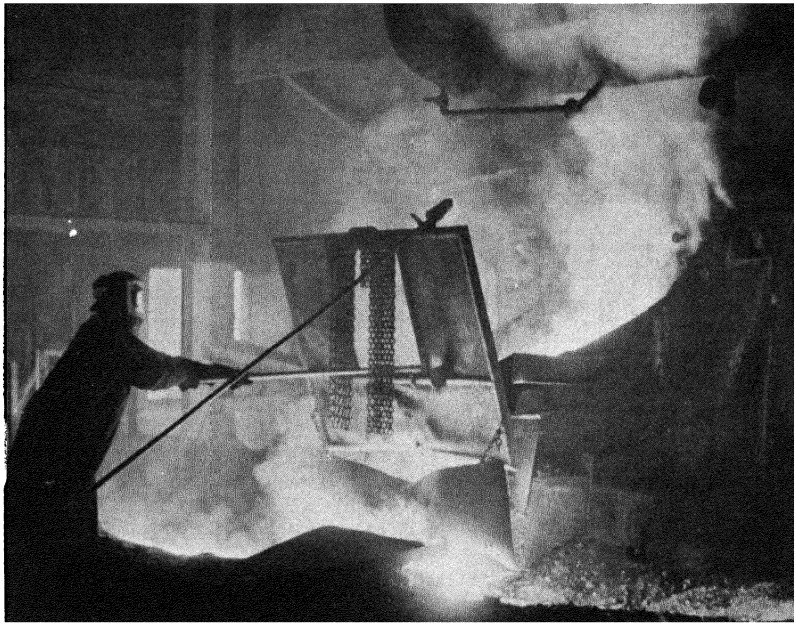


Figure 23–2 Phosphorus in production.

Properties Phosphorus as prepared by this process is a soft, white, waxlike solid which gradually turns yellow in color. When exposed to air, oxidation takes place slowly with the evolution of heat, and the element spontaneously ignites at a temperature of 40° to 45°. The glowing action of phosphorus in the dark is due to the light emitted during the slow oxidation.

The element is insoluble in water but readily dissolves in carbon disulfide and certain other organic solvents. For storage and handling it is placed under water. Great care should be exercised in handling the element; it should always be picked up with tongs or forceps, never with the fingers, since warmth from the fingers may be sufficient to raise the temperature to the kindling point and cause spontaneous ignition. Phosphorus burns are painful and slow to heal.

In contrast to nitrogen, phosphorus is fairly active, combining readily with oxygen, the halogens, and certain metals. Phosphorus burns brightly in the air, producing dense white fumes of the trioxide and pentoxide. In moist air these fumes form droplets of phosphorous and phosphoric acids which appear as a fog or mist. Because of this behavior, the element is used in production of smoke screens in warfare.

When yellow phosphorus is heated in the absence of air to a temperature of 250–300°, it changes to a modification called *red* phosphorus. Red phosphorus is nonpoisonous in contrast to the extremely poisonous character of the yellow form; it ignites in air only at a high temperature and is insoluble in carbon disulfide.

Uses Because of its low kindling temperature, phosphorus finds use as a medium for starting fires. It is used in incendiaries and tracer bullets, and its principal use is in the manufacture of matches. At one time yellow phosphorus was used in matches; its use, however, is now prohibited, since factory workers inhaling air containing poisonous phosphorus vapor developed a dreadful disease causing decay of the bones of the jaw. A compound of phosphorus—phosphorus sesquisulfide, P_4S_3—has been found to be as effective as yellow phosphorus in match manufacture, and since it is nonpoisonous, workers may handle it in safety.

The essential ingredients of a match are (1) phosphorus sesquisulfide, which ignites at a low temperature; (2) a combustible substance such as paraffin, rosin, or antimony sulfide; (3) an oxidizing agent like potassium chlorate or lead dioxide; (4) glue to bind the ingredients; (5) wood stick. For the "strike anywhere" match, the above ingredients constitute the head; friction with a rough surface produces enough heat to ignite the phosphorus compound and initiate the reaction of the combustible substance and oxidizing agent. The flame produced is finally transmitted to the wood stick. The "safety" match is the same as the "strike anywhere" match except that it contains no phosphorus in the head. Instead, the phosphorus compound is placed on the striking surface of the box along with ground glass and glue, and friction causes a bit of the phosphorus to ignite the ingredients of the head.

COMPOUNDS OF PHOSPHORUS

Phosphine The hydride of phosphorus, PH_3, a colorless gas with an offensive odor resembling that of decaying fish, is the analog of ammonia, NH_3. Unlike ammonia, it cannot be prepared by direct combination of the elements but may be obtained by the action of water on calcium phosphide

$$Ca_3P_2 + 6\ H_2O \rightarrow 3\ Ca(OH)_2 + 2\ PH_3\uparrow$$

or by the reaction

$$3\ NaOH + 4\ P + 3\ H_2O \rightarrow \underset{\substack{\text{sodium dihydrogen}\\ \text{hypophosphite}}}{3\ NaH_2PO_2} + PH_3\uparrow$$

The gas is only slightly soluble in water and ignites spontaneously[1] on contact with the air to form smoke ring clouds of phosphoric acid (Figure 23–3):

$$PH_3 + 2\ O_2 \rightarrow H_3PO_4$$

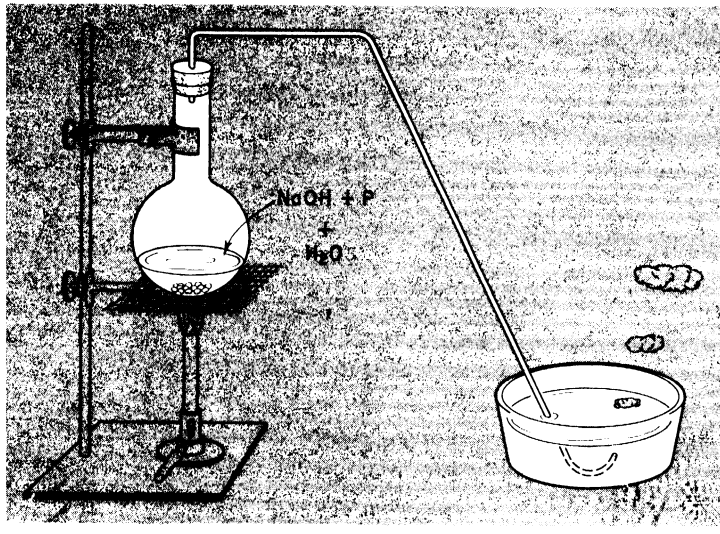


Figure 23–3 Preparation of phosphine.

Oxides of phosphorus The most important oxides are the trioxide, P_2O_3, and the pentoxide, P_2O_5, both white solids.[2] They are obtained by the combustion of phosphorus in air, the trioxide being formed in a limited supply of air, and the pentoxide in an excess of air. The oxides are anhydrides of phosphorous and phosphoric acids, respectively:

$$P_2O_3 + 3\ H_2O \rightarrow 2\ H_3PO_3$$
$$P_2O_5 + 3\ H_2O \rightarrow 2\ H_3PO_4$$

The reaction of the pentoxide and water is particularly vigorous; advantage is taken of this behavior in the use of phosphorus pentoxide as an effective dehydrating agent.

Phosphoric acids Phosphorus pentoxide is the anhydride of three phosphoric acids which differ from one another only in degree of hydra-

[1] It is believed that small amounts of P_2H_4 produced by a secondary reaction are responsible for initiating the combustion.

[2] Evidence indicates these two oxides are actually composed of molecules of P_4O_6 and P_4H_{10}. For simplicity, we shall ordinarily use P_2O_3 and P_2O_5.

tion of the oxide. The relationship between the three acids is shown below:

$$P_2O_5 + 3\,H_2O \rightarrow 2\,H_3PO_4 \quad \text{(orthophosphoric acid)}$$
$$P_2O_5 + 2\,H_2O \rightarrow H_4P_2O_7 \quad \text{(pyrophosphoric acid)}$$
$$P_2O_5 + H_2O \rightarrow 2\,HPO_3 \quad \text{(metaphosphoric acid)}$$

The most hydrated of the acids is the *ortho* acid, the least hydrated the *meta* acid, and the *pyro* acid represents an intermediate degree of hydration. Of these acids, orthophosphoric acid is the one obtained when phosphorus pentoxide is dissolved in water under ordinary conditions. When the ortho acid is heated to relatively high temperatures, the pyro and meta varieties of the acid are formed. In using the term phosphoric acid, the ortho variety is implied unless otherwise specified.

Phosphoric acid is obtained commercially either by ignition of phosphorus in the air and subsequent solution of the resulting oxide in water or by the treatment of phosphate rock with 60 per cent sulfuric acid:

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 \rightarrow 3\,CaSO_4 + 2\,H_3PO_4$$

After filtering off the insoluble calcium sulfate the solution is concentrated to approximately 85 per cent phosphoric acid by evaporation.

Ionization of phosphoric acid The acid is triprotic—that is, it has three replaceable hydrogen atoms—and thus ionizes in three steps:

	IONIZATION CONSTANT
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	$K_1 = 1.1 \times 10^{-2}$
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$	$K_2 = 2 \times 10^{-7}$
$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$	$K_3 = 3.6 \times 10^{-13}$

As is the case with all acids ionizing in stages, each stage of the ionization is less complete than the preceding one; this is evidenced by the ionization constants. H_3PO_4 is the strongest of the three, yet it is a relatively weak acid. $H_2PO_4^-$ would be classed as a very weak acid and HPO_4^{--} as a very, very weak acid. Salts of all the three acids are known; for example, the three sodium salts:

NaH_2PO_4	sodium dihydrogen phosphate
Na_2HPO_4	disodium hydrogen phosphate
Na_3PO_4	normal or trisodium phosphate

Trisodium phosphate is used extensively as a water softener and as a cleansing agent. A mixture of the sodium acid phosphates plays an important part in maintaining a constant *p*H of the blood.

Phosphorus fertilizers Phosphorus, an element vital to the growth of plants, must necessarily be present in fertile soils for successful plant

propagation. One of the most important of the phosphorus fertilizers is *superphosphate*, a mixture of acid calcium phosphate and calcium sulfate, which is prepared by the action of sulfuric acid on rock phosphate according to the equation:

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \rightarrow \underset{\text{superphosphate}}{Ca(H_2PO_4)_2} + 2\ CaSO_4$$

Rock phosphate is too insoluble to be utilized by plants, but the acid salt is soluble, though not soluble enough to be quickly washed from soil; thus it is available for plant metabolism. The sulfuric acid simply renders the phosphorus available by formation of the acid salt. A still more effective phosphate fertilizer per pound is triple phosphate, which is made as follows:

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \rightarrow 3\ Ca(H_2PO_4)_2$$

Ammonium phosphate is another fertilizer containing two important soil elements.

ARSENIC

Occurrence and preparation Although arsenic is found in small quantities in the free state, its principal occurrence is as sulfides: *arsenopyrite*, FeAsS; *orpiment*, As_2S_3; and *realgar*, As_2S_2. Small quantities of arsenic are usually associated with most sulfide ores; as a matter of fact, nearly all of the arsenic produced is recovered as a by-product from the flues of smelters utilizing sulfide ores of zinc, copper, and lead. During the roasting process, the arsenic is converted to volatile arsenious oxide, As_2O_3, which is condensed in the flues as a finely divided solid. The element is easily obtained from the arsenious oxide by reduction with carbon:

$$As_2O_3 + 3\ C \rightarrow 2\ As + 3\ CO$$

Properties and uses Arsenic is a gray crystalline solid with a metallic luster. The solid sublimes to a yellowish, poisonous vapor which has the odor of garlic. The principal use of arsenic is in hardening lead shot. Lead shot is made by pouring molten lead through a screen which breaks up the liquid into small drops. The presence of arsenic lengthens the time of solidification, thereby allowing the drops to attain a more nearly spherical shape, and at the same time the arsenic forms an alloy with the lead to produce a harder product.

Compounds of arsenic Arsenic is very similar to phosphorus in many of its reactions. Arsenic trioxide and arsenic pentoxide dissolve in water to form arsenious and arsenic acids, respectively. *Arsine*, AsH_3,

a very poisonous gas of garlic odor, is the analog of ammonia and phosphine. It is an unstable compound and decomposes when moderately heated into metallic arsenic and hydrogen:

$$2\ AsH_3 \rightarrow 2\ As + 3\ H_2$$

Arsenic trioxide, a white solid commonly called "white arsenic" or simply "arsenic," is the starting material in the preparation of most of the compounds of arsenic. It has a sweet taste and is highly poisonous.[3] Its principal use is in the preparation of insecticides, some of the more common of which are: *lead arsenate,* $Pb_3(AsO_4)_2$, used as a spray for fruits and vegetables; *sodium* and *calcium arsenates* for killing boll weevil in cotton fields; *paris green,* $3\ Cu\ (AsO_2)_2 \cdot Cu(C_2H_3O_2)_2$, an insecticide. Another arsenic compound, *Scheele's green,* $CuHAsO_3$, finds limited application as a paint pigment.

Gutzeit test Since arsenic compounds are so commonly used in fruit tree spraying, rigid state food control laws require that fruit be washed to practically free it of the poisonous arsenic-containing spray residue. Control tests for small amounts of residual arsenic are made by a "Gutzeit test." A sample of macerated fruit peelings is put in a small flask, and zinc and acid are added. Hydrogen is produced which combines with any arsenic present to form arsine. Escaping arsine gas passes over a thin strip of paper which has been soaked in a mercury salt. Arsine will turn the mercury salt to a reddish-yellow color. The

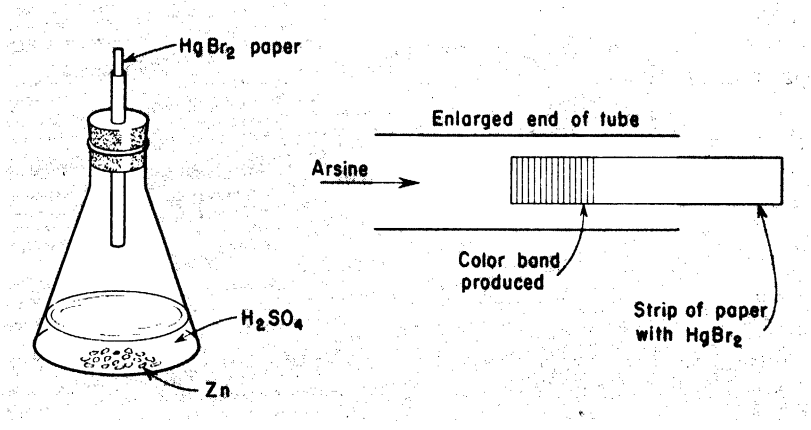


Figure 23–4 Gutzeit test for arsenic.

[3] One of the most notorious women of history, Lucrezia Borgia, used arsenic oxide to poison many men. Roman ladies ate minute quantities of "white arsenic" to enhance the whiteness of their skin and pink of their cheeks. They gradually built up an immunity to the poisonous effects of the arsenic oxide and ultimately could safely take a dose that would "kill a horse."

length of the color band gives a measure of the amount of arsine from a given weight of sample; the amount of arsenic residue on the fruit may be determined down to as little as a few parts per million. Stomach liquid of a poisoned man or animal can be analyzed for arsenic in the same way.

When traces of arsine gas are passed over a white crystal of silver nitrate, the crystal will first turn yellow, then black. Consequently, this reaction constitutes another method which can be used to make a quick test for arsenic.

ANTIMONY

Occurrence and preparation The chief source of antimony is the mineral *stibnite*, Sb_2S_3, although small quantities of the element are found in the free state. Antimony may be recovered from stibnite by heating with finely divided iron:

$$Sb_2S_3 + 3\ Fe \rightarrow 3\ FeS + 2\ Sb$$

The molten products separate into two layers with the lighter ferrous sulfide layer on top.

Stibnite may also be roasted to the oxide, followed by reduction with carbon:

$$2\ Sb_2S_3 + 9\ O_2 \rightarrow 2\ Sb_2O_3 + 6\ SO_2$$
$$Sb_2O_3 + 3\ C \rightarrow 2\ Sb + 3\ CO$$

Properties and uses Antimony is more metallic in its appearance and in its properties than arsenic. However, the element is not metallic enough in character to displace hydrogen from hydrochloric acid, but it reacts with nitric acid to form the trioxide and the pentoxide. Direct combination of the element with sulfur and with the halogens takes place readily. Antimony is brittle and a poor conductor of heat and electricity.

The principal use of antimony is in the preparation of alloys. The addition of antimony to lead gives a much harder product which is useful in making bullets and shrapnel. Type metal is an alloy of lead, tin, and antimony which expands on solidification, thereby filling all parts of the mold to produce a sharp and distinct casting of the type characters.

Compounds of antimony Compounds of antimony are closely related to those of arsenic. *Stibine*, SbH_3, is prepared in a manner similar to arsine. Like arsine, it is a poisonous gas which is unstable toward heat. The oxides, Sb_2O_3, Sb_2O_4, and Sb_2O_5, are more basic than the corre-

sponding oxides of phosphorus and arsenic, since the elements of Group V*A* become more metallic as the atomic weight increases. The trioxide and pentoxide are amphoteric, dissolving in acids to form antimonous and antimonic salts and in strong bases to form antimonites and antimonates.

Antimony chloride, $SbCl_3$, called "butter of antimony" because of the soft, mushy appearance of the crystals, is made by direct combination of the elements. This salt, as well as most of the other salts of antimony, is highly hydrolyzed to produce an insoluble basic salt:

$$SbCl_3 + H_2O \rightleftharpoons SbOCl \downarrow + 2\ HCl$$

When hydrogen sulfide is passed into a solution containing antimony ions, a reddish-orange precipitate of the sulfide is formed. This reaction is often used in testing for the presence of antimony.

BISMUTH

Occurrence and preparation Bismuth occurs in both the free and combined states. Naturally occurring compounds are *bismuth glance*, Bi_2S_3, and *bismite*, $Bi_2O_3 \cdot 3\ H_2O$. Like arsenic and antimony, bismuth may be obtained from the sulfide ore by roasting followed by reduction with carbon. A good deal of bismuth is recovered as a by-product of lead smelters and refineries.

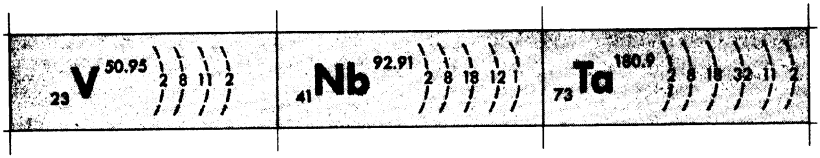
Properties and uses Bismuth is distinctly a metallic element, which is hard and brittle and has a silvery luster with a reddish tinge. Bismuth burns when highly heated in air to form the trioxide, Bi_2O_3, and combines directly with the halogens to form halide salts, although these reactions with the halogens are not vigorous. Unlike the other members of the group V*A* elements, bismuth dissolves in nitric acid to form a nitrate salt.

Bismuth is used in the preparation of several low-melting alloys such as *Rose's metal* (Sn, Pb, Bi), melting point 94°, and *Wood's metal* (Pb, Cd, Sn, Bi), melting point 71°. These alloys are used in electrical fuses, automatic fire sprinklers, safety plugs for boilers, automatic fire alarms, and so on.

Compounds The oxide and hydroxide of bismuth are distinctly basic in character. $BiCl_3$ like $SbCl_3$ is highly hydrolyzed to form the water insoluble basic chloride, BiOCl. Bismuth nitrate when added to water is hydrolyzed to form basic bismuth subnitrate, a compound which is used medicinally in the treatment of certain disturbances of the digestive tract:

$$Bi(NO_3)_3 + H_2O \rightleftharpoons BiONO_3 \downarrow + 2\ HNO_3$$

ELEMENTS OF GROUP VB



ELEMENT	SYMBOL	SP. GR.	MELTING POINT	COMMON OXIDATION STATES
Vanadium	V	5.96	1710°	+2, +3, +4, +5
Niobium	Nb	8.4	1950°	+5
Tantalum	Ta	16.6	2850°	+5

Vanadium, niobium,[4] and tantalum These are transition elements of Group *VB* with a predominant oxidation number of +5. Their occurrence is comparatively rare. Two of the better known minerals containing vanadium are *vanadinite*, $Pb_5(VO_4)_3Cl$, and *carnotite*, $K_2(UO_2)_2(VO_4)_2 \cdot 3\,H_2O$. *Columbite*, $FeO \cdot Nb_2O_5$, and *tantalite*, $FeO \cdot Ta_2O_5$, have been sources of compounds of niobium and tantalum.

These elements combine directly with oxygen, chlorine, and nitrogen to form oxides, chlorides, and nitrides, respectively. A small percentage of vanadium alloyed with steel gives a high tensile strength product which is very tough and resistant to shock and vibration. For this reason vanadium alloy steels are used in the manufacture of high-speed tools and heavy machinery. Vanadium oxide is employed as a catalyst in the "contact process" of manufacturing sulfuric acid. Niobium is a very rare element and has limited use as an alloying element in stainless steel. Tantalum is a steel-gray metal which may be rolled or hammered with difficulty. It has a very high melting point (2850°) and is resistant to corrosion by most acids and alkalies; thus, it may be used as a platinum substitute for certain laboratory utensils. Tantalum carbide is almost as hard as diamond and is a component of some abrasive and cutting mixtures. A marked improvement in rock drilling results from the use of tantalum carbide bits on the end of drill steel.

EXERCISES

1 Approximately how many pounds of As_2O_3 are used in making 1 ton of $Pb_3(AsO_4)_2$? Ans. 440.

2 Write names and formulas of two acids containing antimony.

[4] Formerly called columbium.

3 Write formulas for:
   (*a*) ortho and meta arsenic acids
   (*b*) lead ortho and meta arsenites
   (*c*) stibine
   (*d*) bismuthyl nitrate (also known as bismuth oxynitrate)

4 Write equations for:
   (*a*) calcium phosphide + dilute HCl
   (*b*) hydrolysis of antimony trichloride
   (*c*) preparation of copper arsenite from the raw materials, As_2O_3, H_2O, $CuSO_4$

5 Given As_2S_3, limestone, air, and water; write equations for a practical way of preparing calcium arsenite.

6 A Seattle concern prepares a garden ground rock mixture composed of $(NH_4)_3PO_4$, $CaCO_3$, and granite. The company wants 0.2 per cent phosphorus mixtures. What weight of ammonium phosphate should be in each 100 pounds of the mix? Ans. 1 lb. approx.

7 A ton of rock contains 5 per cent carnotite. On treatment, 90 per cent of the vanadium and uranium is recovered from the ore. What weights of the respective metals are obtained from the rock?

8 An alloy containing one gram atom each of Pb, Cd, Sn, and Bi would have what percentage of bismuth? Ans. 32.3.

9 Discuss the relative merits of superphosphate, ammonium phosphate, and triple phosphate as fertilizers.

10 H_3PO_4 has three ionizable hydrogens while H_3PO_3 has only two. Account for the difference on the basis of different electronic configurations of these two acids.

11 Explain the relationship between P_2O_5, H_3PO_4, $(HPO_3)_x$, and $H_4P_2O_7$ by writing equations for formation of these compounds from P_2O_5 and H_2O.

12 White phosphorus from a bursting shell burns to an oxide, which by hydration forms a white smoke of H_3PO_4 particles. What weight of white smoke can form from burning 1 lb. of phosphorus? Ans. 3.1 lb.

13 Arsenic (at. no. 33, at. wt. 75) occurs in Group *VA* of the periodic table. How many electrons are there in each consecutive orbit? How many protons in the nucleus? What are the oxidation numbers of arsenic as indicated by its structure?

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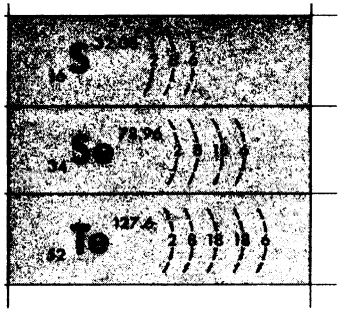
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twenty-four

THE SULFUR FAMILY

ELEMENT	SYMBOL	COLOR	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Sulfur	S	pale yellow	2.07	113° C.	445° C.	−2, +4, +6
Selenium	Se	steel gray	4.8	220° C.	688° C.	−2, +4, +6
Tellurium	Te	metallic	6.24	452° C.	1390° C	−2, +4, +6

The sulfur family includes the elements oxygen, sulfur, selenium, and tellurium which appear in Group VI*A* of the periodic table. Although there appears to be little in common between the yellow solid, sulfur, and the colorless gas, oxygen, we shall find that these elements form many similar compounds.

SULFUR

Occurrence of sulfur Súlfur was known to the ancients as brimstone, which means "burning stone." It is often referred to in the Bible; ancient priests thought of hell as a place not only of fire but of burning brimstone (choking odor of SO_2). The Greek philosophers considered sulfur to be an elementary substance, although their concept of an element was different from the view held today. It was extensively used in the treatment of disease and as a fumigant.[1] Deposits of sulfur are

[1] In the *Odyssey,* it is related that Penelope ordered brimstone burned in the marble halls of her home after her long-absent husband Ulysses came home and killed and scattered about bodies of the men who had wasted his flocks and sought to marry his wife. It is interesting to know that the rudiments of fumigation were known in this early time.

found in Sicily and in Louisiana and Texas, although proved reserves in these areas are being rapidly depleted. Recent discoveries in the Vera Cruz area of Mexico indicate large deposits that will be an important source of supply.

In the combined state, sulfur occurs in the form of metallic sulfides, such as *sphalerite,* ZnS; *galena,* PbS; *chalcocite,* Cu_2S; *chalcopyrite,* $CuFeS_2$; *iron pyrites,* FeS_2; *cinnabar,* HgS; and several other minerals. These compounds are economically important, since they are the sources of the metals Zn, Cu, Pb, Hg, and others. Some combined sulfur exists as sulfates of calcium (*gypsum,* $CaSO_4 \cdot 2\,H_2O$) and barium (*barite,* $BaSO_4$). Many organic compounds contain sulfur; proteins in the body contain small amounts, as do certain compounds in onion, garlic, horseradish, and mustard. Sulfur appears to be one of the elements essential to vital life processes.

The extraction of sulfur In volcanic regions, the sulfur is mixed with soil and rocks, from which it can be separated by heat, which melts the sulfur, leaving the impurities in a solid condition. In Louisiana and Texas the sulfur deposits are found several hundred feet below the surface of the ground. Because these deposits are covered with a layer of quicksand, the sulfur cannot be mined by ordinary means. Herman Frasch, a German-American chemist and engineer, devised an ingenious method for obtaining the sulfur from its underground deposits (Figure 24–1). His method is based on the relatively low melting point of sulfur (113°). A hole is bored into the bed of sulfur and the well is then lined with a series of three concentric pipes, one fitted inside another. Superheated water and air are forced down the well under pressure through two of the pipes. The heat melts the sulfur, which is then forced to the surface in a frothy liquid state by compressed air. The sulfur is allowed to solidify in large blocks at the surface. Each well may produce several hundred tons of sulfur daily, and the product is about 99.5 per cent pure.

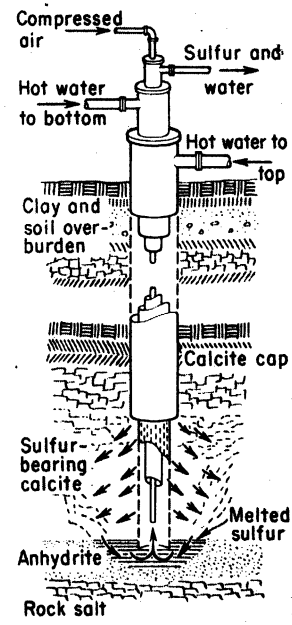


Figure 24–1 Frasch process.

Different forms of sulfur Free sulfur may exist in several forms. The form of sulfur found in nature is called the *rhombic* variety, so called from the shape of the crystals (Figure 24–2). If these crystals are heated to a temperature of 96°, they slowly change into another more needlelike crystalline variety, which is called *monoclinic* sulfur. The temperature at which a given solid will change its crystalline form is known as the *transition point* or *transition temperature.* Thus, 96° is a transition point of sulfur. This property of a substance of existing in more than one physical form in the same physical state is termed *allotropy,* and the different forms are referred to as *allotropes.* Other elements, such as phosphorus and carbon, may exist in allotropic forms.

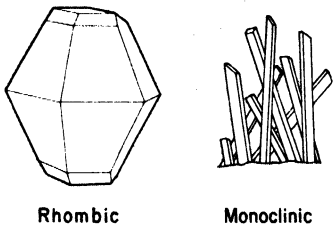
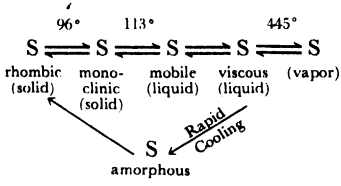


Figure 24–2 Crystals of sulfur: left, rhombic; right, monoclinic.

When rhombic sulfur is heated, it melts at a temperature of 113° to a straw-colored liquid called *mobile* sulfur because it flows freely. When mobile sulfur is allowed to cool slowly and solidify, needlelike crystals of monoclinic sulfur are obtained. If the heating of mobile sulfur is continued, the liquid darkens and becomes thick and sticky, like molasses. This form of sulfur is called *viscous* sulfur. Continued heating changes the liquid sulfur to vapor at a temperature of about 445°. If viscous sulfur is cooled rapidly by immersion in cold water, a rubbery, plastic mass of solid sulfur is obtained, which is called *plastic* or *amorphous* sulfur. (Amorphous means noncrystalline.) Under ordinary conditions, this variety of sulfur will gradually change into rhombic sulfur, the stable form at ordinary temperatures. The relationship which exists between the various forms of sulfur may be represented by the diagram:



The transformations shown in this diagram are reversible, except that of amorphous sulfur to rhombic sulfur; all forms finally revert to the stable rhombic form under ordinary conditions.

Chemical properties Sulfur combines directly with most of the metals to form sulfides. When iron is heated with sulfur, a great deal of heat is evolved, and a vigorous reaction ensues, with the formation of ferrous sulfide. Other metals combine similarly. In some cases, the combination of a metal with sulfur may take place at ordinary temperatures; thus, when mercury and sulfur are ground together in a mortar, black mercuric sulfide is formed:

$$Hg + S \rightarrow HgS \downarrow$$

Sulfur will combine directly with certain of the nonmetals, although the combination does not take place as readily as with metals. Sulfur burns with a blue flame in air or oxygen to form sulfur dioxide:

$$S + O_2 \rightarrow SO_2 \uparrow$$

Examples of other compounds formed by sulfur with nonmetals are carbon disulfide, CS_2, phosphorus sesquisulfide, P_4S_3, and sulfur chloride, S_2Cl_2.

Sulfur exhibits oxidation states of -2, $+4$, and $+6$. As a member of group VI*A*, it tends to acquire two electrons to complete a stable octet configuration in the sulfide ion, S^{--}. Sulfur also forms covalent bonds with various other nonmetals to assume oxidation numbers of $+4$, as in sulfur dioxide and sulfites, and $+6$, as in sulfuric acid and sulfates.

Uses of sulfur Most of the sulfur produced is used in the preparation of sulfuric acid and other compounds of sulfur. Another extremely important use is in the *vulcanization* of rubber. Pure rubber tends to become sticky when slightly warmed and brittle when cold. In the vulcanization process, sulfur is incorporated into the rubber and a product is obtained which extends the temperature at which rubber has the desirable properties of resiliency and toughness. Heated with lime, sulfur forms "lime sulfur spray," which is used as an insecticide. Black gunpowder is a mixture of carbon, sulfur, and saltpeter (KNO_3). Sulfides of phosphorus and antimony have taken the place of free phosphorus in the production of matches. Mixed with rock phosphate fertilizer, sulfur is oxidized slowly in soil to sulfuric acid which converts the fertilizer into a more soluble form. Small amounts of sulfur are employed medicinally in the treatment of certain skin diseases, and sulfur is a constituent of the well-known "sulfa" drugs.

HYDROGEN SULFIDE

Hydrogen sulfide is an odorous gas produced during the destructive distillation of proteins and other sulfur-containing compounds. It is a

constituent of coal gas and sewer gas. The offensive odor of rotten eggs is largely due to the presence of this substance.

Preparation of hydrogen sulfide Sulfur does not combine appreciably with hydrogen at ordinary temperatures, but at an elevated temperature combination takes place readily to form hydrogen sulfide:

$$H_2 + S \rightleftharpoons H_2S$$

The reaction, however, is reversible, and since hydrogen sulfide itself is quite unstable toward heat, the yield is small.

In the laboratory it is most conveniently prepared by the action of a nonoxidizing acid on certain metallic sulfides:

$$FeS + (\text{dilute}) H_2SO_4 \rightarrow FeSO_4 + H_2S\uparrow$$
$$ZnS + 2 HCl \rightarrow ZnCl_2 + H_2S\uparrow$$

These equations are further examples of the general method of preparing an acid by treating a salt of the desired acid with a less volatile acid. Though volatile, hydrochloric acid may be used since it is less volatile than hydrogen sulfide from water solution.

Properties Hydrogen sulfide is a colorless gas at ordinary temperatures, with a foul odor like that of rotten eggs. It may be condensed to a liquid at $-59.6°$ and converted to a solid at $-83°$. It is not very soluble in water—at ordinary temperatures, one liter of water dissolves about three liters of the gas. It is very poisonous, since it paralyzes the nerve centers of the heart and lungs—more than one-half of one per cent in the air may be fatal to humans and animals. Fortunately, it is easily detected even in small quantities because of its characteristic odor.

Hydrogen sulfide reacts with water to form a solution with acidic properties:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad K_i = 1.2 \times 10^{-7}$$
$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{--} \qquad K_i = 1 \times 10^{-15}$$

or

$$H_2S + 2 H_2O \rightleftharpoons 2 H_3O^+ + S^{--}$$

The ionization is very slight; consequently, hydrosulfuric acid is classed as a weak acid. It exhibits typical weak acid reactions, reacting with bases to form salts; for example,

$$2 NaOH + H_2S \rightleftharpoons Na_2S + 2 H_2O$$

Hydrogen sulfide burns in the air with a blue flame, producing sulfur dioxide and water:

$$2 H_2S + 3 O_2 \rightarrow 2 H_2O + 2 SO_2$$

If combustion takes place in a limited supply of air (for example, in an open bottle) free sulfur is deposited:

$$2\ H_2S + O_2 \rightarrow 2\ H_2O + 2\ S$$

Hydrogen sulfide is a good reducing agent; note these reactions:

$$3\ H_2S + (\text{dilute})\ 2\ HNO_3 \rightarrow 3\ S + 2\ NO + 4\ H_2O$$
$$H_2S + I_2 \rightarrow S + 2\ HI$$
$$H_2SO_4 + H_2S \rightarrow S + SO_2 + 2\ H_2O$$
$$2\ H_2S + SO_2 \rightarrow 3\ S + 2\ H_2O$$

Certain metallic ions produce sulfides with hydrogen sulfide, such as lead sulfide (black), copper sulfide (black), cadmium sulfide (yellow), antimony sulfide (orange), manganese sulfide (pink). The formation of a colored sulfide may be used as a basis for a test for the presence of hydrogen sulfide. If a piece of filter paper saturated with lead nitrate solution is placed in a stream of hydrogen sulfide gas, a black deposit of lead sulfide is formed on the paper:

$$Pb^{++} + H_2S \rightarrow PbS\downarrow + 2\ H^+$$

This test is useful in locating breaks in sewer lines, as well as in pipes carrying coal gas or natural gas, which usually contain a little hydrogen sulfide.

Uses of hydrogen sulfide The use of hydrogen sulfide is confined largely to the chemical laboratory, where it is employed in the separation and identification of metallic ions. Its use as an analytical reagent is very important. Let us consider for a moment the way in which it functions as a qualitative reagent.

The equilibrium

$$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2\ H^+ + S^{--}$$

may be shifted by the addition of an acid or base. If acid is added, repression of ionization occurs, resulting in a decrease of the sulfide ion concentration. The addition of hydroxyl ions from a base causes a shift in equilibrium to the right because of the formation of un-ionized water by the combination of hydrogen and hydroxyl ions. This results in an increase of the sulfide ion concentration. It is evident, then, that the sulfide ion concentration can be controlled by proper adjustment of the acidity or basicity of the solution. Since the metallic sulfides have different solubility product constants, theoretically we could successively precipitate the metallic ions as sulfides by proper control of the acidity of the solution. Actually, in qualitative analysis the concentration of hydrogen ion is adjusted to 0.3 molar, in which solution the sulfides of

arsenic, antimony, mercury, tin, lead, copper, bismuth, and cadmium are precipitated. Other metallic sulfides are not precipitated because the sulfide ion concentration in the solution is not sufficient to exceed the solubility product of these other sulfides. By making the solution basic, the sulfide ion concentration is increased to the point where another group of sulfides precipitate. By means of hydrogen sulfide, the metallic ions may be readily separated into three groups: (1) those sulfides which are insoluble in dilute acid; (2) those sulfides which are insoluble in basic solution; and (3) those sulfides which are soluble in both acidic and basic solutions.

OXIDES AND ACIDS OF SULFUR

Sulfur forms several oxides, only two of which will be considered here. Sulfur dioxide and sulfur trioxide are the acid anhydrides of sulfurous acid and sulfuric acid, respectively.

Preparation of sulfur dioxide (*a*) *By burning sulfur.* Sulfur burns with a blue flame in air to produce sulfur dioxide:

$$S + O_2 \rightarrow SO_2$$

(*b*) *By roasting sulfides.* Roasting consists in heating a metallic sulfide in the presence of air or oxygen, thus converting the metal to an oxide. This process is very important in the metallurgy of ores, since it represents one step in the production of a metal from its sulfide ore:

$$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2$$
$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$$
$$4\ FeS_2 + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2$$

(*c*) *Reduction of sulfuric acid.* Metals react with hot concentrated sulfuric acid to form sulfur dioxide:

$$Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2\ H_2O$$

(*d*) *Action of acids on sulfites.* Sulfur dioxide is conveniently prepared in small quantities by treatment of a sulfite or bisulfite salt with an acid, for example,

$$Na_2SO_3 + 2\ HCl \rightarrow 2\ NaCl + \underbrace{H_2SO_3}_{\rightarrow SO_2 + H_2O}$$

or

$$NaHSO_3 + HCl \rightarrow NaCl + \underbrace{H_2SO_3}_{\rightarrow SO_2 + H_2O}$$

The sulfurous acid is unstable and decomposes into sulfur dioxide and

water. As a result of the unstable character of sulfurous acid, sulfite salts effervesce on addition of acids.

Properties of sulfur dioxide Sulfur dioxide is a gas at ordinary temperatures and has a disagreeable, penetrating odor. The gas is about twice as heavy as air and may be liquefied easily by cooling in a salt-ice mixture. The boiling point of the liquid is $-10°$. The gas is quite soluble in water; 1 liter of water dissolves about 80 liters at 0°. It reacts with water, forming a solution of weakly acidic properties:

$$SO_2 + 2\ H_2O \rightleftharpoons H_3O^+ + HSO_3^- \qquad K_i = 1.7 \times 10^{-2}$$
$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{--} \qquad K_i = 6.2 \times 10^{-8}$$

Sulfurous acid has not been isolated, but its salts (sulfites) are well known. A solution of sulfurous acid gives typical acid reactions, reacting with metals above hydrogen in the activity series and with bases:

$$Zn + H_2SO_3 \rightarrow ZnSO_3 + H_2$$
$$2\ NaOH + H_2SO_3 \rightarrow Na_2SO_3 + 2\ H_2O$$

Sulfurous acid slowly absorbs oxygen from the air, forming sulfuric acid:

$$2\ H_2SO_3 + O_2 \rightarrow 2\ H_2SO_4$$

Sulfur dioxide is a good reducing agent, as illustrated by the following reactions:

$$5\ SO_2 + 2\ H_2O + 2\ KMnO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 2\ H_2SO_4$$
$$2\ H_2O + 3\ SO_2 + 2\ HNO_3 \rightarrow 2\ NO + 3\ H_2SO_4$$

Use of sulfur dioxide and sulfites The most important use of SO_2 is in the preparation of sulfuric acid. A solution of sulfurous acid is a mild bleaching agent and may be used for bleaching straw, silk, or wool. The bleaching action is probably due to the reducing property of the acid. Sulfur dioxide is also used as a refrigerant. *Calcium bisulfite,* $Ca(HSO_3)_2$, and *magnesium bisulfite,* $Mg(HSO_3)_2$, are used extensively in the paper and pulp industry for dissolving lignin, a resinous substance which holds the wood fibers together.

Sulfur trioxide and sulfuric acid The preparation of sulfuric acid involves the preparation of its anhydride, sulfur trioxide, and the solution of the anhydride in water to form H_2SO_4. Two methods are now employed for the commercial preparation of H_2SO_4.

(*a*) *Contact process.* Sulfur dioxide does not combine with oxygen appreciably at room temperature, but at a temperature of about 400° in the presence of a catalyst, the reaction is about 98 per cent complete:

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$$

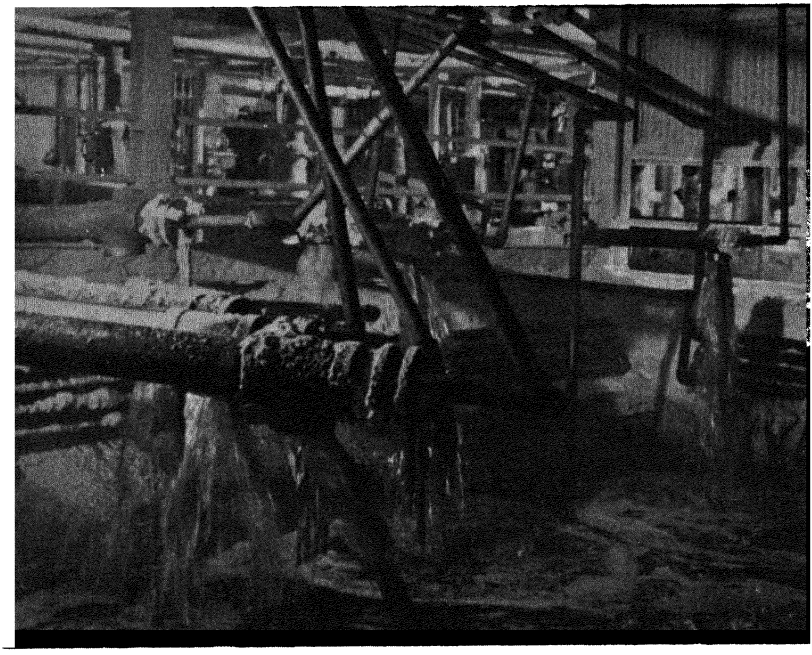


Figure 24–3 Molten sulfur being pumped to a large vat area in which it will solidify.

Platinum is used as a catalyst, but owing to the ease with which the platinum becomes poisoned (rendered inactive), this metal may be replaced by a mixture of various metallic oxides with vanadium pentoxide, V_2O_5. The sulfur trioxide is absorbed in concentrated sulfuric acid, in which it is readily soluble, forming pyrosulfuric acid:

$$SO_3 + H_2SO_4 \rightarrow \underset{\substack{\text{pyrosulfuric acid}\\ \text{(fuming sulfuric acid)}}}{H_2S_2O_7}$$

Pyrosulfuric acid is then converted into sulfuric acid by adding water:

$$H_2S_2O_7 + H_2O \rightarrow 2\,H_2SO_4$$

The acid produced by this process is 100 per cent.

(*b*) *Lead chamber process.* In this process, a mixture of sulfur dioxide, air, oxides of nitrogen (NO and NO_2), and steam is allowed to react in lead-lined chambers. The reactions taking place are somewhat complex; the ultimate changes may be represented by the reactions:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$2\,NO + O_2 \rightarrow 2\,NO_2$$

Intermediate in the formation of H_2SO_4 there is formed a compound with the formula $H(NO)SO_4$, called nitrosyl sulfuric acid, which forms as white crystals in the lead chambers, especially when insufficient steam is being used.

The oxides of nitrogen are not destroyed in the reactions and may be used over and over again. A solution containing 60 to 70 per cent sulfuric acid is obtained by this process. Although the chamber process is the older of the methods for making sulfuric acid, the contact process now produces most of the supply of commercial acid, since it makes 100 per cent pure acid and requires less investment in equipment. However, in the chamber process, impure sulfur dioxide can be used; the sulfur dioxide used in the contact process must be relatively pure.

Properties of sulfuric acid Pure sulfuric acid is a heavy, viscous liquid (sometimes called "oil of vitriol"), with a density of 1.84. Sulfuric acid exhibits three distinct sets of chemical properties.

(*a*) *Acid properties.* Dilute sulfuric acid exhibits typical acid reactions. It reacts with metals above hydrogen

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

and neutralizes bases to form salts:

$$2\ NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O$$
$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ H_2O$$

Concentrated sulfuric acid reacts with salts by double decomposition to produce salts and acids (this is the general method of preparing volatile acids):

$$2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl\uparrow$$
$$2\ NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HNO_3\uparrow$$

(*b*) *Oxidizing agent.* Hot concentrated sulfuric acid acts as an oxidizing agent, reacting with some metals below hydrogen in the activity series:

$$Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2\ H_2O$$
$$2\ Ag + 2\ H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2\ H_2O$$

Some metals above hydrogen act in the same manner with hot concentrated acid:

$$Zn + 2\ H_2SO_4 \rightarrow ZnSO_4 + SO_2 + 2\ H_2O$$

Sulfuric acid reacts with metals below hydrogen in the activity series, not because of its acid property but because of its oxidizing action.

(*c*) *Dehydrating agent.* Concentrated sulfuric acid has a great affinity

for water. If an open container nearly full of the acid is allowed to stand in contact with the air for some time, the liquid in the container increases in volume and may even flow over the top. Since the acid absorbs water from the air, concentrated sulfuric acid is often used in a closed space to produce a virtually dry atmosphere.

When concentrated sulfuric acid is added to sugar, a charred mass of carbon is formed. Sugar is a compound in which the ratio of hydrogen to oxygen is the same as in water—that is, two atoms of hydrogen to one atom of oxygen:

$$C_{12}H_{22}O_{11} \rightarrow 12\ C + 11\ H_2O$$

The hydrogen and oxygen are removed from the sugar molecule in the form of water because of the affinity of the sulfuric acid for water. The acid probably is not changed chemically in the reaction but is diluted by the water formed. Wood is blackened in contact with sulfuric acid because of a similar reaction:

$$C_6H_{10}O_5 \rightarrow 6\ C + 5\ H_2O$$

The manufacture of explosives (discussed in Chapter 22) involves the use of concentrated sulfuric acid. The action of concentrated nitric acid on such compounds as glycerin seems to be markedly hastened by concentrated sulfuric acid because water is removed from the reaction

$$\underset{\text{glycerin}}{C_3H_5(OH)_3} + 3\ HNO_3 \xrightarrow{H_2SO_4} \underset{\text{nitroglycerin}}{C_3H_5(NO_3)_3} + 3\ H_2O$$

Uses of sulfuric acid There is hardly an industry which is not directly or indirectly dependent upon the use of sulfuric acid. Annual consumption in tons of 100 per cent acid in the various industries of the United States is shown in Table 24–1.

SELENIUM AND TELLURIUM

Selenium and tellurium closely resemble sulfur, though tellurium exhibits more metallic properties than other members of the group. This is in accord with the general tendency of nonmetallic elements to show increasing metallic properties as the atomic weight increases.

Selenium is obtained as a by-product of the roasting of pyrites. Selenium, along with tellurium, is also obtained as a by-product from the electrolytic refining of copper, lead, and other metals. Selenium is used in the production of red glass and in certain electrical devices, since it becomes an increasingly better conductor of an electric current according to the strength of light impinging on it. Tellurium has no major use at present. Some use is made of relatively insoluble selenates

TABLE 24–1 Use of Sulfuric Acid in the United States*

INDUSTRY	TONS (100% acid)	USE
1. Fertilizer	6,300,000	Production of ammonium sulfate and superphosphate
2. Petroleum refining	1,800,000	Purifier of petroleum by removing dark-colored products, especially sulfur compounds
3. Chemicals	4,195,000	Preparation of hydrochloric and nitric acids, metal sulfates, ether, and so on
4. Iron and steel	1,160,000	Removal of rust on iron and steel before galvanizing or enameling
5. Metallurgy	248,000	Refining of metals by electrolysis
6. Paints and pigments	1,400,000	
7. Explosives	450,000	Dehydrating agent in the nitration of organic compounds
8. Rayon and cellulose film	750,000	
9. Miscellaneous	705,000	
Total	17,008,000	

* From *Chemical Engineering*, August 1955.

and tellurates by incorporating them into paints for ship bottoms to lessen the growth of barnacles and other organisms.

EXERCISES

1 How could you demonstrate experimentally that a given yellow solid is sulfur and not Sb_2S_3, $BaCrO_4$, or AgI?

2 Point out chemical similarities and differences of the elements sulfur and oxygen.

3 What physical properties of sulfur are taken advantage of in the separation of sulfur from other substances with which it is associated in nature?

4 Summarize the different kinds of evidence indicating that sulfur is a nonmetal.

5 Write equations for the combustion of hydrogen sulfide in (*a*) excess oxygen; (*b*) a limited supply of oxygen. Calculate the volume of air (20 per cent oxygen) necessary for the combustion of 10 liters of hydrogen sulfide. Ans. 75 l.

6 How would you demonstrate experimentally that H_2S

(*a*) is an acid
(*b*) contains sulfur
(*c*) has a molecular weight of 34
(*d*) is a reducing agent

7 Write equations for four different methods of preparing SO_2. Which of these methods are commercially important?

8 Calculate the weight of SO_2 obtainable by the roasting of 100 pounds of an ore, 60 per cent of which is zinc sulfide. Calculate also the volume of this weight of SO_2 at standard conditions. (22.4 cu. ft. is ounce molecular volume.)
Ans. 39.5 lb.; 220 cu. ft.

9 What conditions of temperature and pressure would be most favorable to the production of SO_3 by the reaction:

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3 + 44{,}000 \text{ calories}$$

10 Even though silver is a metal below hydrogen in the activity series, silverware is tarnished on coming in contact with H_2S. Explain.

11 Calculate the number of milliliters of H_2S gas at standard conditions necessary to precipitate PbS from 100 ml. of a 2 molar solution of lead nitrate.

Ans. 4480.

12 Given the following chemicals in the laboratory and no others: water, ferrous sulfide, concentrated H_2SO_4, barium chloride, air. Write equations to show reactions you might carry out to prepare (*a*) H_2S; (*b*) $BaSO_4$; (*c*) SO_2.

13 A certain sample of sulfur-containing mineral is analyzed by converting the sulfur to sulfate ion and then precipitating $BaSO_4$. If 0.5 g. of sample yielded 0.547 g. $BaSO_4$, what was the percentage of sulfur in the sample? Ans. 15.

14 Write balanced equations which illustrate the use of H_2SO_4 in the following ways: (*a*) where the SO_4^{--} acts as an oxidizing agent, (*b*) where the H^+ ion is the oxidizing agent, (*c*) where H^+ behaves as an acid toward some basic substance.

15 List in order of increasing weight (consider gases at STP): (*a*) 20 liters of NH_3 (*b*) 18×10^{23} molecules of H_2S (*c*) 100 ml. conc. H_2SO_4 (*d*) 2,240 cu. ft. of He (*e*) 10 liters N_2 (*f*) 5 liters SO_2 (*g*) 100 kg. of H_2.

16 Write the equations and state conditions of the reactions for the manufacture of H_2SO_4 by the contact process.

17 Why is H_2SO_4 not prepared from a sulfate of a metal treated with an acid?

18 Describe briefly an experiment, writing equations and telling of the phenomena observed, to show (*a*) that a certain gas is hydrogen sulfide and not sulfur dioxide; (*b*) that a certain solution contains sodium sulfate and not sodium chloride.

19 In the burning of sulfur, how many liters of oxygen would be required to produce 150 liters of SO_2?

20 Write balanced chemical equations illustrating the use of H_2SO_4 in the fertilizer industry, making bulk chemicals, in the iron and steel industry, and in the explosive industry.

21 Explain how you would proceed in the laboratory to prove that a remedy paste for the face contained some elemental powdered sulfur in it.

22 In preparation of fuel gas in a western city, the gas is passed through a bed of wood chips impregnated with $FeSO_4$. What volume of H_2S would theoretically be taken from the gas by 648 pounds of $FeSO_4$?

23 A match mixture is made of 20 pounds of Sb_2S_3, 70 pounds of $KClO_3$, 10 pounds of starch. What is the per cent of sulfur in the mixture?

24 Acid that has been used to dry Cl_2 gas has a density of 1.6 and is 60 per cent H_2SO_4. What volume in liters of the acid contains 2000 pounds of H_2SO_4?

25 Ten cubic centimeters of battery acid (density 1.21) was diluted to 100 cc. Thirty cubic centimeters of the dilute solution was neutralized by 45 cc. of 0.5 *N* base. What was the normality of the diluted acid? its strength in terms of grams per liter? What was the strength of the undiluted 1.21 density acid in terms of grams per liter? its percentage strength?

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twenty-five

CARBON AND ITS OXIDES

Carbon appears in Group IV*A* of the periodic table, centrally located between those elements that act distinctly as metals and those elements that act distinctly as nonmetals. Carbon in some forms possesses certain properties characteristic of metals and in others exhibits properties usually associated with nonmetals.

Occurrence Carbon is nineteenth in abundance among the chemical elements, yet its percentage in the earth's crust is only .027. It is widely distributed in both the free and combined states. Elementary carbon is found as diamond, graphite, and in the various forms of coal. Its compounds are almost innumerable; every living cell, plant or animal, contains carbon compounds; petroleum is a mixture of compounds of carbon and hydrogen (hydrocarbons); most of our food and clothing consist of mixtures of carbon compounds; and many carbonate minerals occur on the earth's surface.

Carbon forms compounds only by sharing electrons—all of its compounds are covalent. Not only does it share electrons with other elements but it also has great ability to share electrons with itself. Many carbon atoms may cluster together to form molecules of great complexity. The chemistry of these compounds is so extensive that it comprises the special field of organic chemistry, which is discussed in Chapters 39 and 40. More compounds of carbon are known than of any other element except oxygen and hydrogen, with which carbon itself forms numerous compounds.

It is estimated that there is 30,000 times as much carbon in rocks of the earth's crust and as carboniferous deposits as there is carbon in the air as carbon dioxide. We can infer from this that the percentage of carbon dioxide in the air in earlier geologic times was much higher than the 0.035 per cent now present.

Allotropic forms Carbon exists in three allotropic forms. Two of these are definitely crystalline: *graphite* and *diamond,* which will be considered in more detail later. The third allotropic form, *amorphous* carbon, has a number of common names—coke, charcoal, soot, lampblack, sugar charcoal, and boneblack—as we encounter it with various impurities. These forms of carbon have been shown by X-ray analysis to be minutely crystalline, but the crystals are too small to give the substance any apparent crystalline properties.

Destructive distillation of wood and coal Heating a substance in the absence of air to form volatile and nonvolatile products is called *destructive distillation.* If wood is covered with sand to exclude air and heated, volatile material is given off and charcoal remains. The properties of the charcoal depend largely on the kind of wood used. A more modern process is to heat wood in airtight ovens in which it decomposes into charcoal, water vapor, and a poor-burning gas. From this gas, wood alcohol, acetic acid, and acetone may be condensed.

The biggest industrial application of destructive distillation is heating suitable coal in ovens to yield coke and volatile products. The coke retains the nonvolatile mineral matter of the coal, but it also contains a high percentage of carbon and so is much used in metallurgical operations, in making gas, and in home furnaces. Volatile products from destructive distillation of coal are coal gas, benzene, coal tar, and ammonia. Benzene and coal tar are raw materials for chemical industries which produce medicinals, dyes, explosives, certain kinds of plastics, and in general, many organic compounds.

Formation of coal Coal is the result of change of fossil plant material which has been protected from complete decay by overlying water-washed earthy deposits. Since at one time in the earth's history, during the so-called Carboniferous era, the air had a much higher carbon dioxide content than at the present time, the average earth surface temperature was higher, and vegetation grew in profusion. The carbon dioxide content of the air in generations of time was lessened as it was used by growing plants and by conversion into carbonate rocks. Today plants make use of the 0.035 per cent CO_2 in the air.

During the time that the carboniferous material was beneath a cover of earth, changes were effected by pressure, heat, and other factors. The original plant material probably had a composition somewhat like that of wood. Preliminary decomposition of such material gives a product called *peat,* which may be dug from its deposits and burned. However, peat constitutes a rather poor fuel. In its formation, carbon dioxide and methane are the principal gases evolved. The methane is known as marsh gas, since it occurs in the bubbles coming up through the water

in boggy regions where organic decomposition takes place. Further loss of carbon dioxide, water, and minor amounts of other gases from the underground organic mass brings about an increase of the percentage of carbon with the resultant formation of coal. Various grades of coal differ, according to the amount of metamorphosis the carboniferous deposit underwent during geological time.

Fuels Wood, coal, and oil, man's most useful fuels, are mixtures composed largely of carbon or carbon-containing compounds. Their combustion gives usable heat energy, with carbon dioxide and water as the main products. Results of chemical analysis of a number of varieties of fuels are given in Table 25–1.

TABLE 25–1 Fuels

FUEL	ULTIMATE ANALYSIS (per cent)						PROXIMATE ANALYSIS (per cent)				CAL. PER GRAM
	C	H	N	O	S	Si, Fe, Mg Oxides	Moisture	Volatile Matter	Fixed C	Ash	
Anthracite	82.	0.5	0.1	1.8	0.9	14.7	4.5	3.0	78.7	13.8	7100
Pa. Bituminous	71.5	5.3	1.3	9.1	3.1	9.7	1.8	32.8	47.3	18.2	7200
Ore. Subbituminous	51.1	5.5	1.2	28.2	0.8		16.1	31.1	39.6	13.2	5500
N. D. Lignite	37.4	6.4	0.6	45.0	0.2		36.9	24.9	27.7	10.4	5000
Coke									89.0	10.2	7200
Charcoal									97.0	3.0	7700
Wood	40.0	7.2	0.8	50.7		1.3					4500
Petroleum	84.0	13.									10400

Ultimate analysis aims at ascertaining the percentages of the elements in a mixture such as wood or coal. *Proximate analysis,* which is much more rapid, is a practical means of evaluating coal for its different uses. Bituminous coal, with a high percentage of volatile matter, gives a higher yield of coal gas and coal tar than an anthracite coal. The lignite coals, with high percentage of moisture and low percentage of carbon, make mediocre fuels.

Petroleum is a naturally occurring mixture of compounds of carbon and hydrogen (Chapter 39). Wood is largely composed of lignin and cellulose, compounds containing carbon, hydrogen, and oxygen.

In general, the higher the hydrogen content of fuel, the greater the heat liberated per unit of it burned; and the higher the oxygen content of fuel, the lower the heating value of it. *Calorific value* is the measured amount of heat liberated per unit quantity of a substance burned, and may be measured in calories or British thermal units.[1]

[1] A British thermal unit (B.T.U.) is the amount of heat required to raise the temperature of one pound of water one degree Fahrenheit.

Gaseous fuels find marked demand because of their convenient pipe delivery. *Natural gas* which is obtained from bore holes in many parts of the country, chemically is composed of the lighter hydrocarbon molecules. Methane, CH_4, is a high-percentage constituent of natural gas. *Coal gas* from the destructive distillation of coal is used for heating and cooking in urban areas and as an industrial fuel. Coal gas is carefully treated to remove hydrogen sulfide, ammonia, and small particles of solid or liquid matter, and, as distributed for use, is about 50 per cent hydrogen, 30 to 35 per cent methane, 8 per cent carbon monoxide, about 2 per cent other hydrocarbons, and the remainder mainly nitrogen.

Properties and uses of carbon Since a small weight of charcoal has a large surface area because of its high porosity, it is widely used as an adsorbent. *Adsorption* is the tendency exhibited by all solids to condense selectively upon their surfaces a layer of gas or liquid with which they are in contact. It has long been a practice of farmers to suspend a gunnysack of charcoal in a cistern to adsorb smelly gases. Similarly, gas mask cannisters for wartime use contain specially prepared charcoal of high adsorptive capacity. A brownish impure sugar solution is rendered colorless by filtering it through charcoal. It should be stressed that adsorption by a given solid is selective. For example, charcoal adsorbs coloring matter but not sugar from solution; charcoal adsorbs a high percentage of hydrogen sulfide gas from an atmosphere containing it but adsorbs only a small percentage of nitrogen.

Other uses for various kinds of amorphous carbon are printer's ink, filler for rubber, shoe polish, paints, and enamels.

Chemical properties At ordinary temperatures, carbon does not readily unite with other elements, but at higher temperatures it combines with many metals and nonmetals. Carbon heated in air burns to form CO_2 with evolution of about 7900 calories per gram of carbon. Carbon is thus a good fuel. If it is heated in a limited amount of air or at a very high temperature, carbon monoxide is produced rather than CO_2 according to the equation

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

Carbon monoxide is a dangerous gas resulting from incomplete combustion of carbon or its compounds. When carbon or its compounds burn in open air where a large volume of oxygen is available, CO, if first formed, readily burns to CO_2.

Carbon disulfide, a liquid compound formed by sulfur vapor in contact with hot carbon, is in increasing demand to make "viscose," an intermediary substance in rayon production. It is also used to kill rodents. Since it is a readily volatile and inflammable liquid, it must be kept away from open flames.

Carbon tetrachloride is a noninflammable liquid used as a solvent for oils and greases. Carbon does not form this compound, however, by direct union with chlorine. Carbon tetrachloride may be made by chlorination of carbon disulfide:

$$CS_2 + 3\,Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

It is used as a solvent in dry cleaning and as a filler in certain fire extinguishers with the trade name Pyrene.

Reducing action Carbon and carbon monoxide, the cheapest reducing agents available, are extensively used to obtain metals from metal ores in the metallurgical industry; for example,

$$ZnO + C \rightarrow Zn + CO$$
$$Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2$$

Carbides The more active metals cannot be prepared from their oxides in this manner because of their tendency to unite with hot carbon to form carbides. Aluminum would be a much cheaper metal if it could be obtained by heating aluminum oxide with carbon. The chemical change which does take place is

$$2\,Al_2O_3 + 9\,C \rightarrow 6\,CO + Al_4C_3$$

Certain other metals unite with carbon to form similar carbides. Such carbides react with water to yield CH_4, methane gas;

$$Al_4C_3 + 12\,H_2O \rightarrow 4\,Al(OH)_3 + 3\,CH_4\uparrow$$

In a similar manner, by heating sand and coke in an electric furnace, silicon carbide, called *carborundum,* may be made:

$$SiO_2 + 3\,C \rightarrow SiC + 2\,CO$$

The impure blue-black, iridescent, crystalline carborundum is almost as hard as diamond and is used widely as an abrasive in the form of powder, whetstones, or grinding wheels.

Carbon and lime heated together in an electric furnace form calcium carbide, which will react with water to produce acetylene gas, the basis of an important industry:

$$CaO + 3\,C \rightarrow CO + CaC_2$$
$$CaC_2 + 2\,H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$$

In the iron and steel industry, other carbides are encountered. Steels may contain some Mn_3C or some Fe_3C *(cementite),* a hard crystalline substance largely accountable for the hardness and brittleness of a high-carbon steel.

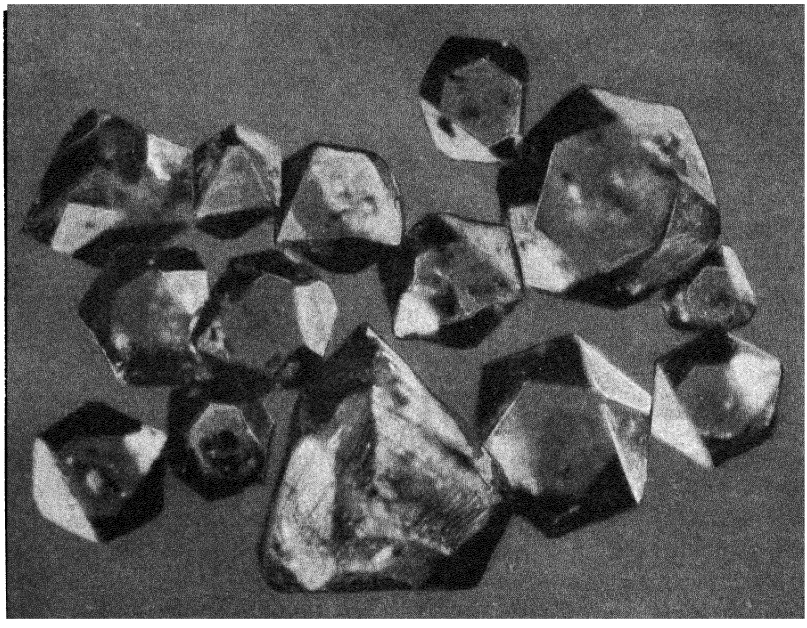


Figure 25–1 Considerably magnified view of man-made diamonds.

Graphite This shining black, soft, slippery feeling, flaky, crystalline form of carbon occurs in widely separated deposits. It is mined in Ceylon, Siberia, and to a lesser extent on the North American continent. Naturally occurring graphite has the mineral name *plumbago.* Plumbago deposits have probably resulted from heating of carbonaceous material to high temperature underneath a covering of rock. Simulating nature, man produces graphite by heating hard coal in an electric furnace, under cover of sand, to a temperature of 3500°. At this temperature carbon seems to vaporize quite readily, and the condensing carbon vapor molecules form hexagonal crystals of graphite.

Figure 12–8 on page 164 shows the hexagonal structure of carbon atoms of graphite in one plane as compared to the less closely interbonded third dimension. This structure helps to account for the flaky nature of graphite and the fact that it can be oxidized to various six-carbon atom organic compounds. The interplanar bonding electrons allow graphite to exhibit a relative softness and some degree of electrical conductivity.

Since graphite is a better conductor of the electric current than other forms of carbon and is resistant to heat and chemical change, it has

numerous uses. Electrodes and crucibles are made of it. The scalelike crystals readily slip over each other, and graphite thus makes a good lubricant. A suspension of graphite powder in water for lubricating purposes is known as "aquadag." Stove polish contains graphite to inhibit oxidation of the iron. Lead pencils contain as a core a mixture of graphite and clay, the hardness being determined by the percentage of clay and the texture of the mix.

Diamond Diamond is a colorless solid capable of being cut into brilliant stones, although it occurs naturally as a lusterless crystal. That it is pure carbon may be demonstrated by burning it in oxygen at 700°, yielding only carbon dioxide as a product.

Diamond is the hardest substance known. Its conduction of heat and electricity is very poor. These properties may be attributed to the tetrahedral structure of the crystals; see Figure 12-7, page 163. The closely packed atoms account for the hardness and relatively high density; the four covalent bonds per atom effectively tie down the valence electrons, which explains the insulating properties.

Diamonds are found in several localities; the principal deposits are in South Africa, the East Indies, and Brazil. About one quarter of those mined are suitable for gem stones; the remainder are used industrially for rock drill-bits, polishing and cutting, and as pivot supports in precision instruments.

Man-made diamonds of a quality suitable for industrial applications became commercially available in 1957. Pressures greater than 1,500,000 pounds per square inch and temperatures of about 2700° must be utilized to produce diamond artificially.

The weight of a diamond is expressed in carats. A carat is about 0.2 gram and has an average value of about $600.

CARBON DIOXIDE

Carbon dioxide is present in the air to the extent of 3.5 parts in 10,000. This amount is constantly being added to by burning carbon compounds, decay, fermentation, respiration, and volcanic gases. In turn, some of the carbon dioxide of the air is being absorbed by plants, dissolved by water, and fixed into such minerals as calcium or magnesium carbonate. There are some gas wells in the central United States and Mexico from which carbon dioxide issues at considerable pressure. Escaping carbon dioxide from ground waters in a cave near Naples, Italy, builds up such a concentration that a small dog walking into the quiet air of the cave will suffocate. A man walking upright, however, will have little discomfort, since carbon dioxide is about 1.4

times as heavy as air, and the concentration at the cave floor is much higher than at the five-foot level. Carbon dioxide is not a poison, but in a moderately high concentration a person suffers from lack of oxygen and inability to get rid of carbon dioxide from the body.

Preparation (*a*) Carbon dioxide is the product of the complete burning of carbon or its compounds. Most vaporizable or gaseous carbon compounds, when mixed with air, form an explosive mixture. Occasionally, serious explosions occur when a suspension of finely divided solid carbon compounds in air (coal dust, flour dust, and so on) is subjected to a spark or flame. Precautions must be taken in mills that are grinding organic material so that sparks or flame do not contact the organic dust-laden air. The slow oxidation processes of rotting and respiration form carbon dioxide as a product.

(*b*) Fermentation of carbohydrate compounds results in the formation of alcohol and carbon dioxide. Yeast cells secrete an organic compound called "zymase," which hastens the fermentation process. Such an organic substance, which is produced by living cells and which catalyzes specific chemical changes is called an *enzyme:*

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} 2\ \underset{\text{alcohol}}{C_2H_5OH} + 2\ CO_2 \uparrow$$

(*c*) Carbon dioxide is produced when metal carbonates (except those of the alkali metals such as Na_2CO_3 or K_2CO_3) are heated. Heating limestone to produce lime constitutes a large industry:

$$CaCO_3 \rightarrow CaO + CO_2$$

This chemical change requires a temperature of about 900°. The reaction is reversible, so a draft is used to keep removing the CO_2.

(*d*) The most convenient laboratory method of preparing carbon dioxide is by action of an acid on a carbonate or bicarbonate:

$$CaCO_3 + 2\ H^+ \rightarrow Ca^{++} + H_2O + CO_2$$
$$Na_2CO_3 + 2\ H^+ \rightarrow 2\ Na^+ + H_2O + CO_2$$
$$NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2$$

Physical properties

Molecular weight	44
Solubility at 15° and 1 atm. pressure	1 vol in 1 H_2O
Critical pressure	72 atm.
Critical temperature	31.4°
Melting point	−56°
Sublimes at	−79°

Carbon dioxide gas is $1\frac{1}{2}$ times as heavy as air and, since it is noninflammable, may be used to blanket a flame and extinguish it. A 4 per cent carbon dioxide atmosphere over burning wood, even if 17 per cent oxygen is present, will smother the flame. It is moderately soluble in water under ordinary conditions and markedly more soluble under pressure. Its solubility is enhanced by the combination:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Carbonic acid, which has a slightly sour or biting taste, is used in carbonated or soda water.

Carbon dioxide may be liquefied by pressure and is transported as a liquid in steel cylinders. If the nozzle of such a cylinder is opened, with the nozzle end lower than the rest of the cylinder, liquid carbon dioxide is ejected into the air. The liquid under the reduced pressure immediately boils. Since a boiling liquid absorbs its heat of vaporization from the surroundings, a marked cooling takes place. If the liquid is allowed to squirt into a cloth bag so that the cooling is confined, some of the carbon dioxide liquid will cool to the solid state. Solid carbon dioxide, which commercially is called "dry ice," is made in this fashion. The solid carbon dioxide gasifies in air at a temperature of about $-79°$.

A convenient low-temperature mixture may be prepared by making a mush of solid carbon dioxide and ether. Its use may be demonstrated as follows:

Into a crystallizing dish containing a mush of ether and carbon dioxide, place a small matchbox or pillbox. Fill the box with mercury. As the mercury begins to solidify, insert a small wooden stick so that the mercury freezes around it. The box mold may then be torn from the solid mercury. One now has a mercury hammer with which nails may be driven.

Chemical properties Carbon dioxide is a very stable substance except at exceedingly high temperatures, where it decomposes:

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

Carbon dioxide from the atmosphere is constantly dissolving in water over the earth's surface; thus, natural water is really a dilute solution of carbonic acid. This dilute acid has much to do with the disintegration of rocks. Minerals are acted on by the dilute acid, and today there are enormous deposits of limestone, $CaCO_3$, and dolomitic limestone, $CaCO_3 \cdot MgCO_3$.

Carbon dioxide is tested for on the basis of the chemical change:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

A calcium hydroxide solution (lime water), when subjected to carbon dioxide, becomes milky as calcium carbonate precipitates. If carbon dioxide is added to a fine suspension of calcium carbonate, the milkiness will clear up, since calcium acid carbonate, which is water soluble, is formed:

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

This chemical change is a most important one in the problem of water softening. Naturally occurring limestone is constantly being slowly dissolved by carbonic acid in ground water to form soluble calcium acid carbonate (also called calcium bicarbonate). See Chapter 30.

In Chapter 21, mention was made of photosynthesis, the process whereby plants synthesize carbohydrates from carbon dioxide and water. It is to be assumed that photosynthesis would be much faster if plants had available a higher concentration of carbon dioxide than the 0.035 per cent in air. Increased temperature and increase of sunlight would also hasten the growing process. By subjecting growing corn in a hothouse to an atmosphere containing more carbon dioxide than is present in ordinary air, some phenomenally rapid rates of plant growth are obtained.

CARBON MONOXIDE

We most commonly hear of carbon monoxide as a product of the incomplete burning of gasoline:

$$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O \text{ (complete combustion)}$$
$$2\ C_8H_{18} + 17\ O_2 \rightarrow 16\ CO + 18\ H_2O \text{ (incomplete combustion)}$$

With insufficient oxygen, a gasoline compound such as octane, C_8H_{18}, will give off a large quantity of carbon monoxide.

Pure carbon monoxide may be prepared by heating oxalic acid in the presence of concentrated sulfuric acid:

$$H_2C_2O_4 \rightarrow H_2O + CO_2 + CO$$

The carbon dioxide can be dissolved from the carbon monoxide by solution in potassium hydroxide solution.

Carbon monoxide is a light gas, very slightly soluble in water. It is an insidious poison since it has no odor to warn of its presence. Whereas oxygen combines with hemoglobin to form a compound that readily decomposes again to yield oxygen to body tissue, carbon monoxide unites with hemoglobin to form a stable compound. When carbon monoxide is inhaled, hemoglobin combines with it, and insufficient

hemoglobin remains to function in its oxygen-carrying capacity. A person suffocates for lack of enough body oxygen when about one-third of his hemoglobin has been combined with carbon monoxide.

As carbon burns, carbon monoxide is almost always an intermediate oxidation product:

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

The blue flame surrounding burning carbon and observable in the inner cone of a Bunsen burner flame is due to the oxidation of carbon monoxide:

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

Good draft in a furnace allows for complete burning of carbon; a dampered furnace may yield considerable carbon monoxide, which escapes up the chimney.

Since carbon monoxide is formed by incomplete combustion of carbon or its compounds, and since it is a cumulative poison, some means should be employed to warn of its presence. Canaries are sometimes kept in garages as they are more sensitive to suffocation than man. Rather than relying on a canary, it is better to ensure sufficient ventilation of the building and to minimize the running of automobile motors indoors.

CYANIDES

Hydrogen cyanide, called *prussic acid,* is very poisonous and is the gas used in the lethal chambers for capital punishment in some states. It may be prepared by adding an acid to a cyanide salt:

$$2\ NaCN + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCN\uparrow$$

The gas is also used in fumigation. Since HCN has the rather pleasant smell of bitter almonds or crushed peach leaves, it is customary in fumigation to add to it some cyanogen chloride, CNCl, which is also toxic but because of its irritating odor warns of the presence of poison. The ancient Egyptians boiled peach leaves and seeds to obtain a poisonous solution which was dilute HCN. Certain tropical trees emit small concentrations of HCN into the air.

Sodium and potassium cyanides may be prepared in several ways on a commercial scale:

$$2\ NH_3 + 2\ Na \rightarrow 2\ NaNH_2 + H_2 \qquad (1)$$

$$2\ NaNH_2 + 2\ C \text{ at red heat} \rightarrow 2\ H_2 + 2\ NaCN$$

$$CaCN_2 + C + Na_2CO_3 \xrightarrow{\text{heat}} CaCO_3\downarrow + 2\ NaCN \qquad (2)$$

Cyanides are used in dissolving gold and silver from ores, in cleaning silverware, as insecticides or rodenticides, in electroplating, and in case-hardening steel. Alkali cyanides have a marked tendency to unite with cyanides of higher-valence metals:

$$4\ KCN + Fe(CN)_2 \rightarrow 4\ KCN \cdot Fe(CN)_2 \quad \text{or} \quad \underset{\text{potassium ferrocyanide}}{K_4Fe(CN)_6}$$

An antidote for a cyanide, if taken soon enough, is a solution of a ferrous compound:

$$FeSO_4 + 2\ KCN \rightarrow Fe(CN)_2 + K_2SO_4$$
$$Fe(CN)_2 + 4\ KCN \rightarrow K_4Fe(CN)_6$$

From an ionic standpoint:

$$Fe^{++} + 6\ CN^- \rightarrow Fe(CN)_6^{----}$$

The latter ion does not have the poisonous qualities of CN^-

Salts such as potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$, are important in analytical chemistry. If finely divided scrap iron, nitrogenous animal refuse, and K_2CO_3 are heated together, $K_4Fe(CN)_6$ may be dissolved from the residue. This constitutes a method for its preparation.

Certain South American natives throw NaCN into a stream above a deep pool; fish are poisoned and float downstream to be scooped from the water. Any residual cyanide in the fish is probably converted to harmless cyanate during the cooking:

$$2\ NaCN + O_2 \rightarrow 2\ NaCNO$$

When it is necessary to kill undesired fish in a lake or pond prior to restocking, cyanide may be used. In running streams, cyanides are oxidized to cyanates as shown in the above equation.

When heated, a cyanide will similarly unite with finely divided sulfur to yield thiocyanates:

$$KCN + S \rightarrow KCNS$$

A few metal cyanides tend to decompose, yielding a lower valence cyanide of the metal:

$$2\ Cu(CN)_2 \rightarrow 2\ CuCN + (CN)_2\uparrow$$

Cyanogen is the name for $(CN)_2$ gas, which is poisonous, water soluble, and in chemical behavior resembles Cl_2:

$$(CN)_2 + H_2O \rightleftharpoons HCN + HCNO$$

When cyanogen gas is heated to 400° C., it polymerizes to form paracyanogen, $(CN)_x$, a white solid.

EXERCISES

1 What weight of 90 per cent pure calcium carbide, CaC_2, is needed to prepare 896 liters of acetylene, C_2H_2? Ans. 2840 g.

2 Will an atmosphere containing 5 per cent carbon dioxide, 15 per cent oxygen, and 80 per cent nitrogen support the combustion of wood?

3 Explain how certain physical properties of carbon dioxide make it useful as a refrigerant.

4 Complete and balance these equations:

(*a*) $CO_2 + OH^- \rightarrow$ (*b*) $Na_2C_2 + H_2O \rightarrow$ (*c*) $CO_2 + C \rightarrow$

(*d*) $NaHCO_3 + \text{heat} \rightarrow$ (*e*) $Ca(OH)_2 + CO_2 + H_2O \rightarrow$

5 Given 88 g. of CO_2 at S.T.P., determine the following: (*a*) number of moles present; (*b*) number of liters present; (*c*) number of molecules present.

6 If one wishes to be exact in statement, why cannot charcoal, coke, and bone-black be called amorphous carbon?

7 What is the percentage composition of $(C_6H_{10}O_5)_x$? What is the percentage composition of the product as it loses 2 and 4 molecules of water, respectively? This is somewhat analogous to woody material becoming coal in geological time.

8 Given 100 tons of 20 per cent ZnS, 80 per cent siliceous ore. Write equations for reactions involved in obtaining zinc metal. Assuming 5 per cent metal loss in operation, what weight of zinc may be obtained? Ans. 12.7 t.

9 Give a formula for a metal hydride and for a metal carbide. What is Fe_3C?

10 The density of liquid CO_2 is 0.81, as it exists under pressure in a cylinder. A liter of this CO_2 liquid will expand to what volume of CO_2 gas measured at standard conditions? Ans. 412 l.

11 Write formulas for six molecular or ionic particles present in an aqueous solution of carbon dioxide.

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twenty-six

SILICON AND GLASS

Silicon appears with carbon in Group IV*A* of the periodic table and, like carbon, has four valence electrons in its outer orbit. Silicon is nonmetallic and acid forming like carbon, and many silicon analogs of carbon compounds are known. Unlike carbon, the element is not found in the free state. Silicon is found in nearly all rocks and minerals and appears as the central element of the mineral kingdom in the same way that carbon is the central element of the animal kingdom.

Occurrence of silicon Silicon is second only to oxygen in abundance, constituting approximately 26 per cent of the earth's crust. Since practically all the silicon occurs combined with oxygen as SiO_2 (or as compounds of SiO_2 with metal oxides), this compound comprises over 50 per cent of the weight of all matter available to us.

The outer zone of the earth is composed largely of what are called *siliceous rocks.* Rocks that have probably resulted from solidification of liquid on or near the earth's surface are known as *igneous* rocks. The weathering of these rocks, erosion, and deposition by water have resulted in vast deposits of *sedimentary* rocks such as sandstone, shale, and limestone. As new intrusions of hot liquid rock have penetrated the earth's crust, heat and marked pressure effects have caused alteration of igneous and sedimentary rocks to *metamorphic* rocks. When a sandstone is subjected to marked heat and pressure effects, it crystallizes to a more compact rock called quartzite; limestone by heat and pressure is altered to the metamorphic rock, marble.

The chemistry of igneous rocks is the chemistry of many complex silicates. Liquid, glassy masses which originally covered all or part of the earth (some lavas still exist in the earth) are metal oxides dissolved in, or combined with, silicon dioxide. When a water solution of many salts freezes, one finds many different salt crystals throughout the ice.

Similarly, a magma (molten rock), on solidifying, contains crystalline compounds throughout the quartz, SiO_2, or the SiO_2 may be part of the compound.

Granite is a good example of an igneous rock. A molten mass of SiO_2, Al_2O_3, K_2O, Na_2O, Fe_2O_3, and H_2O may solidify to the minerals *feldspar*, $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$ or $Na_2O \cdot Al_2O_3 \cdot 6\,SiO_2$; *mica*, $K_2O \cdot 2\,Al_2O_3 \cdot Fe_2O_3 \cdot 6\,SiO_2 \cdot 2\,H_2O$; and *quartz*, SiO_2. Close examination of a good granite building stone will reveal cream-colored feldspar, black flaky mica, and white quartz. As varying compositions of molten magmas solidify or are altered chemically by weathering, hundreds of different minerals may form. Other common silicates are *wollastonite*, $CaSiO_3$; *asbestos*, $Mg_3Ca(SiO_3)_4$; *talc*, $H_2Mg_3(SiO_3)_4$; *zircon*, $ZrSiO_4$; *clay*, $2\,H_2O \cdot Al_2O_3 \cdot 2\,SiO_2$. These types of siliceous rock comprise most of our surface rock and soil particles.

Preparation Silicon may be prepared by the reduction of silicon dioxide with an active metal like magnesium or aluminum at an elevated temperature

$$SiO_2 + 2\,Mg \rightarrow Si + 2\,MgO$$

More commonly, silicon is prepared by reducing the oxide with carbon in an electric furnace:

$$SiO_2 + 2\,C \rightarrow Si + 2\,CO\uparrow$$

The proportions of the reactants must be carefully regulated to prevent the formation of silicon carbide.

Properties and uses Silicon as ordinarily prepared is a brownish powder but may exist also as hard gray crystals with a metallic luster. The element is relatively inactive at ordinary temperatures. When heated with oxygen, it combines readily to form the dioxide; however, the action soon stops as a tightly adhering protective coating forms on the surface and prevents further action. The element readily reacts with the halogens at elevated temperatures to form volatile halides; for example,

$$Si + 2\,Cl_2 \rightarrow SiCl_4\uparrow$$

Silicon alloyed with iron as *ferrosilicon* finds extensive application in the manufacture of steel as a deoxidizing agent for dissolved gases. The alloy is prepared by heating together ferric oxide, silicon dioxide, and carbon. Silicon in small amounts in steel gives a softer, easily magnetized steel used in magnets and transformers. When silicon is alloyed with iron in larger amounts, a product is obtained which is highly resistant to the action of acids and chemicals. *Duriron* (15 per cent Si, 85 per cent Fe) is used for laboratory drain pipes and sinks. A fragment of pure silicon (or germanium) is the vital element in transistors—new electronic

devices which give promise of cheaper television sets, tiny radios, improved electric motors, and desk-size electronic brains. A wafer of elemental silicon is used in the conversion of solar energy to electrical energy in the solar battery.

Silicon is not attacked by acids, but does react as a nonmetal with strong bases to liberate hydrogen:

$$Si + 4\,OH^- \rightarrow SiO_4^{----} + 2\,H_2\uparrow$$

A small amount of industrial hydrogen is produced in this way.

Silicon dioxide Of silicon products, silicon dioxide or *silica* is the most abundant. Sand and sandstone are very high in silica. A crystalline form, *quartz,* is widely disseminated through other rock minerals, and quartz itself composes some large rock masses. Several varieties of quartz are known. A clear transparent form is *rock crystal;* colored varieties include *amethyst, rose quartz, onyx,* and a hydrated form called *opal.* The colors of the latter varieties are probably due to traces of certain metallic oxides. *Flint* is an opaque quartz.

Silica appears to be important in certain biological processes. The ashes of certain grains such as oats and barley and the feathers of certain birds contain appreciable quantities. The supporting structure of the *diatom,* a tiny organism which thrives in sea water, is largely composed of silica. In certain areas skeletons of diatoms have accumulated in deposits several hundred feet deep. This finely divided silica is called *diatomaceous earth* or *infusorial earth.* It is used as a filtering medium for certain dye products and as a mild abrasive in scouring powders.

Silica has a melting point of approximately 1700° C. When the fused compound is allowed to cool, it solidifies to a clear colorless glass. Since it has the lowest coefficient of expansion of any known substance, it finds considerable application in the preparation of beakers, flasks, and other chemical apparatus. A quartz beaker or flask may be heated red hot and plunged into cold water without breakage. Quartz window glass is finding use in hospitals since it does not filter out beneficial ultraviolet rays as does ordinary glass. Articles made of fused silica or quartz are relatively expensive as compared with similar articles made from ordinary glass.

Silicic acids and silicates Many silicates both simple and complex are known. Silicon dioxide is insoluble in water and does not react with water to form a silicic acid; nevertheless, it may be considered as the anhydride of the many possible silicic acids. Although free silicic acids (except possibly H_4SiO_4) have not been isolated, many salts of the hypothetical acids are known. A theory of the formation of the acids, from which the salts are presumably derived, is as follows:

Combination of one molecule of water with one molecule of silica would produce H_2SiO_3; two molecules of water would yield H_4SiO_4. Two or more molecules of H_4SiO_4 may condense together and then lose one or more molecules of water, giving rise to a large number of *polysilicic acids;* thus, loss of a molecule of water from two molecules of H_4SiO_4 will yield $H_6Si_2O_7$, a disilicic acid:

$$2\ H_4SiO_4 - H_2O \rightarrow H_6Si_2O_7$$

Loss of a second molecule of water would yield $H_4Si_2O_6$:

$$H_6Si_2O_7 - H_2O \rightarrow H_4Si_2O_6$$

Condensation of three molecules of silicic acid and successive losses of a molecule of water would yield a series of trisilicic acids:

$$3\ H_4SiO_4 - 2\ H_2O \rightarrow H_8Si_3O_{10}$$
$$H_8Si_3O_{10} - H_2O \rightarrow H_6Si_3O_9$$
$$H_6Si_3O_9 - H_2O \rightarrow H_4Si_3O_8$$

Many salts of $H_4Si_3O_8$ are found in nature, such as *orthoclase,* $KAlSi_3O_8$, and *albite,* $NaAlSi_3O_8$.

Silica possesses very definite acidic properties, reacting with bases and metallic oxides to form silicate salts. If silica is fused with sodium carbonate, the equation for the reaction may be written:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

Carbon dioxide escapes as a gas, and Na_2SiO_3 is easily soluble in water. The solution of sodium silicate, called *water glass,* is used as a cement or adhesive for fibrous materials such as wood and asbestos, as a fireproofing agent for stage scenery, as a detergent, and as a preservative for eggs. The commercial substance represented by the formula Na_2SiO_3 is probably a mixture of various hydrated sodium silicates.

When an acid is added to a solution of sodium silicate, a jellylike colloidal suspension of hydrated SiO_2 is obtained, which gradually loses water when warmed or allowed to stand in the open air. The acid, H_2SiO_3, does not appear to exist, and the formula for the jellylike mass should be written as $x\ SiO_2 \cdot y\ H_2O$. When this product is dehydrated to five per cent water or less, a granular, porous solid remains. This solid, termed *silica gel,* is widely used as an adsorbent for gases and as a carrier for platinum and other catalysts in certain contact catalytic reactions.

X-ray examination of silicate minerals reveals that the basis of their structure is the silicate ion, SiO_4^{----}. Metal ions are interspaced with the negative silicate ions. The SiO_4^{----} ion has a tetrahedral structure with

an atom of silicon at the center of the tetrahedron and an oxygen atom at each of the four corners. The silicon atom is much smaller than the oxygen atoms and fits into a so-called "tetrahedral hole." By a sharing of oxygen atoms between silicons, these tetrahedrons appear to be able to condense in two-dimensional or three-dimensional patterns, which explains many of the characteristic properties of some of the more complex silicates. Thus silicate tetrahedral ions may arrange themselves in two-dimensional sheets which would explain the cleavage of mica and talc into thin sheets. The arrangement of these units in long chains explains the fibrous nature of asbestos. Three-dimensional structures may also be produced, giving rise to large and complex molecules. Other silicate ions such as $Si_3O_9^{-6}$ or $Si_6O_{18}^{-12}$ exist in spatial relation to metal ions.

Other silicon compounds Silica, while resistant to the action of the strong mineral acids HCl, H_2SO_4, and HNO_3, is rapidly attacked by hydrofluoric acid with the formation of gaseous SiF_4:

$$SiO_2 + 4\,HF \rightarrow SiF_4 \uparrow + 2\,H_2O$$

SiF_4 is readily hydrolyzed with water to form fluosilicic acid, H_2SiF_6;

$$3\,SiF_4 + 4\,H_2O \rightarrow H_4SiO_4 + 2\,H_2SiF_6$$

Fluosilicic acid is used as an analytical reagent in the determination of sodium and potassium, since Na_2SiF_6 and K_2SiF_6 are among the few water-insoluble salts of these elements *Sodium fluosilicate* finds use as a germicide; *lead fluosilicate,* as an electrolyte in the electrolytic refining of lead

Silicon tetrachloride, which may be formed by the direct action of chlorine on silicon, is a volatile liquid which fumes strongly in moist air with the formation of a smoke or cloud of finely divided ortho silicic acid:

$$SiCl_4 + 4\,H_2O \rightarrow H_4SiO_4 + 4\,HCl$$

If ammonia gas is added, the density of the smoke is increased by the formation of ammonium chloride.

GLASS

When a mixture of limestone, sodium carbonate, and sand is fused, a clear homogeneous mixture of sodium and calcium silicates is produced. When the fused liquid is cooled it becomes more and more viscous and finally hardens to a transparent rigid mass called *glass.* During the cooling process the transition from liquid to solid does not take place at any definite temperature. Similarly, in the reverse process, when the glass

is warmed, it gradually softens and shows no definite transition temperature which is characteristic of the change from the solid state. X-ray examination reveals no definite pattern or orientation of atoms characteristic of the solid state. Glass then is really a solid solution.

The proportions of raw materials in glass may be varied within wide limits, and, by the substitution of other metal oxides, a great variety of glasses may be obtained. Common glass is a soda-lime glass consisting of a mixture of sodium and calcium silicates with an excess of dissolved silica. It is often called soft glass since it melts at a relatively low temperature. The substitution of potassium for sodium results in a harder glass which has a higher melting point and is more insoluble in water and alkalies. The substitution of lead oxide for calcium oxide yields *flint* glass, which has a high refractive index and is used in the production of lenses and other optical glass. If a part of the silica is replaced by boric oxide and the metal oxide content reduced, a product with a low coefficient of heat expansion is obtained. *Pyrex* is one variety of the borosilicate glasses. Colored glasses may be obtained by incorporating small amounts of certain substances either in true solution or as a colloidal suspension. A colloidal dispersion of gold or selenium produces a red glass; cobalt oxide gives a blue glass; chromium or ferrous oxide produces a greenish colored glass.

The general procedure for the manufacture of glass is as follows: The ingredients are heated in a furnace until a homogeneous solution is obtained. The glass is removed from the furnace as a semi-fluid mass and fashioned into various shapes by molding, rolling into sheets, blowing or pressing. Many of these operations were formerly done by hand, but nearly all glass shapes are now turned out by machinery. To relieve strains set up by rapid cooling, the glass must be *annealed* by a very slow and gradual cooling over a period of hours or days. Annealing the huge 200-inch reflecting telescope lens on Mount Palomar, California, took almost a year.

Safety glass is produced by cementing together two thin sheets of ordinary glass with a transparent resinous plastic. When the glass breaks, it does not shatter, as the broken pieces stick to the plastic binding.

EXERCISES

1 Discuss the similarities and differences in properties of carbon and silicon.
2 Contrast the differences in composition and properties of the following types of glasses: ordinary soft glass; pyrex; optical glass; safety glass; colored glasses; quartz.
3 List several varieties of silicon dioxide.

4 How does SiO_2 behave chemically? Explain the action of limestone as a flux to remove SiO_2 in various smelting operations.
5 How is ferrosilicon prepared? For what is it used?
6 Give the formula for the acid formed when three molecules of water are liberated as three molecules of silicic acid condense. Substitute symbols of metal atoms for the hydrogen atoms of this acid to represent a complex silicate.
7 Write the formula for calcium orthosilicate; for zinc metasilicate.
8 Write equations for the reactions:
(*a*) $Mg_2SiO_4 + HF \rightarrow$ (*b*) Fusion of K_2CO_3, $CaCO_3$, and SiO_2
9 Germanium (at. no. 32, at. wt. 72.6) is in the same family of the periodic table as carbon and silicon. How many electrons in its outer orbit? Write formulas for three possible compounds of the element. Write the formula for orthogermanic acid; for sodium metagermanate.

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twenty-seven

THE COLLOIDAL STATE OF MATTER

What is a colloid? When sugar is dissolved in water, individual molecules from the crystalline sugar are dispersed or scattered throughout the water. Such a mixture of two or more substances molecularly or ionically dispersed is termed a *true solution.*

If finely ground clay is mixed with water, a *suspension* results, in which the clay will slowly settle out. The larger the particles of clay, the faster the settling will occur. It is impossible to reduce the size of the clay particles to molecular size, and we say that the clay is insoluble. The mixture of sugar and water is said to be homogeneous, while the mixture of clay and water, since the clay particles are not of molecular dimensions, is said to be heterogeneous.

Between true solutions and ordinary suspensions, there may exist mixtures of two substances, the particles of which are so finely divided that they do not settle and cannot be filtered by ordinary means. The particles in such a mixture are smaller than those in a suspension, but larger than those in true solutions. These mixtures are referred to as colloidal dispersions or *colloidal solutions.*

Size of colloidal particles In discussing the size of colloidal particles, we shall introduce a very small unit of linear measurement, the *millimicron,* designated mμ (m stands for milli and μ for micron) and defined as one millionth of a millimeter. If we assume that molecules are spherical in shape, the diameter of an average size molecule would be about $\frac{1}{10}$ mμ. Particles of clay dispersed in water would have an average size of 1000 mμ or more in diameter. Dispersed particles of a diameter ranging between 1 mμ and 100 mμ have properties characteristic of the

"colloidal state." Differences between true solutions, colloidal solutions and suspensions are largely a matter of size of the dispersed particles. There is no sharp dividing line between the three kinds of mixtures. Molecules of some compounds are large enough to come within the size range of colloidal particles, and indeed these large molecules exhibit properties characteristic of the colloidal state.

The colloidal state is not peculiar to any class of substances; any material may be brought into a colloidal state under the proper conditions. One limitation must be imposed for the formation of a colloidal solution; the *dispersed phase* (the substance which is suspended) and the *dispersion medium* (the substance in which another substance is suspended) *must be mutually insoluble.* A colloidal solution of sugar in water is impossible, since when sugar and water are mixed, the sugar is dissolved—that is, the particles are reduced to molecular size. However, sugar may be brought into colloidal solution in some liquid in which the sugar does not dissolve.

The particles in a colloidal solution are made up of aggregates or clusters of molecules. A single particle may be made up of a hundred or a thousand molecules of a substance. Even the smallest of colloidal particles will consist of many molecules.

Kinds of colloidal solutions In Chapter 15, the various kinds of true solutions were listed. Similarly, we may list the possible types of colloidal solutions with examples of each:

1 *Gas dispersed in gas.* Gases mix in all proportions, forming a homogeneous mixture or solution; consequently there are *no* colloids of this type.
2 *Gas dispersed in a liquid.* Foams and whipped cream are examples.
3 *Gas dispersed in a solid.* Gases adsorbed by charcoal are colloidally dispersed. White flowers and white hair contain air which is colloidally dispersed.
4 *Liquid dispersed in a gas.* Fog is composed of liquid water particles dispersed in air.
5 *Liquid dispersed in a liquid.* This type of dispersion is called an *emulsion.* Milk contains butterfat in water; mayonnaise salad dressing consists of oil dispersed in vinegar.
6 *Liquid dispersed in a solid.* Cheese contains a dispersion of butterfat in casein; pearl consists of calcium carbonate in which sea water is colloidally dispersed.
7 *Solid dispersed in a gas.* Smoke and dust particles dispersed in the air may be of colloidal size.
8 *Solid dispersed in a liquid.* This is the most common type. Coffee, tea, and paints are colloidal solutions of a solid dispersed in a liquid.

9 *Solid dispersed in a solid.* Certain colored glasses and porcelain are examples.

Of the above types, we shall consider in detail only (5) and (8). A liquid colloidal solution is called a *sol;* if the liquid is water, the solution is called a *hydrosol.*

Preparation of colloidal solutions Two general methods are available for the preparation of colloidal solutions: (1) *dispersion* and (2) *condensation* Dispersion methods involve the breaking up of large particles into particles of colloidal size. Condensation refers to the condensing of molecules (which are smaller than colloidal particles) to particles of colloidal size.

increasing particle size (condensation) →

Molecules → Colloids ← Precipitates and Large Particles

← decreasing particle size (dispersion)

1. *Dispersion* Certain devices, called *colloid mills,* are available for reducing the size of coarse particles to colloidal size. These mills are essentially pulverizing devices. Certain chemicals, called *peptizing agents,* aid in attaining dispersion of the particles to the colloidal state. Clay particles may be peptized with an alkaline solution.

2. *Condensation.* Condensation methods may employ chemical reactions, in which the starting materials are in true solution. The chemical reaction forms an insoluble substance in which molecules cluster together to form a particle of colloidal size If a solution of ferric chloride is allowed to drip slowly into boiling water, a reddish colored dispersion of iron hydroxide is obtained:

$$FeCl_3 + 3\ H_2O \rightarrow Fe(OH)_3 \downarrow + 3\ HCl$$

Arsenic sulfide is insoluble in water and may be produced in a colloidal condition by passing hydrogen sulfide gas into a saturated solution of arsenic oxide in water·

$$As_2O_3 + 3\ H_2S \rightarrow As_2S_3 \downarrow + 3\ H_2O$$

Gold and silver colloids may be prepared by the action of certain reducing agents upon solutions of salts of these metals.

The importance of colloids A few typical examples may illustrate the importance of colloids in everyday life. The protoplasm of living cells and tissue is a colloidal substance; most of the body fluids, glandular secretions, and blood are colloidal; and many foods are colloidal. Thus the essential vital processes—nutrition, digestion, and secretion—are concerned with colloidal solutions.

Jellies of all kinds are colloidal dispersions. The color of the sky is

due to a colloidal dispersion of dust. The action of soap in removing dirt and grease is due to a colloidal phenomenon.

Dispersions of solids in liquids If a small amount of gelatin is dissolved in hot water and the solution cooled, the whole changes to a semisolid jellylike mass, pectin added to sugared fruit juices causes the solution to jell The dispersed particles in these two instances have an attraction for the dispersion medium. A large shell of the dispersion medium may be formed about each colloidal particle, thus preventing the free movement of these particles (Figure 27-1). In some cases the dispersed phase may surround minute pockets of the liquid. Much as beeswax encases honey, a colloidal substance in film form may enclose small droplets of the liquid dispersion medium. As a result the colloidal system assumes a semisolid state Colloids in which the dispersed phase has an attraction for the dispersion medium are called *lyophilic* colloids. If the liquid is water, the colloid is said to be *hydrophilic* Lyophilic colloids are usually organic; examples are starches, soaps, glues, and gums.

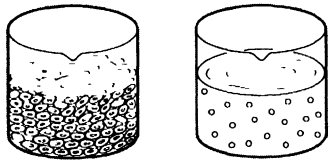


Figure 27-1 Colloidal particles: left, lyophilic colloid; right, lyophobic colloid

Substances of an inorganic character usually form *lyophobic* colloidal solutions—a dispersion in which there is no attraction between the two phases If arsenic sulfide is dispersed in water, the water has little attraction for the arsenic sulfide, and the solution has almost exactly the same properties as water itself.

Lyophilic colloids are reversible—that is, if the colloid is precipitated, the solid may again be dispersed in a colloidal condition when the dispersion medium is added. If albumen is precipitated without heat coagulation by means of a salt solution and is then washed free of the salt and water is added, the albumen becomes dispersed again in the colloidal state. Lyophobic colloids are not reversible.

Characteristics of colloidal solutions Colloidal systems exhibit certain properties which enable us to differentiate them from true solutions.

(*a*) *The Tyndall effect.* If a beam of light is passed through a colloidal solution, a very definite path of the light is visible through the solution (Figure 27-2) The light ray is made visible by the scattering of light by the suspended particles. This phenomenon is not observed in true solutions because the molecules present are too small to scatter the light. This property of colloidal solutions was first called to attention by Tyndall, an English physicist. If the beam of light is observed at right

angles by means of a high-powered microscope, the *ultramicroscope,* the diffraction or scattering of light by the individual particles in suspension can be seen. Although the particles in suspension cannot actually be seen, a study of the tiny specks of light leads to many interesting conclusions as to the size and properties of the particles. The Tyndall effect is analogous to the scattering of light entering a darkened room in which dust particles are suspended in the air. A well-defined path of light is visible because of the scattering of light by the suspended dust particles. The observation of light flashes from colloidal particles in the ultramicroscope is analogous to the transmission of signals from a considerable distance by sunlight flashes from a pocket mirror, even though the mirror itself is too small to be seen.

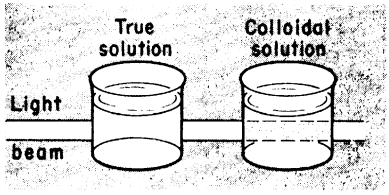


Figure 27–2 Tyndall effect.

(*b*) *The Brownian movement.* When a colloidal solution is viewed under an ultramicroscope, the suspended particles are seen as tiny specks of light dancing about in the solution. They appear to move at random, first one way, then another. This zigzag motion was first observed by the botanist, Brown, in a suspension of pollen dust. It is believed that this motion is due to a bombardment of the suspended particles by molecules in the solution. The molecules in a liquid move at relatively high speeds, and when they collide with a larger particle (of colloidal size), the larger particle is moved in one direction or another. Since, on the average, a particle will not receive the same number of hits on all sides at the same time, the net result is a zigzag motion. The Brownian movement appears to be a stability factor of colloidal solutions; the particles are kept from settling out because of this ceaseless molecular bombardment.

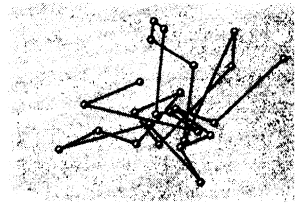


Figure 27–3 Brownian movement is random movement of a particle through the dispersion medium.

(*c*) *Electric charge.* Colloidal solutions act as fair conductors of an electric current. If a current is passed through a solution between a pair of electrodes (as in electrolysis, for example), the colloidal particles will all move toward either the positive or the negative pole. This indicates that the particles in suspension carry an electric charge. The particles are discharged at one of the electrodes, and as a result the colloid is pre-

cipitated. This movement of the colloidal particles toward one of the electrodes is termed *electrophoresis*. The charge carried by the colloidal particles depends on the nature of the colloid itself. Most of the metals and their sulfides form negatively charged colloids; metallic hydroxides in general are positive.

The charge on a colloidal particle is probably due to the adsorption of ions from the dispersion medium. *Adsorption* means that the adsorbed substance forms a layer of one molecule or one ion thickness on the surface of the adsorbing medium. Adsorption differs from absorption. When a sponge absorbs water by capillary action, the columns of water in the pores of the sponge are many molecular diameters in size.

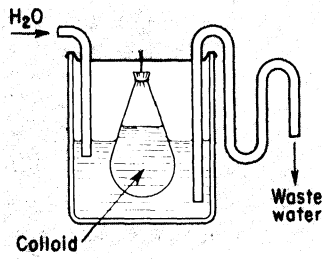


Figure 27–4 Purification of a colloid by dialysis.

A single colloidal particle probably adsorbs many ions. Certain dispersed substances adsorb positive ions and as a result become positively charged; others adsorb negative ions and become negatively charged. When a colloid is subjected to the potential difference between electrodes, the colloid particles move toward the anode or cathode depending upon the specific nature of the adsorbed charge on the colloid particle.

The charge on the colloidal particle is another important reason why the solutions are stable and do not settle out. Since like charges repel, the force of repulsion will prevent the particles from coalescing to form larger particles and precipitating.

The precipitation of colloidal particles It is reasonable to assume that if the charge on the colloidal particle could be removed or neutralized, this would allow the particles to come together and form larger particles. Eventually the particles would be large enough to settle out in the form of a precipitate; neutralization of the charge should result in coagulation of the colloid. This appears to be the case, since the addition of electrolytes (substances which ionize) causes the colloid to precipitate. Ions of opposite charge to those borne by the colloidal particle are probably adsorbed, thereby neutralizing the charge on the particle. The higher the charge of the ion adsorbed, the more effective the precipitating electrolyte.

Coagulation may also be effected by the addition of a colloid of opposite charge. Thus, iron hydroxide colloid, which is positive, added to arsenic sulfide colloid, which is negative, results in coagulation of both colloidal solutions. This process is termed *mutual coagulation.*

Dialysis In order to prepare a stable colloidal system, it is necessary to remove substances in the ionic state which would tend to precipitate the colloid. This separation may be effected by a process called *dialysis*. It is based on the fact that colloidal particles are much larger than ions. If an animal membrane bag containing the colloidal solution contaminated with electrolytes is immersed in a bath of distilled water, the ions will diffuse through the membrane until the concentration of the ions is the same inside and outside the membrane, colloidal particles are retained within the bag (Figure 27–4). By renewing the water on the outside frequently, practically all the electrolyte may be removed from the colloidal solution. Dialysis is really a kind of filtration, since one kind of substance is retained on one side of the membrane, while the other passes through. Membranes used for this purpose include certain animal membranes, parchment paper, and collodion film.

Protective colloids In many cases a colloidal system may be stabilized by the addition of a second colloid. The second colloid probably forms a protective film around the particles and adsorbed ions of the first colloid, thereby preventing the particles from coming together and coalescing. These protective colloids are of the lyophilic type. Gelatin may be added to an ice cream mixture to prevent the formation of large crystals. Gelatin is also employed in the photographic industry to form a film about the silver bromide particles which are dispersed on the photographic plates. Protective colloids find application also in the preparation of inks.

Emulsions If two mutually insoluble liquids are vigorously shaken together, small droplets of one will be dispersed in the other. Thus when kerosene and water are shaken together, the kerosene is dispersed as small droplets throughout the water medium. The kerosene particles soon coalesce, and finally separation of the oil and water into two distinct layers takes place. Such a temporary emulsion may be made more permanent by the addition of an *emulsifying agent* such as soap. An emulsifying agent is a protective colloid which forms a film about each oil particle, preventing coalescence. Milk is an emulsion of drops of butterfat in water, with casein acting as an emulsifying agent. The yolk of eggs acts as an emulsifying agent in an emulsion of olive oil in dilute vinegar (mayonnaise dressing).

Applications of colloids Smoke, which is a colloidal dispersion of solid particles in air, constitutes a nuisance around manufacturing centers. The smoke from smelters and certain other industrial plants is particularly undesirable. Such smoke may be treated by a Cottrell precipitator, which makes use of the fact that colloidal smoke particles in general have like adsorbed electrical charges and may be precipitated as a

powder by passing the smoke between highly charged plates or electrodes (Figure 27–5) In addition to eliminating the smoke nuisance, valuable materials may be recovered as by-products from the precipitated smoke powder. For example, one of our main sources of industrial arsenic oxide is the dust that is recovered from smelter smoke by a Cottrell precipitator.

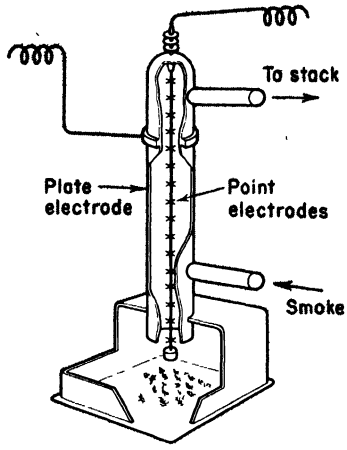


Figure 27–5 Cottrell precipitator

Colloids, as mixtures of minute particles of one substance insoluble but dispersed throughout another, are finding innumerable applications in the preparation of paints, salad dressings, glass and chinaware, oils and lubricants, photographic emulsions, and drugs.

EXERCISES

1 Give an example of (general name or specific example) a lyophilic colloid; a liquid-in-gas colloid, a solid-in-gas colloid, a liquid-in-liquid colloid, a gas-in-solid colloid, electrophoresis, adsorption

2 List and describe four ways in which you could distinguish between a yellow arsenic sulfide colloid and a yellow K_2CrO_4 solution Tell how both the colloid and K_2CrO_4 would act in each case

3 What are the two general methods for preparing colloidal solutions?

4 What do you understand by the terms colloidal solution, dialysis, adsorption, electrophoresis, emulsifying agent, lyophobic, lyophilic, emulsion, true solution?

5 List a number of common substances having colloidal characteristics

6 Differentiate between smoke and mist, hydrophilic colloid and hydrophobic colloid, dialysis and electrolysis, adsorption and absorption, microscope and ultramicroscope, electrophoresis and osmosis

7 Would 342 g. of colloidal gold in 10 l of water have as much effect on boiling point and freezing point as 342 g of sugar ($C_{12}H_{22}O_{11}$)? Explain

8 Colloidal gold in water gives a purple sol $KMnO_4$ in water gives a purple solution Aside from the slight difference in colors, list tests in which the colloidal gold and $KMnO_4$ solution will act differently

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twenty-eight METALS, METALLURGY

In previous chapters of this book, nonmetals and their compounds have been more specifically discussed than metals and metallic compounds. During the discussion of salts and bases (Chapter 10), metals were briefly considered, since cations are almost exclusively metal ions.

Metals are those elements having in their outer orbit few electrons, which are comparatively readily given up to form ions; for example,

$$\underset{\text{atom}}{Na} \rightarrow \underset{\text{ion}}{Na^{+}} + e$$

$$Zn \rightarrow Zn^{++} + 2e$$

$$Al \rightarrow Al^{+++} + 3e$$

The electromotive series (page 437) lists the metals in order of their comparative tendencies to give up electrons to form ions. As nonmetallic or negative radical ions associate themselves with these positive metallic ions, salts result; with OH^- ions, a base results.

In this chapter, we shall concern ourselves particularly with the physical and chemical properties of metals as a class; the properties of specific metallic elements will be covered in following chapters.

Metallic properties and atomic structure The physical and chemical properties of metals must be basically a manifestation of the atomic structure of the respective metals. The outer electron structure is a dominant factor in determining many physical as well as chemical properties. In a given periodic family group, however, there is a somewhat progressive change from the lightest to the heaviest element; for example, lithium to cesium or beryllium to radium. Consult periodic table inside back cover.



The valence or outer electron of cesium is much further removed from the positive nucleus than the valence electron of lithium. Accordingly, the outer electron of cesium is less tightly held; this manifests itself in the fact that cesium has the lowest ionization potential for gaseous atoms (ionization potential is a measure of the ease with which electrons may be removed from gaseous atoms). It follows that many *physical and chemical properties are related to atomic size and the lability of outer electrons.* (See page 61.) This is not a definite rule, however, as other factors are involved when dealing with a bulk metal rather than with single atoms. For example, one would expect cesium to be an excellent conductor of electricity and better than lithium in this respect. The fact is that lithium is a considerably better conductor than cesium. Apparently the nature of the *interatomic bonding between atoms of a given metal is also a basic factor in the comparative physical and chemical properties of metals.*

Although beryllium and radium have the same valence, radium is a more chemically active metal than beryllium and, although both of these elements exhibit similar physical properties, size and comparative valence electron mobility can account for degrees of difference in these properties.

In the case of families III*A* to VI*A* of the periodic table, the lighter elements possess more nonmetallic properties and progress toward distinctly metallic properties in the heavier atoms. This is readily related to the fact that the smaller, lighter atoms of these families, with outer electrons in an orbit not distant from the positive nucleus, hold on to their electrons and even tend to acquire more to become negative ions; whereas the heavier, larger atoms of these families, from a comparative standpoint, more easily lose outer electrons which are quite distant from the nucleus and thus act as metals. Family VII*A* elements, because of need of only one electron to fill the outermost orbit of 8, always act as nonmetals.

Bonding forces of metals and nonmetals Nonmetals have several electrons in the outer orbit of their atoms. As a result, nonmetal atoms are probably held together in the solid state by covalent linkages—that is, a sharing of electrons. Even in the vapor state, nonmetal atoms are frequently associated as in O_2, S_2, S_4, S_8, C_x. On the other hand, vapors of metals are *monatomic.* In the solid state, it seems likely that metal atoms, which have relatively few outer electrons, probably are not held together by covalent linkages—and certainly not by electrovalent forces; yet there is some binding force which holds metal atoms together in crystals.

The terms *metallic bond* or *metallic valency* have been coined for use in considering intermetallic bonding tendency. A marked feature of

metallic bonding is the fact that bonding remains or is instantaneously renewed on mechanical deformation of the metal. For example, a crystal of copper may be drawn into a long wire. This may in part be explained by the tendency of metals to assume a very close-packed cubic crystalline structure in which a large number of planes of flow or slippage allow for deformation, but with instantaneous renewal of metallic bonding without detracting from the strength of the interatomic attraction.

The exact nature of the interatomic attraction between metallic atoms has not yet been ascertained. This is a good example of the sort of problem that arises to challenge the scientist. Until he had learned something of the structure of the atom, he did not realize that the problem even existed, and it is almost certain that the successful solution of this problem will raise others equally difficult.

Physical properties of metals Various physical properties of metals are basically dependent on the mobility of the outer electrons. Metals are good *electrical conductors* as compared to nonmetals. An electrical current in a metal wire is presumed to be a movement of the outer electrons from one atom to another down the wire. Such elements as silver, sodium, and copper, which have only one or two valence electrons, are among the best of conductors. On the other hand, sulfur, which is a nonmetal with six outer electrons, tends to hold its outer electrons and even capture electrons and consequently acts as an *insulator* material.

Heat conductivity of elements closely parallels electrical conductivity; metals are good heat conductors, and this may be because of the capacity of the outside electrons to absorb energy and readily move from atom to atom in the solid metal.

Malleability, or the ease with which metals may be deformed or pounded into shape, is related to the weakness or mobility of bonding between metallic atoms. Gold, for example, is a very malleable element; it can be pounded into gold leaf as thin as $\frac{1}{300{,}000}$ inch. Lead is also very malleable. A *ductile* element is one that can be easily pulled into wire; copper and aluminum are very ductile. These two properties, malleability and ductility, determine the usefulness of metals for various purposes. The opposite of malleability and ductility is *brittleness.* Diamond, which is typical of nonmetals in that the atoms are held together by covalent linkages, is the *hardest* element and is very brittle.

Another useful property of metals is their *elasticity.* They may be deformed to a considerable extent, yet they spring back to their original state; or they may be deformed to such an extent that the *elastic limit* or *yield point* is exceeded so that the piece will no longer spring back to

its original dimensions but undergoes permanent deformation, though it remains as one piece. Whatever the binding force between the metal atoms, within limits it remains after deformation. There is a sort of *plastic flow* as metals undergo stretching or pounding. Contrast the fact that a crystal of a nonmetal or of a salt fractures when slightly distorted; the elastic limit is soon reached. This fracturing of salts and crystalline nonmetals occurs when these brittle substances are ground with a mortar and pestle. Plastic flow of metals accounts for the capacity to fashion them into various shapes by pounding, rolling, pulling, or drawing through a die, extruding or squirting under high pressure through an orifice, pressing, or bending. If the force pulling on a piece of metal is increased sufficiently, it will rupture the metal. The magnitude of the force necessary to pull apart a piece of known cross-sectional area is a measure of the *tensile strength.* The yield points and tensile strengths of a number of metals are shown in Table 28–1. In general, heat treatment and mechanical working such as rolling or drawing increase the strength of a metal.

TABLE 28–1 Yield Point and Tensile Strength of Metals

MATERIAL	YIELD POINT lb. per sq. in.	ULTIMATE TENSILE STRENGTH lb. per sq. in.
Aluminum (cold rolled)	18,700	20,900
Lead (cast)		1,780
Nickel (cast)	25,000	60,000
Nickel (cold rolled)	120,000	160,000
Iron (wrought)	25,000	48,000
Steel	36,000–170,000	50,000–200,000
Alloy steel	39,000–276,000	60,000–340,000
Zinc	12,800	17,000–42,000

Metals are capable of giving a polished surface which reflects a high percentage of impinging light. Since smooth metal surfaces reflect light, metals are said to have *metallic luster,* whereas nonmetals are not lustrous and at times are even transparent.

Metals are, of course, selectively used according to such desired physical properties as tensile strength, malleability, ductility, electrical and heat conductivity, melting temperature, hardness, resistance to corrosion, and density. There are marked differences in properties of the various metals; for example, the metal lithium has a density (0.534) which is little more than one-half that of water, while osmium has a density of 22.48. Table 28–2 lists some common physical properties of certain of the important metals. A more comprehensive listing of the

TABLE 28–2 Physical Properties of Some Important Metals

METAL	MELTING POINT °C.	BOILING POINT °C.	DENSITY AT 20° C.	RADIUS* OF METAL ION IN CRYSTALS cm.	ELECTRICAL RESISTANCE AT 20° ohm-cm.	SPECIFIC HEAT cal./gram
Lithium	179	1372	0.534	0.6×10^{-8}	9.3×10^{-6}	0.80
Sodium	97.5	892	0.97	0.95	4.6	0.25
Potassium	63.5	774	0.86	1.33	7.0	0.18
Cesium	28.4	690	1.90	1.69	20.	0.05
Beryllium	1300	1530	1.73	0.31	18.5	0.42
Magnesium	650	1107	1.75	0.65	4.46	0.25
Calcium	851	1487	1.55	0.99	4.6	0.145
Strontium	757	1384	2.6	1.13		
Barium	850	1640	3.75	1.35		0.07
Radium	960	1140	6.0			
Copper	1083	2310	8.92	0.96	1.69	0.09
Silver	960	1950	10.5	1.26	1.62	0.055
Gold	1063	2600	19.3	1.37	2.4	0.031
Zinc	420	907	7.14	0.74	6.	0.092
Mercury	−38.9	357	13.6	1.1	95.8	0.033
Aluminum	659	2057	2.71		2.62	0.22
Tin	231.8	2260	7.3	0.71	11.4	0.054
Lead	327.5	1620	11.3	0.84	21.9	0.032
Bismuth	271	1420	9.8	0.74	119.	0.03
Chromium	1550	2470	7.1	0.52	2.6	0.11
Manganese	1220	2150	7.2		5.	0.11
Iron	1530	2730	7.8	0.75	10.	0.11
Nickel	1452	2730	8.9	0.69	6.9	0.10
Platinum	1770	4400	21.45		10.5	0.032

* The radius of a metal ion in a crystal will in general be considerably smaller than the radius of the metal atom.

various physical properties of metals is given in various handbooks of chemistry and physics.

Periodicity of properties Many properties of the elements are periodic functions of their atomic numbers. For example, atomic radii show a definite periodicity as the atomic number increases (Figure 28–1). It is evident that the alkali group occupy maxima while members of other families occupy lower but similar relative positions on the curve.

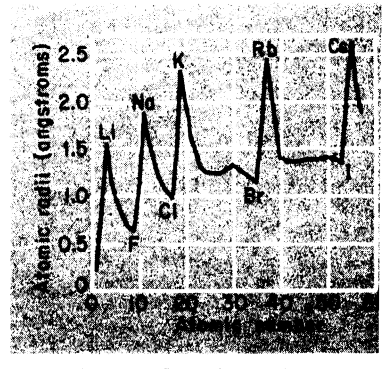


Figure 28–1 Periodicity of atomic radii.

The alkali metals, which have relatively large atomic radii, have comparatively low melting points. Elements such as the covalent-bonded nonmetals carbon and silicon have very high melting points. Melting points generally decrease as atomic size increases within a group in which there are one or two

electrons in the outer orbit of an atom—Groups I*A*, I*B*, II*A*, and II*B*. For other groups of the periodic table, melting points increase with increasing atomic size. Discontinuities occur in the cases in which there are changeovers in properties from nonmetallic to metallic within a group. Boiling points and heats of sublimation (the amount of heat necessary to convert one mole of a substance from a solid to a gas) exhibit the same pattern of periodicity as do melting points.

Periodicity of such properties as heat expansivity, heat and electrical conductivity, magnetic susceptibility, compressibility, hardness, and distribution of spectral lines has also been observed.

Alloys The product obtained by melting together two or more metals and allowing the mixture to solidify is called an *alloy*. Much as the fundamental colors may be blended to many tints, a great diversity of properties of metal products is obtained by alloying. For example, copper has a melting point of 1083° C. and costs about three times as much as zinc per pound. *Brass* is an alloy of about 66 per cent Cu and 34 per cent Zn, and melts at 900° C. This alloy, then, is easier to remelt than copper and has good mechanical working qualities. An alloy of approximately 14 per cent silicon and 86 per cent iron, known as *ferrosilicon* or *duriron*, is very resistant to corrosion and to the action of acids. Accordingly, it is used in laboratory drain pipes. Several of the more common alloys and their compositions are shown in Table 28–3.

TABLE 28–3 Common Alloys

TRADE NAME	PER CENT COMPOSITION
Aluminum bronze	90 Cu, 10 Al
Babbitt	90 Sn, 7 Sb, 3 Cu
Bearing bronze	82 Cu, 16 Sn, 2 Zn
German silver	60 Cu, 25 Zn, 15 Ni
Gold coinage	90 Au, 10 Cu
Magnalium	90 Al, 10 Mg
Manganese bronze	95 Cu, 5 Mn
Nickel coinage	75 Cu, 25 Ni
Pewter	85 Sn, 6 Bi, 7 Cu, 2 Sb
Red brass	90 Cu, 10 Zn
Silver coinage	90 Ag, 10 Cu
Solder	50 Pb, 50 Sn
Type metal	82 Pb, 15 Sb, 3 Sn
Yellow brass	67 Cu, 33 Zn
Wood's metal	50 Bi, 25 Pb, 12.5 Sn, 12.5 Cd

Binary alloys (of two metals) may be of several types depending on the following factors: complete solubility, partial solubility or insolubility of the given metals in the solid state; and possible compound formation between the metals. Intermetallic compounds in alloys are fairly numerous; for example, Al_2Mg_3, Ag_3Sb, CuMg, $CuMg_2$.

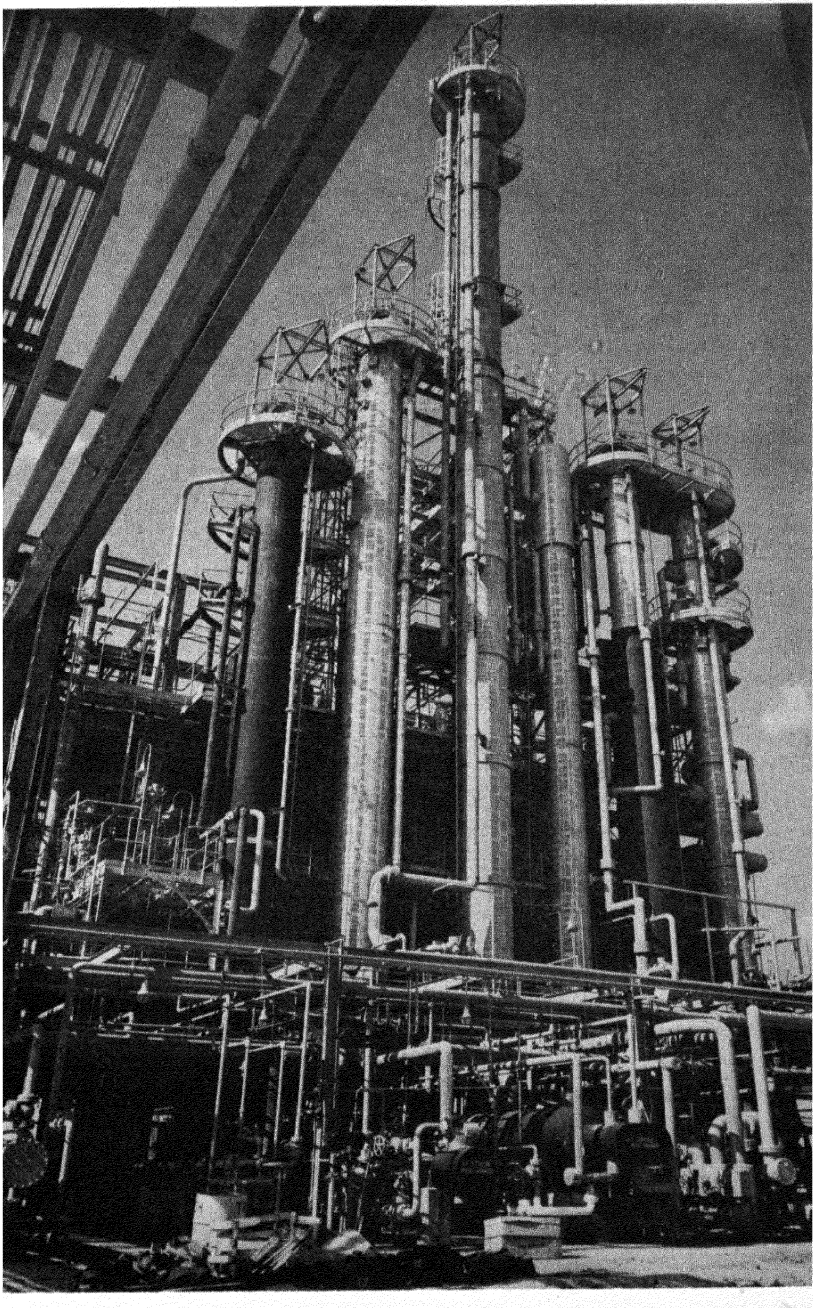


Figure 28–2 Alloys play an important part in large-scale industrial equipment.

If two metals completely soluble in the melted state are also completely soluble in the solid state, a homogeneous alloy is obtained. A homogeneous alloy may also be prepared if the melt of the two metals has the exact composition of a compound of the two. For various purposes a homogeneous alloy is best; most alloys, however, are heterogeneous and for many uses this is an advantage. The desired surface hardness and wearing quality of some steel is due to hard needlelike crystals of Fe_3C throughout an iron matrix. The bearing metal called babbitt (90 Sn, 7 Sb, 3 Cu) has a hard antimony-containing needlelike component embedded in a softer tin component. On wear, the soft component of babbitt smears the surface so there is little bearing friction, while the harder component gives rigidity. Babbitt is a ternary alloy.

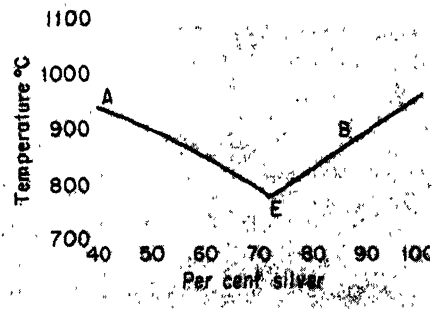


Figure 28–3 Freezing-point curve for solutions of copper and silver.

Alloys are frequently analyzed by etching a polished metal surface with weak acid followed by microscopic examination. The different components of a smooth alloy surface react at different rates with weak acids and thus a new irregular surface is formed. Acid resistant sections will be microscopic plateaus as compared with degrees of depression of the more acid soluble components.

Eutectics Much as a dissolved substance lowers the freezing point of water, one metal dissolved in the liquid of a second metal lowers the freezing point of the latter. This is evident from Figure 28–3.

As silver is dissolved in liquid copper, the freezing point or melting temperature of the alloys formed is progressively lower as the percentage of silver increases; as copper is dissolved in liquid silver, the freezing point or melting temperature of the alloy progressively decreases. Necessarily, a mixture exists which is the *alloy of lowest melting point.* It is called the *eutectic* alloy and is represented in Figure 28–3 by *E*, which shows a composition of 28 per cent copper and 72 per cent silver. If a solution of composition *A* is cooled, copper begins to crystallize out, and the composition of the solution alters along the curve toward *E*. At *E* the entire mass, which consists of the copper which has crystallized out and the eutectic mixture (28 per cent Cu, 72 per cent Ag) solidifies. Simi-

larly if a solution of composition *B* is cooled, silver crystallizes out with concomitant change in composition of the liquid until *E* is reached, when the entire mass solidifies.

Occurrence of metals Only those metals that have little affinity for oxygen or other nonmetals occur in the elemental state in nature. Gold and platinum are found as nuggets or specks in rock or in alluvial gravel. Silver, copper, and mercury are occasionally found in the free (not chemically combined) state, but these metals usually occur in the combined state. The more active metals always occur in nature as compounds. The naturally occurring compounds are usually those which are water insoluble, with oxides, sulfides, and silicates predominating. Metal oxides act basic toward the very abundant acidic compound silica, SiO_2; as a result, silicate rocks (which are made up of various metal oxide-silica compounds) comprise the bulk of earth material. Thus the metal elements occur mainly as silicates; for example, sodium feldspar, $Na_2O \cdot Al_2O_3 \cdot 6\,SiO_2$; potassium feldspar, $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$; wollastonite, $CaSiO_3$, ferrous silicate, $FeSiO_3$; mica, $K_2O \cdot 2\,Al_2O_3 \cdot Fe_2O_3 \cdot 6\,SiO_2 \cdot 2\,H_2O$. Silicates are not usually satisfactory sources of the metals because of the cost of extracting the metal. Weathering of rocks in geological time has effected decomposition of much rock silicate, and there are resultant metal oxide deposits. Bauxite, $Al_2O_3 \cdot 2\,H_2O$, is an example of a natural metal oxide mineral resulting from silicate weathering. Much of the reds or browns in soil is due to iron oxide or hydrated iron oxide that was once part of a silicate rock.

In long periods of geological time, ground waters containing dilute acids have selectively dissolved salts from the silicate minerals. These have found their way into the sea or have been deposited in arid regions. Large deposits of the salts NaCl, Na_2CO_3, $NaNO_3$, K_2SO_4, $MgSO_4$, $Na_2B_4O_7$ are found on the earth's surface.

Rock deposits of metal compounds may also result from precipitations as diverse ground water solutions flow together. Suppose a mineral water which contained H_2S joined a ground water solution which contained Cu^{++} ions:

$$Cu^{++} + S^{--} \rightarrow CuS \downarrow$$

Deposits of copper sulfide mineral would accrue as these diverse waters continued to meet over thousands of years. *Sulfide* minerals such as ZnS (sphalerite), PbS (galena), Cu_2S (chalcocite), As_2S_3 (orpiment), HgS (cinnabar) constitute some of the principal minerals from which metals are obtained.

Carbonic acid is among the most important of the ground water acids,

and it is natural that rock deposits of water-insoluble *carbonates* occur. There are mountainous deposits of $CaCO_3$ (limestone) or $CaCO_3 \cdot MgCO_3$ (dolomite) found in many regions of the world, and $FeCO_3$ (siderite) is an important iron mineral.

Thus, it is evident that most of our minerals are water-insoluble sulfides, oxides, carbonates, or silicates. Water-insoluble metal compounds of most of the other acid radicals exist in varied amounts; examples are $BaSO_4$ (barite), $Ca_3(PO_4)_2$ (phosphorite), and $PbWO_4$ (lead tungstate).

Minerals and ores A *mineral* is defined as a naturally occurring inorganic compound. Silicon dioxide, SiO_2, is the most abundant of all minerals and, according to its form of occurrence, is variously called silica, quartz, diatomaceous earth, and other names. According to our definition, naturally occurring water is a mineral. Usually when one refers to a mineral, he has in mind some naturally occurring metal-nonmetal compound. Metal minerals are commonly classed according to the nonmetal with which they are united. Metal oxides, sulfides, carbonates, and silicates are examples of important classes of minerals.

An *ore* is a naturally occurring mineral mixture from which a metal may be extracted economically. While both clay and bauxite are minerals of aluminum, only bauxite is termed an ore, since aluminum on a commercial basis is extracted from bauxite but not from clay.

Metallurgy The science which considers the extraction of metals from ores is called *metallurgy*. All those processes of breaking, grinding, pulverizing, and sizing of ore particles, and of concentrating the desired mineral from the unwanted rock mass in which it occurs, comprise what is known in metallurgical industry as *ore dressing*. When a mineral concentrate has been obtained, appropriate chemical changes to obtain the desired metal or metals must be carried out. Processes of *pyrometallurgy, hydrometallurgy,* or *electrometallurgy* may be involved. The names are in themselves explanatory, as heat, water, or electric current are used in obtaining the metal from its ore.

Suppose a company has an ore which is 5 per cent galena (PbS) and 95 per cent quartz (SiO_2). After it is mined, broken, crushed, and ground, the rock might be subjected to *gravity* concentration. Taking advantage of the difference in specific gravity between the heavy PbS particles and the lighter SiO_2 particles, the use of running water in suitable concentration machines could effect a considerable separation of the ore and silica. A product of such concentration machines from the raw ore might assay 50 per cent PbS and 50 per cent SiO_2. Most of the silica in the original rock could be discarded with only a small loss of PbS. This is evident from the following:

500 lb PbS	concentration machines →	475 lb PbS	+	25 lb PbS
9,500 lb SiO_2		475 lb SiO_2	+	9,025 lb. SiO_2
10,000 lb ore		950 lb concentrate		9,050 lb reject

It may be noted that most of the PbS is now concentrated in less than one-tenth the original amount of rock material. If this ore concentration is effected in a mill at the mine, much haulage and transportation of waste material is saved. At the smelter to which the concentrated ore is shipped, less heat will be required in the subsequent pyrometallurgy.

To obtain metallic lead, the concentrate may now be heated in suitable furnaces in the presence of air, in which case the following chemical changes take place:

$$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2$$
$$2\ PbO + PbS \rightarrow 3\ Pb + SO_2$$

The process of heating an ore in contact with air is called *roasting*. This is one of the more important pyrometallurgical processes of treating metallic sulfide ores.

Carbon is commonly used to obtain a metal from its oxide. When the oxide is heated with carbon, it is reduced; for example,

$$ZnO + C \rightarrow Zn + CO$$
$$PbO + C \rightarrow Pb + CO$$
$$Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO$$

Carbon monoxide is also an effective reducing agent for a metallic oxide.

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

Smelters or reduction plants get their name from the fact that melted metal is usually the product of their pyrometallurgical operations.

Most metal-containing minerals, when mined, are mixed with a bulk of worthless siliceous material. Even after concentration processes, much undesired impurity may remain with the metal mineral. Worthless mineral is referred to as *gangue*. In the smelting processes, chemicals called *fluxes* may be added to convert the gangue to some fluid material, usually called a *slag*. The common flux for a siliceous gangue is limestone, which forms a glassy slag of calcium silicate:

$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2$$

An example of hydrometallurgical treatment would be as follows: Suppose an ore contained about 2 per cent of a copper oxide-copper carbonate mineral intermixed with 98 per cent of worthless silica or silicate rock. The crushed ore could be put into large vats and treated with

dilute sulfuric acid. The dilute acid would act on the copper minerals to give water-soluble $CuSO_4$, the solution of which could be drained from the gangue. This particular use of a water solution (a hydrometallurgical process) may be called *leaching*. Leaching consists essentially of a selective dissolving of one mineral or group of minerals from an ore.

The copper sulfate solution could be electrolyzed in a cell to obtain metallic copper This would be an example of electrometallurgy. In the ultimate refining of metals, electrometallurgy is commonly used, the impure metal of the anode being deposited electrolytically as pure metal on the cathode.

Most of our metals may be obtained from their ores by appropriate selection of processes of ore dressing, pyrometallurgy, hydrometallurgy, or electrometallurgy

Flotation concentration Gravity concentration has been mentioned as an early step in the quest of metals from low percentage ores. Many modern ore dressing mills use a so-called *flotation* process for the elimination of gangue. The process is based on the selective wetting of surfaces by various liquids or selective attraction or repulsion between liquids and solids. To illustrate, consider the liquids water and mercury in contact with a solid such as glass. Water spreads out on a clean surface and wets the glass. Mercury, on the other hand, does not spread out but forms a globule which does not wet the glass. Certain organic liquids such as pine oil or various organic sulfur compounds have a marked tendency to wet and cling to metal or metal sulfide surfaces but do not cling to siliceous matter. Powdered ore suspended in water is fed into a vat into which is placed a mechanism to beat or blow air bubbles into the suspension A chemical such as cresylic acid is added to produce a froth and to stabilize

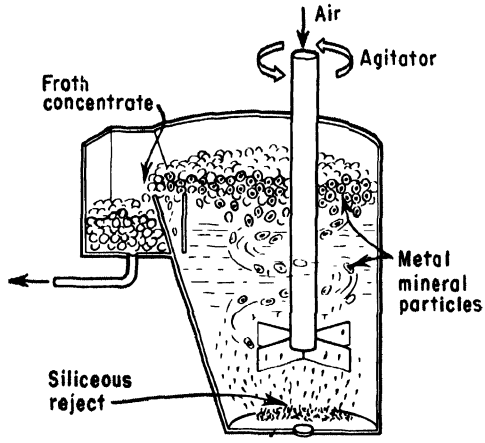


Figure 28–4 Apparatus for flotation concentration

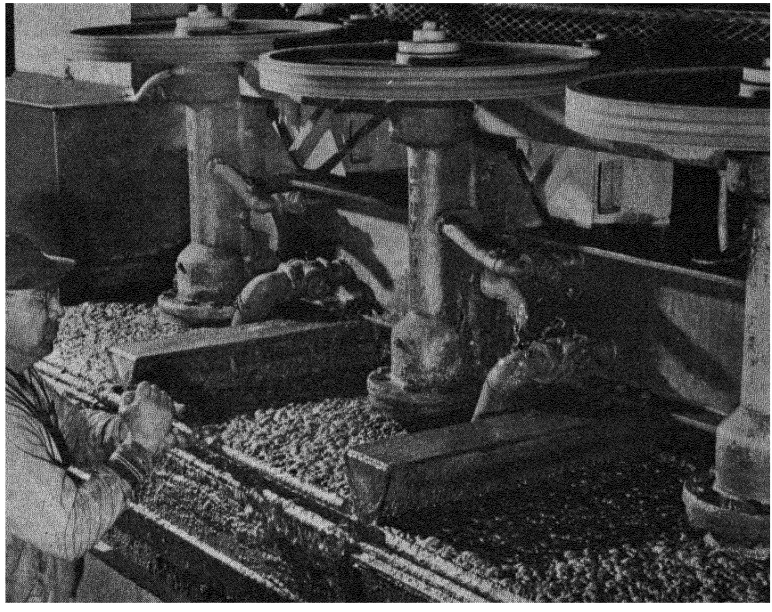


Figure 28–5 Molybdenum sulfide being froth floated from gangue.

the bubbles. Next, an organic chemical such as ethyl xanthate is added in amount as little as 0.1 pound per ton of ore. The xanthate adheres to metal and metal sulfide mineral as well as to the air bubbles, and the powdery metal-containing particles are floated to the surface as the air bubbles rise. They are then scraped off in a froth which, when dried, gives a metal mineral concentrate. The siliceous particles do not collect against the air bubbles but drop to the bottom of the vat (Figure 28–5).

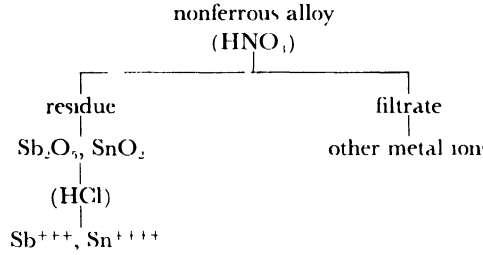
Nonaqueous electrometallurgy Electrometallurgy for such active metals as sodium or aluminum is carried out with nonaqueous solutions, since sodium or aluminum, if freed as cathode products in the presence of water, would react with the water. Sodium is obtained by electrolysis of fused NaCl; aluminum is produced by electrolysis of aluminum oxide dissolved in hot molten cryolite, Na_3AlF_6.

Chemical properties of metals Metals unite with nonmetals under appropriate conditions of temperature and contact to form binary compounds called salts; for example, FeS, Zn_3P_2, $AuCl_3$.

Contingent upon their position in the electromotive series, metals may take part in replacement chemical changes. Action of dilute acids on metals above hydrogen in the activity series are examples of replacement. One of the best ways to get a metal or alloy into solution is by use of an

acid. Hydrochloric acid is satisfactory for most metals above hydrogen in the activity series. Metals below hydrogen require the use of an oxidizing acid for solution; nitric acid is most commonly used. Gold and platinum metals do not react with nitric acid; aqua regia is the common solvent.

Alloys are commonly classified as *ferrous* and *nonferrous*. In dissolving an alloy for analysis, filings or cuttings from a specimen are taken rather than putting the bulk piece in acid. Hydrochloric acid is the appropriate solvent to use in dissolving *ferrous alloys* (alloys of iron or ironlike metals). Since *nonferrous alloys* often contain metals such as copper, lead, mercury, and silver which are insoluble in hydrochloric acid, nitric acid is best used for their solution.



In this treatment with nitric acid, tin and antimony are converted to white oxides or hydrated oxides, which are insoluble in the solution, however, they may be dissolved in hydrochloric acid.

Certain metals react with strong bases; for example,

$$Zn + 2\ OH^- \rightarrow ZnO_2^{--} + H_2$$
$$2\ Al + 2\ OH^- + 2\ H_2O \rightarrow 2\ AlO_2^- + 3\ H_2$$

A mixture of powdered aluminum and solid sodium hydroxide has been put into holes bored in the frozen ground of Alaska placer gold mines, and the heat of the reaction has thawed out the surrounding area. Similarly, some use of this mix has been made in thawing frozen water pipes.

Metal ions (cations) As noted previously, a fundamental property of metals is their ability to release electrons, resulting in the formation of positively charged ions termed *cations*. Therefore, metals act as *electron donors*. This release of electrons may be accomplished in various ways. If a metal atom reacts with water or an acid, *electrons are transferred from the metal to* H^+, producing free hydrogen; for example,

$$2\ Na + 2\ H^+ \rightarrow 2\ Na^+ + H_2$$
$$Zn + 2\ H^+ \rightarrow Zn^{++} + H_2$$

A metal may combine directly with certain nonmetals, in which case *electrons are transferred from the metal to the nonmetal atom*, for example,

$$2\ Au + 3\ Cl_2 \rightarrow 2\ Au^{+++} + 6\ Cl^-$$

An active metal will displace a less active metal from its solution, a process in which *electrons are transferred from the more active metal to the less active metal ion* (cation), for example,

$$2\ Al + 3\ Cu^{++} \rightarrow 3\ Cu + 2\ Al^{+++}$$
$$Zn + 2\ Ag^{+} \rightarrow 2\ Ag + Zn^{++}$$

Electron interchange may result from certain *intermetallic ion reactions;* for example,

$$2\ Fe^{++} + Sn^{++++} \rightarrow 2\ Fe^{+++} + Sn^{++}$$
$$2\ Hg^{+} + Sn^{++} \rightarrow Hg_2^{++} + Sn^{++++}$$

A salt is a compound composed of positive and negative ions and is formed when a solution containing cations and anions is evaporated sufficiently. Where a salt is quite insoluble, addition of a dilute solution of the positive ions of the salt to a dilute solution of negative ions of the salt results in the formation of a precipitate, for example,

$$Ag^{+} + Cl^{-} \rightarrow AgCl \downarrow$$
$$3\ Cu^{++} + 2\ PO_4^{---} \rightarrow Cu_3(PO_4)_2 \downarrow$$

Salts are usually classed according to the anion with which the cation combines—for example, chlorides, sulfates, phosphates, chromates, and so on. The solubility rules (page 186) are helpful in predicting the precipitation of salts from solution

In those cases in which an element exhibits several positive oxidation states—for example, Mn—metallic characteristics are more pronounced in the lower states; indeed, in the higher oxidation states the element may appear as part of an anion, in which case it may be said that the element is acting in the capacity of a nonmetal rather than a metal Although manganese exhibits many metallic properties, it also forms manganates and permanganates in which the Mn appears as part of the anion. *These changes in oxidation number,* of course, *involve an electron transfer;* for example, when permanganate ion is reduced with Fe^{++}, the oxidation-reduction reaction may be written:

$$5\ Fe^{++} \rightarrow 5\ Fe^{+++} + 5\ e\ \text{(oxidation)}$$
$$5\ e + MnO_4^{-} + 8\ H^{+} \rightarrow Mn^{++} + 4\ H_2O\ \text{(reduction)}$$

A further example is the reduction of ferrate ion (FeO_4^{--}) with stannite ion (SnO_2^{--}):

$$6\ OH^- + 3\ SnO_2^{--} \rightarrow 3\ SnO_3^{--} + 3\ H_2O + 6\ e \text{ (oxidation)}$$
$$6\ e + 2\ FeO_4^{--} + 5\ H_2O \rightarrow Fe_2O_3 + 10\ OH^- \text{ (reduction)}$$

Metal oxides and hydroxides Most metallic oxides and hydroxides are quite water-insoluble. (See solubility rules, page 186.) The alkali (Na, K) oxides and hydroxides are very soluble and produce strong alkaline solutions. Alkaline earth (Mg, Ca, Sr, Ba) oxides and hydroxides are sparingly soluble.

Amphoterism There are many slightly soluble hydroxides that may act either as an acid or as a base, and, accordingly, may be dissolved by either a base or an acid. For example, $Al(OH)_3$ is soluble either in hydrochloric acid or sodium hydroxide.

$$Al(OH)_3 + 3\ H^+ \rightarrow Al^{+++} + 3\ H_2O$$
$$(H_3AlO_3) \text{ or } Al(OH)_3 + 3\ OH^- \rightarrow Al(OH)_6^{---} \rightarrow AlO_3^{---} + 3\ H_2O$$
or
$$(H_3AlO_3) \text{ or } Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \rightarrow AlO_2^- + 2\ H_2O$$

The solubility in the strong base is due to the formation of a complex ion, in this case the ortho-aluminate ion, AlO_3^{---}, or meta-aluminate ion, AlO_2^-.

Compounds such as $Al(OH)_3$ (H_3AlO_3), which may act as an acid or a base, are said to be *amphoteric*, or to exhibit amphoterism.

Various industrial separations or purifications are based on this property of amphoterism. For example, there is the dissolving of bauxite, $Al_2O_3 \cdot 2\ H_2O$ in NaOH, away from hydrated iron oxide impurity in aluminum ore (see page 470).

Other amphoteric hydroxides are $Zn(OH)_2$, $Sn(OH)_2$, $Sn(OH)_4$, $Cr(OH)_3$. These will all act with H^+ as if they were typical bases, but the following equations show their action with OH^- as if they were acids.

$$Zn(OH)_2 + 2\ OH^- \rightarrow Zn(OH)_4^{--} \text{ or } ZnO_2^{--} \cdot 2\ H_2O \text{ (zincate ion)}$$
$$Sn(OH)_2 + 2\ OH^- \rightarrow Sn(OH)_4^{--} \text{ or } SnO_2^{--} \cdot 2\ H_2O \text{ (stannite ion)}$$
$$Sn(OH)_4 + 2\ OH^- \rightarrow Sn(OH)_6^{--} \text{ or } SnO_3^{--} \cdot 3\ H_2O \text{ (stannate ion)}$$
$$Cr(OH)_3 + 3\ OH^- \rightarrow Cr(OH)_6^{---} \text{ or } CrO_3^{---} \cdot 3\ H_2O \text{ (chromite ion)}$$

Metal hydrides Compounds of hydrogen with nonmetals—for example, HCl, H_2S, H_3P—are not considered unusual. Compounds between metals and hydrogen exist only between active metals and hydrogen and have come into industrial importance only recently. Sodium hydride, NaH; lithium hydride, LiH; lithium aluminum hydride, $LiAlH_4$; and calcium hydride, CaH_2, are commercially produced and are strong reducing agents in organic preparations.

EXERCISES

1 Write a brief summary of what might be done to obtain pure copper from a mine ore that contains about 20 pounds Cu as Cu_2S per ton The gangue is mainly granite and quartz

2 Discuss how galena (PbS) ore, containing 2 per cent PbS and 98 per cent siliceous matter, could be concentrated How would metallic lead be obtained from the concentrate?

3 Explain the meaning of eutectic, ternary alloy, elastic limit, yield point

4 What factors enter into the question of whether a two-foot thick ledge of quartz assaying $20 per ton in gold is an ore or not?

5 Compare physical properties, such as melting point, boiling point, atomic volume, for a family of elements such as the alkali metals or a Group III family

6 Complete and balance

$$Ag + HNO_3 \rightarrow$$
$$Pb + HNO_3 \rightarrow$$
$$Sn + HNO_3 \rightarrow$$

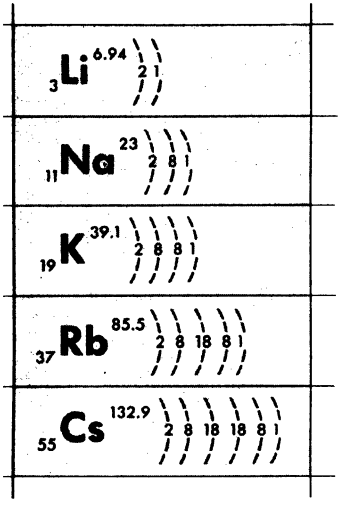
7 From the later chapters of this book, pick two examples of pyrometallurgy, two of electrometallurgy, one of hydrometallurgy

8 Write ionic equations illustrating a metal as an electron donor to hydrogen ion, a metal as electron donor to a nonmetal, a metal as an electron donor to a metal ion

9 A siliceous rock assays 1 per cent copper, 3 per cent zinc, and 0.3 oz gold per ton 100 tons of this ore is shipped to a concentration mill After gravity and flotation concentration, there remains 10 tons of concentrate, assaying 35 per cent copper, 20 per cent zinc, and 2.5 oz gold per ton Some metal values were lost in the discarded 90 tons What percentage of each metal was recovered in the concentrate?

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twenty-nine

THE ALKALI METALS

METAL	SYMBOL	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Lithium	Li	0.53	186	1200	+1
Sodium	Na	0.97	97.5	880	+1
Potassium	K	0.87	62.3	760	+1
Rubidium	Rb	1.53	38.5	700	+1
Cesium	Cs	1.87	26.5	670	+1

The alkali metals constitute a closely related family of metals in Division *A* of Group I of the periodic table. The metals are all very active, the activity (except for Li which is nearly as active as Cs) gradually increasing as the atomic weight increases. The elements are called *alkalies,* since their hydroxides give strongly alkaline solutions. All exhibit an electrovalence of +1, which indicates one valence electron in the outermost orbit of the atom. The densities of these metals are relatively low, a property not usually associated with metals; yet from a chemical standpoint these elements are the most metallic of all. Because of their extreme activity, the alkali elements are never found in

the free state, and liberation from their compounds is accomplished with some difficulty. All may be prepared by electrolysis of the fused chlorides or hydroxides. The metals themselves are relatively unimportant, since they are too active for most purposes; but their compounds are exceedingly important, particularly those of sodium and potassium, the most abundant of the alkali metals.

SODIUM

History and occurrence In 1807, Davy first prepared the element sodium by the electrolysis of fused sodium hydroxide. Davy's experiments involving the preparation of sodium and other alkali metals by means of electrolysis was the beginning of a new field in chemistry—electrochemistry.

Sodium is one of the more abundant of the chemical elements and comprises 2.6 per cent of the earth's crust. While never found in the free state because of its extreme activity, its compounds are nevertheless widely distributed. Most silicate rock masses contain sodium minerals; *soda feldspar* or *albite,* $Na_2Al_2Si_6O_{16}$, is an abundant mineral. Enormous deposits of *rock salt,* NaCl, are found in various parts of the world. Sea water contains about 3 per cent of mineral matter, most of which is sodium chloride. Because of the solubility of most sodium salts, they are leached out by streams and ground waters and eventually find their way to the sea. Alkaline lakes in Nevada and California contain large quantities of sodium carbonate which may be obtained by evaporation.

Preparation of metallic sodium Although some sodium is still produced by Davy's original process, this method has been largely supplanted at the present time by the electrolysis of fused sodium chloride. The electrolysis is carried out in an electrolytic cell, a cross section of which is shown in Figure 29–1. The anode, which is placed at the center of the cell, is composed of carbon. The cathode consists of an iron

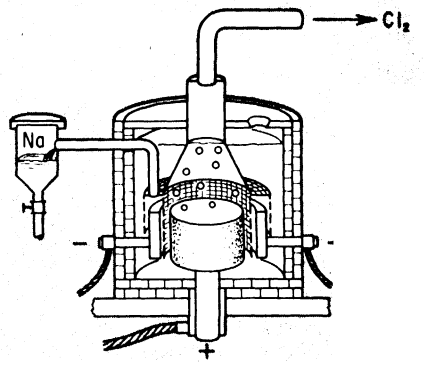


Figure 29–1 Electrolytic cell for producing metallic sodium.

cylinder, which surrounds the anode and is separated from it by an iron gauze, which keeps the products of electrolysis separated. The electrolyte is fused sodium chloride to which calcium chloride has been added to lower the melting point from 800° to about 600°. The cell is so arranged that chlorine, which is formed at the anode, may be drawn away into a compartment just above the carbon anode Meanwhile, metallic sodium, which is formed at the cathode, rises to the surface of the cell since its density is less than that of the fused electrolyte Here it is collected in a special receptacle

Properties Sodium is a soft metal and may be easily molded into any desired form. When cut with a knife, it reveals a silver-white surface. It is very light, having a density of 0.97. The property of lightness is usually not associated with metals, yet here is a metal which is less dense than water Sodium melts at 97° and boils at 880°

Chemically, sodium is one of the most active metals; it reacts vigorously with water, displacing hydrogen:

$$2\,Na + 2\,HOH \rightarrow 2\,Na^{+} + 2\,OH^{-} + H_2$$

The metal combines readily with oxygen and if heated will burn in the air. With the halogens and other nonmetals, it combines readily to form salts. The metal amalgamates quickly with mercury to form a liquid alloy which is useful as a reducing agent since the action is less vigorous than with pure sodium Sodium imparts a characteristic yellow coloration to a flame, a property which serves as a delicate test for the presence of sodium or its compounds

Uses Most of the sodium prepared commercially is used in the preparation of certain salts which are more easily prepared from the free metal than from its compounds. Sodium peroxide is prepared by passing oxygen over aluminum trays containing metallic sodium Tetraethyl lead is made from a lead-sodium alloy as starting material. Sodium is an effective reducing agent in the synthesis of certain organic compounds. Recently, sodium metal has been used as a heat transfer agent in power applications of nuclear reactors. Liquid sodium is used as a coolant for the nuclear reactor; the heat which is removed is later used to run a steam generator. Liquid sodium is used instead of water for this purpose since it does not become dangerously radioactive in the process as does water

COMPOUNDS OF SODIUM

Sodium chloride Sodium chloride is one of the most abundant minerals of the earth. The compound is widely distributed and vast deposits have been found in many localities. These large deposits have

probably been formed as a result of evaporation of inland bodies of water in desert or arid regions. The high salt content of the Great Salt Lake in Utah was noted earlier (Chapter 16). One of the largest deposits in the United States is a layer several hundred feet deep and covering an area of many thousand square miles in Kansas, Oklahoma, and Texas. These deposits lie below the surface and the salt is obtained by pumping water into the salt bed where a saturated solution of the salt is formed. This saturated solution then is pumped to the surface and evaporated.

Sodium chloride may be recovered from sea water by evaporation, though this method is not practicable except in certain localities because of the cost involved in evaporating the relatively dilute solution. Of course, the plan is feasible if the solution can be evaporated by the sun's rays. Solar evaporation of sea water is practical in certain areas where the evaporation exceeds the total rainfall. Sodium chloride obtained by this method is usually impure and contains other salts in small percentages. The impurities in general are more soluble than sodium chloride and remain in the mother liquor during the crystallization of the common salt. One of the most troublesome impurities in salt is magnesium chloride, which is hygroscopic and causes the salt to cake in a moist atmosphere. Such caking of salt can be alleviated somewhat by the addition of starch, which coats the salt particles and prevents them from sticking together.

Sodium chloride serves as the source for its constituent elements, sodium and chlorine, and is the starting material in the preparation of most of the compounds of sodium. It is believed to be an essential constituent of animal food, and its use as a seasoning agent dates back to ancient times. It has been estimated that the human body requires about 29 pounds of salt per year in a direct or indirect form. "Salt torture" in which the victim was given plenty of food but deprived of salt was one of the ancient methods of torture. Sodium chloride plays an important role in the proper functioning of the human body, since it is a source material from which the body prepares hydrochloric acid in the gastric juices of the stomach for the digestion of food. It is also present in the blood and in case of severe shock and loss of blood a physiological salt solution (0.8 per cent aqueous solution of sodium chloride) may be introduced into the blood stream.

Sodium carbonate As an industrial chemical, sodium carbonate is second only to sulfuric acid in importance and use. Some naturally occurring sodium carbonate is found with other salts in certain desert regions. The oldest known deposits are in Egypt. Near Death Valley in California, deposits of *trona,* $Na_2CO_3 \cdot NaHCO_3 \cdot 2\,H_2O$, have been found

associated with borax and other salts. While some sodium carbonate is obtained from natural sources, by far the greater portion is manufactured from sodium chloride as a starting material. The commercial product is known as "soda" or "soda ash." Two methods are now used for the production of soda on a commercial scale (1) Solvay process, (2) electrolytic process.

Solvay process. This process was developed about 1860 by Ernest Solvay, a Belgian manufacturer, and since that time has provided most of the world's supply of soda. The process takes place in several distinct steps as follows

1. Limestone is heated to furnish carbon dioxide and lime·

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$

2 Carbon dioxide and ammonia gases are bubbled into a saturated solution of sodium chloride, resulting in the formation of ammonium bicarbonate·

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$$

3 Ammonium bicarbonate reacts with the salt in solution to form sodium bicarbonate.

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 \downarrow + NH_4Cl$$

The reaction proceeds to the right since sodium bicarbonate is sparingly soluble at 15° C., the temperature used, and precipitates in a finely divided form

4 Sodium bicarbonate is heated to convert it to sodium carbonate

$$2\,NaHCO_3 \xrightarrow{heat} Na_2CO_3 + CO_2 \uparrow + H_2O$$

5 Ammonia is recovered from the ammonium chloride by treatment with lime, CaO, from step 1:

$$2\,NH_4Cl + CaO \rightarrow CaCl_2 + 2\,NH_3 \uparrow + H_2O$$

A careful study of the reactions involved in this process proves the economic feasibility of the method The raw materials are limestone and salt, both very cheap materials. While ammonia is used in the process and is relatively costly, nearly all of the ammonia is recovered from the operation The limestone functions not only as a source for carbon dioxide but provides the base for the liberation and recovery of ammonia in step 5. One disadvantage of the process is the production of calcium chloride, a compound for which there is little demand.

Electrolytic process This process is becoming increasingly popular in this country as the result of development of large quantities of hydro-

electric power. It will be recalled that the electrolysis of an aqueous solution of sodium chloride produces chlorine at the anode and hydrogen gas at the cathode. Sodium hydroxide is left in solution. Treatment of this solution with CO_2 results in the formation of sodium carbonate or sodium bicarbonate depending on the amount of carbon dioxide added:

$$2\,NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$
$$NaOH + CO_2 \rightarrow NaHCO_3 \text{ (excess } CO_2\text{)}$$

Uses of sodium carbonate As a result of the hydrolysis of *sodium carbonate*, hydroxyl ions are formed; consequently sodium carbonate exhibits a distinctly basic reaction in aqueous solution.

$$2\,Na^+ + CO_3^{--} + H_2O \rightleftharpoons 2\,Na^+ + OH^- + HCO_3^-$$

The salt neutralizes strong acids, liberating carbon dioxide. When crystallized from aqueous solution, the decahydrate is obtained, $Na_2CO_3 \cdot 10\,H_2O$. This compound is commonly known as *washing soda*. It is an efflorescent salt decomposing slowly into the monohydrate, $Na_2CO_3 \cdot H_2O$.

The estimated consumption of soda ash in the United States in a recent year by industries, in short tons, is shown in Table 29–1.

TABLE 29–1 Estimated U. S. Consumption of Soda Ash

CONSUMING INDUSTRY	SHORT TONS	PER CENT OF TOTAL
Glass	1,490,000	28.6
Soap	88,000	1.6
Caustic and bicarbonate	704,000	13.5
Other chemicals	1,281,000	24.6
Cleansers and modified sodas	154,000	3.0
Pulp and paper	312,000	6.0
Water softeners	117,000	2.2
Petroleum refining	33,000	0.6
Textiles	31,000	0.6
Nonferrous metallurgy	487,000	9.4
Exports	164,000	3.1
Miscellaneous	352,000	6.8
Total	5,213,000	100.0

Sodium bicarbonate Sodium bicarbonate, or *baking soda* as it is commonly called, is produced as an intermediate substance in the Solvay process or may be produced in the electrolytic soda process by treating sodium hydroxide with an excess of carbon dioxide (see above). Its reaction with acids is similar to that of soda, liberating carbon dioxide and forming a sodium salt of the acid added. An aqueous solution is mildly

alkaline, as the bicarbonate ion reacts with water (hydrolysis) to form weak carbonic acid and hydroxyl ions:

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

Baking soda, as the name implies, is often used in cooking. Its function is to furnish carbon dioxide, which acts as a leavening agent. A weak acid such as lemon juice, vinegar, or sour milk, added to sodium bicarbonate, liberates carbon dioxide.

Baking powders Baking powders are mixtures of three essential ingredients:

1. Sodium bicarbonate, which furnishes carbon dioxide.
2. Some substance which will furnish hydrogen ions to react with the sodium bicarbonate and liberate carbon dioxide when water is added to the baking powder.

$$HCO_3^- + H^+ \rightarrow CO_2 \uparrow + H_2O$$

3. A substance such as starch to prevent intimate contact and reaction between ingredients 1 and 2.

All baking powders are alike in ingredients 1 and 3 but the second ingredient is variable. *Cream of tartar*, $KHC_4H_4O_6$, an acid salt, is a constituent of certain baking powders. In water solution this reaction takes place:

$$NaHCO_3 + KHC_4H_4O_6 \rightarrow NaKC_4H_4O_6 + H_2O + CO_2 \uparrow$$

Phosphate baking powders contain primary calcium acid phosphate which acts on sodium bicarbonate:

$$2\ NaHCO_3 + Ca(H_2PO_4)_2 \rightarrow CaHPO_4 + Na_2HPO_4 + 2\ CO_2 \uparrow + 2\ H_2O$$

Alum baking powders contain potash alum. Because of the hydrolysis of aluminum sulfate contained in the alum, hydrogen ions are produced which react with the bicarbonate to liberate carbon dioxide. Certain baking powders may contain mixtures of alum and calcium acid phosphate.

Sodium hydroxide Sodium hydroxide, commonly called *caustic soda* or *lye,* is a compound of major importance in industry. Its strongly basic properties are familiar. Two methods of manufacture are employed at the present time:

1. The electrolytic method is the more modern method and has already been discussed (page 201).
2. The older method consists in treating a suspension of slaked lime with sodium carbonate:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2\ NaOH$$

Calcium carbonate precipitates and may be filtered off; the filtrate is evaporated to dryness to remove water. The solid sodium hydroxide is easily melted and is cast into sticks, in which form it is usually marketed. Major uses include the manufacture of artificial silk, soap, and other chemicals.

Other salts of sodium Other important compounds of sodium with their sources and uses are shown in Table 29-2.

TABLE 29-2 Compounds of Sodium

COMPOUND	SOURCE	USE
$NaNO_3$ (Chile saltpeter)	Natural deposits in Chile	Preparation of HNO_3 and KNO_3
NaCN	Synthetically produced from soda, C, and N_2	Extraction of gold and silver from ores; electroplating
$Na_2B_4O_7$	Occurs native	Washing powder and water softener
$Na_2S_2O_3$ (thiosulfate, "hypo")	Made from Na_2SO_3	Photography (fixing agent)
Na_2O_2	$Na + O_2$	Oxidizing agent
Na_2SO_4	By-product in HCl manufacture	Preparation of Na_2S for paper and glass industries

POTASSIUM

History and occurrence Potassium is only slightly less abundant than sodium; its percentage in the earth's crust is 2.4. Although the element itself was not isolated until 1807, many of its compounds have been known and used for a very long time. The cleansing properties of extracts from the ashes of wood and plant matter and their value as a fertilizer have been known since early times. Compounds of potassium are widely distributed in rocks; two of the more important ones are *orthoclase*, $KAlSi_3O_8$, and *leucite*, $KAlSi_2O_6$. Gradual ground water leaching of these silicates and similar compounds results in soluble potassium salts in the soil. Potassium appears to be necessary for the growth of plants, and soils which have been depleted in this element must be furnished with artificial fertilizer in the form of potassium salts. In soils containing both sodium and potassium salts, the potassium salts are selectively absorbed by the plant, leaving the sodium salts to be leached out and carried away in ground waters. Consequently potassium compounds concentrate in land plants, while sodium compounds find their way to the sea and are utilized by sea plants. When wood or plant material is burned, the potassium salts of the organic acids present in the plant fiber are converted to potassium carbonate, or *potash*. Thus the extraction of wood ashes was the first important source of potash.

Occurrence *Sylvite*, KCl, and *carnallite*, $KCl \cdot MgCl_2 \cdot 6\ H_2O$, are the most important potassium bearing salts. Germany, France and the United States are the leading producers of potassium compounds. Salt deposits have been found at Searles Lake in California which contain considerable quantities of potassium salts. Some potassium compounds are recovered as by-products from the fermentation of molasses, from cement kilns, and from blast furnaces, and some potassium has been successfully recovered from *greensand* and *alunite*, complex minerals.

Preparation of metallic potassium Potassium may be obtained by the electrolysis of either the fused hydroxide or the fused chloride. The preparation is similar to that of sodium. There is little demand for the metal, since sodium, which is produced much more cheaply, will usually serve the same purpose. Potassium is very similar to sodium in properties, and what has been said about sodium will in general apply to potassium. Like sodium, potassium is soft and may be cut with a knife or molded into shape. A freshly cut surface is bluish, but contact with the air tarnishes it rapidly. Potassium is above sodium in the activity series and is the most active of the common metals. Water is decomposed violently with the evolution of hydrogen; sufficient heat is produced to ignite the hydrogen gas. Potassium and its compounds impart a violet color to a flame.

COMPOUNDS OF POTASSIUM

Potassium halides Potassium chloride is used for fertilizers and is also the starting material in the preparation of most of the compounds of potassium. Potassium chloride, *sylvite*, is obtained from the natural salt deposits or may be obtained from carnallite, $MgCl_2 \cdot KCl \cdot 6\ H_2O$.

Potassium bromide and potassium iodide are prepared by treating potassium hydroxide with free halogen; with iodine the reaction is

$$6\ KOH + 3\ I_2 \rightarrow KIO_3 + 5\ KI + 3\ H_2O$$

The mixture of iodate and iodide is heated with carbon, which reduces the iodate to iodide. The salt is purified by recrystallization. Both potassium bromide and iodide find use in photography and as medicinals.

Potassium hydroxide Potassium hydroxide may be obtained by the electrolysis of an aqueous solution of potassium chloride (similar to the preparation of sodium hydroxide) or by the treatment of slaked lime with potassium carbonate. The solid is prepared by evaporating the solution to dryness, after which the solid is melted and cast into sticks. In contrast to sticks of sodium hydroxide, which are practically anhy-

drous, the sticks of potassium hydroxide may contain a quantity of water. Potassium hydroxide is very hygroscopic and may be used as a drying agent. Its chemical properties are very much like those of sodium hydroxide. There is relatively little demand for potassium hydroxide, since the cheaper product, sodium hydroxide, will serve as well for most purposes. Its principal use is in the preparation of soft soaps.

Potassium nitrate Potassium nitrate, or *saltpeter,* is first referred to in literature in connection with the preparation of gunpowder. It was used in medieval times, as references to its use in gunpowder are numerous after the twelfth or thirteenth century. Deposits of the salt have been found in dry and arid countries of the East, particularly in the neighborhood of villages where organic matter and refuse had been allowed to accumulate. The action of bacteria on this organic matter resulted in the formation of the salt. KNO_3 is usually prepared from *Chile saltpeter,* $NaNO_3$, and potassium chloride:

$$NaNO_3 + KCl \rightarrow NaCl + KNO_3$$

The preparation is based upon the fact that the solubilities of the three salts, KCl, KNO_3, and $NaNO_3$, increase rapidly as the temperature is raised, while the solubility of sodium chloride is only slightly greater in hot water than in cold water. Thus, if sodium nitrate and potassium chloride are brought into contact in a relatively small amount of hot water, they will dissolve. Double decomposition takes place, since the sodium chloride which is formed crystallizes from solution. The precipitated sodium chloride is filtered from the hot solution and the solution cooled. Very little more sodium chloride crystallizes from solution as cooling proceeds (since the solubility of the salt changes only slightly); however, crystallization of nitrate takes place because it is much less soluble in the cold solution. Thus a product is obtained which contains a small amount of sodium chloride. Recrystallization of this product results in potassium nitrate of a high degree of purity. Reference to the solubility curves (page 187) will clarify this procedure.

Until the beginning of the twentieth century large amounts of saltpeter were used in the preparation of black gunpowder. This powder was prepared by mixing powdered saltpeter, carbon, and sulfur intimately. When ignited, sulfur and carbon are very rapidly oxidized by the potassium nitrate, producing several gaseous products. The rapid change in volume (because of the expansion of these gases with heat) results in an explosion. In recent years, black gunpowder has been replaced largely by smokeless powders prepared from organic nitrogen compounds. Some black powder is still employed as a blasting agent in soft rock mining operations.

Potassium nitrate is a particularly effective fertilizer because it contains both potassium and nitrogen. Potassium nitrate is also used in preserving meats.

Potassium tartrates As noted on page 378, potassium acid tartrate, $KHC_4H_4O_6$, commonly called *cream of tartar*, is used in some baking powders. The main source of cream of tartar is the crystalline crusts deposited by grape juice during fermentation. This salt of potassium is sparingly soluble. Potassium antimonyl tartrate, $KSbOC_4H_4O_6$, called *tartar emetic*, is used medicinally.

OTHER ALKALI METALS

Lithium Lithium is a relatively rare element, although its compounds are rather widely distributed. It is found in certain mineral waters and some soils. Chief naturally occurring compounds are *lepidolite*, a complex silicate, and *amblygonite*, $LiAlFPO_4$. Certain plants such as tobacco and sugar beets seem to absorb lithium compounds from soil as the element is found in the ashes of these plants.

Chemically, the element is very similar to sodium and may be prepared by electrolysis of the fused chloride. It is the lightest metal known, with a specific gravity of about 0.5. The metal has about the same oxidation potential as cesium and is thus one of the most active of the alkali metal family. It decomposes water vigorously to form hydrogen. In certain respects lithium resembles magnesium in the alkaline earth family. Lithium hydroxide, LiOH, lithium phosphate, Li_3PO_4, and lithium carbonate, Li_2CO_3, in contrast to corresponding compounds of the other alkali metals, are relatively insoluble, similar to corresponding compounds of magnesium. Lithium compounds yield a crimson color when heated in a flame. Lithium compounds are used in the preparation of special glasses and in fireworks. Lithium hydride is important in considerations of nuclear energy; see the discussion of the hydrogen bomb on pages 422 and 423.

Rubidium and cesium Small amounts of these elements are found in certain mineral waters, and in ashes from tobacco, tea, and coffee. Both elements were discovered by Bunsen; cesium in 1860 and rubidium in 1861; the names of the elements refer to the color of the Bunsen flame when their salts are heated therein. Rubidium produces a dark red color and cesium a blue color. Both elements are very much like sodium and potassium but are more active. Cesium oxidizes in air with almost explosive violence, and it also reacts vigorously with water. Small amounts of cesium are used in the manufacture of radio tubes and photoelectric cells.

EXERCISES

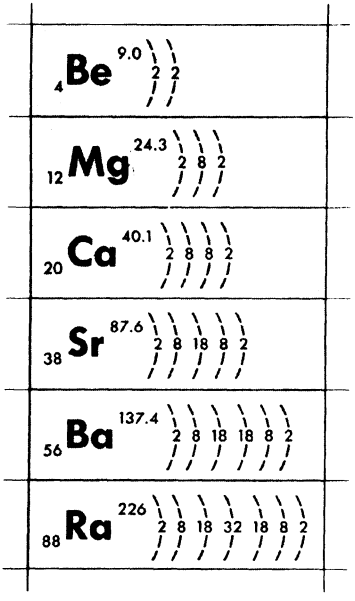
1 Summarize the general properties of the alkali metals. Point out differences between members of the alkali group.
2 List various products which chemical industry manufactures from NaCl as a raw material.
3 By equations show how you might prepare a sample of K_2CO_3, starting with KCl; $NaNO_3$, starting with NaCl.
4 From a consideration of properties of the alkali metals, predict the properties of element No. 87.
5 10.6 g. of Na_2CO_3 is dissolved in water and the solution diluted to 1 liter. What is the normality of the solution? 25 ml. of this solution required 20 ml. of H_2SO_4 solution for complete neutralization. Calculate the normality of the sulfuric acid solution. Ans. 0.2; 0.25.
6 Suggest a method of recovering pure NaCl from sea water.
7 A bath salt is a mixture of NaCl and $Na_2CO_3 \cdot 10\ H_2O$. A one gram sample is dissolved in water and neutralized with 12.5 ml. of 0.4 *N* HCl. What is the weight of Na_2CO_3 in the sample? Assume the HCl reacts with all of the Na_2CO_3 in the sample.
8 Calculate the volume of CO_2 measured at standard conditions which would be obtained by heating 0.5 mole $NaHCO_3$. Ans. 5.6 l.
9 A cleaner is known to be a mixture of NaOH and SiO_2. A 1 g. sample of the cleaner required 50 cc. of 0.3 *N* H_2SO_4 to neutralize it. What weight of NaOH is in the gram sample, and thus what percentage of NaOH?
10 One gram of a mixture of NaCl and LiCl is analyzed for chloride by precipitation of AgCl. 2.728 g. of AgCl is obtained. Calculate the percentage of LiCl in the original mixture of chlorides. Ans. 30%.

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thirty

THE ALKALINE EARTH FAMILY

METALS	SYMBOL	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Beryllium	Be	1.84	1280	1500	+2
Magnesium	Mg	1.70	651	1110	+2
Calcium	Ca	1.55	810	1240	+2
Strontium	Sr	2.54	800	1150	+2
Barium	Ba	3.75	850	1140	+2
Radium	Ra	5.00	960	1140	+2

The term "earth" was originally applied to those substances which are relatively insoluble in water and which do not undergo change when heated. Typical "earths" were alumina (aluminum oxide) and ferric oxide. A few other "earths" were slightly soluble in water and

gave an alkaline solution; accordingly, they were called the alkaline earths. Inasmuch as they resisted all efforts of the early chemists to decompose them they were thought to be elements. We now know the "alkaline earths" to be oxides of the metals listed in the above table. Because of certain unusual properties of radium, this element is considered separately in Chapter 31.

The metals of this group are quite active; their activity increases with increasing atomic weight. The only oxidation state exhibited by members of the group is +2, indicating two electrons in the outermost orbit of their atoms. In general, compounds of these elements are more important from a practical standpoint than the free metals; magnesium, however, is extremely important in the metallic state.

Beryllium, the first member of the group, resembles aluminum in some respects. Although its valence is two, the hydroxide of beryllium is amphoteric like aluminum hydroxide.

CALCIUM

History and occurrence Compounds of calcium were known and used for a long time before the element itself was isolated. Davy first prepared it in 1808 by electrolysis.

Calcium is the fifth most abundant of the chemical elements and the third most abundant metal; the earth's crust contains 3.4 per cent. The metal is too active to exist in the free state, but its compounds are numerous and widely distributed. Of these, calcium carbonate, $CaCO_3$, is the most abundant. Many forms of the carbonate are known: *limestone, chalk, pearl, calcite, coral, marble,* and others. Other important naturally occurring compounds are *gypsum,* $CaSO_4 \cdot 2\ H_2O$; *anhydrite,* $CaSO_4$; *dolomite,* $CaCO_3 \cdot MgCO_3$; *fluorite,* CaF_2; *apatite,* $(CaF)Ca_4(PO_4)_3$ or $(CaCl)Ca_4(PO_4)_3$; and *phosphorite* or *phosphate rock,* $Ca_3(PO_4)_2$. Sea water contains some calcium salts, usually the sulfate, chloride, or bicarbonate, and these salts are the source of calcium utilized by marine animals in building up their shells, which are mainly calcium carbonate. A certain amount of calcium is required for human and animal nutrition, as bones and teeth are composed largely of calcium phosphate. Rich food sources of calcium are milk, leafy and root vegetables, egg yolk, potatoes, and peas.

Preparation, Properties, and Uses Calcium metal is prepared by the electrolysis of fused calcium chloride. The metal is silver white, harder than lead, with a density of 1.55. It is malleable and ductile, for it may be hammered into plates or drawn into wire. The metal is stable in

dry air but oxidizes in moist air. Calcium is one of the more active metals and will react with cold water slowly:

$$Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2$$

At high temperatures, the metal burns vigorously in the air to form both calcium oxide and calcium nitride, Ca_3N_2. The metal reacts rapidly with dilute mineral acids to produce hydrogen.

Calcium is not extensively used industrially because of the difficulty and cost of producing it. The metal is an active reducing agent and may be employed in the reduction of certain metallic oxides, such as those of chromium and tungsten. An alloy with lead containing about 0.1 per cent calcium is used in the manufacture of storage battery plates and as a bearing metal. Calcium may also be used to remove traces of nitrogen and oxygen in producing high vacua.

COMPOUNDS OF CALCIUM

Calcium carbonate Calcium carbonate is by far the most abundant and most widely used compound of calcium. Two crystalline forms are known: (1) *aragonite,* which crystallizes in the rhombic system, and (2) *calcite,* or *Iceland spar,* which forms rhombohedral crystals. *Limestone* is a more or less impure form of the carbonate, usually containing iron and magnesium carbonates and other impurities. *Marble* consists of a compact and coherent mass of small crystals of nearly pure calcium carbonate. *Dolomite* is a natural-occurring compound of equal molecular proportions of calcium and magnesium carbonates, $CaCO_3 \cdot MgCO_3$. Marine shells, pearls, and coral, as well as eggshells, are composed largely of calcium carbonate. *Stalactites,* which form on the roofs of certain caves, and *stalagmites,* which form on the floors beneath, are composed of calcium carbonate. Calcium carbonate is soluble in water containing carbon dioxide to form calcium bicarbonate. The pressure is reduced when the bicarbonate solutions enter the caves, carbon dioxide escapes, and calcium carbonate is precipitated and deposited.

Calcium carbonate finds extensive application in many industrial processes. Certain forms of limestone and marble are used as building materials. Limestone in large quantities is used in the production of cement (page 389) and soda ash (page 376). It serves as a basic flux in the smelting of certain metals, notably iron (page 365).

Calcium oxide When limestone is heated (technically called *burning*), carbon dioxide and calcium oxide (*lime* or *quicklime*) are formed:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

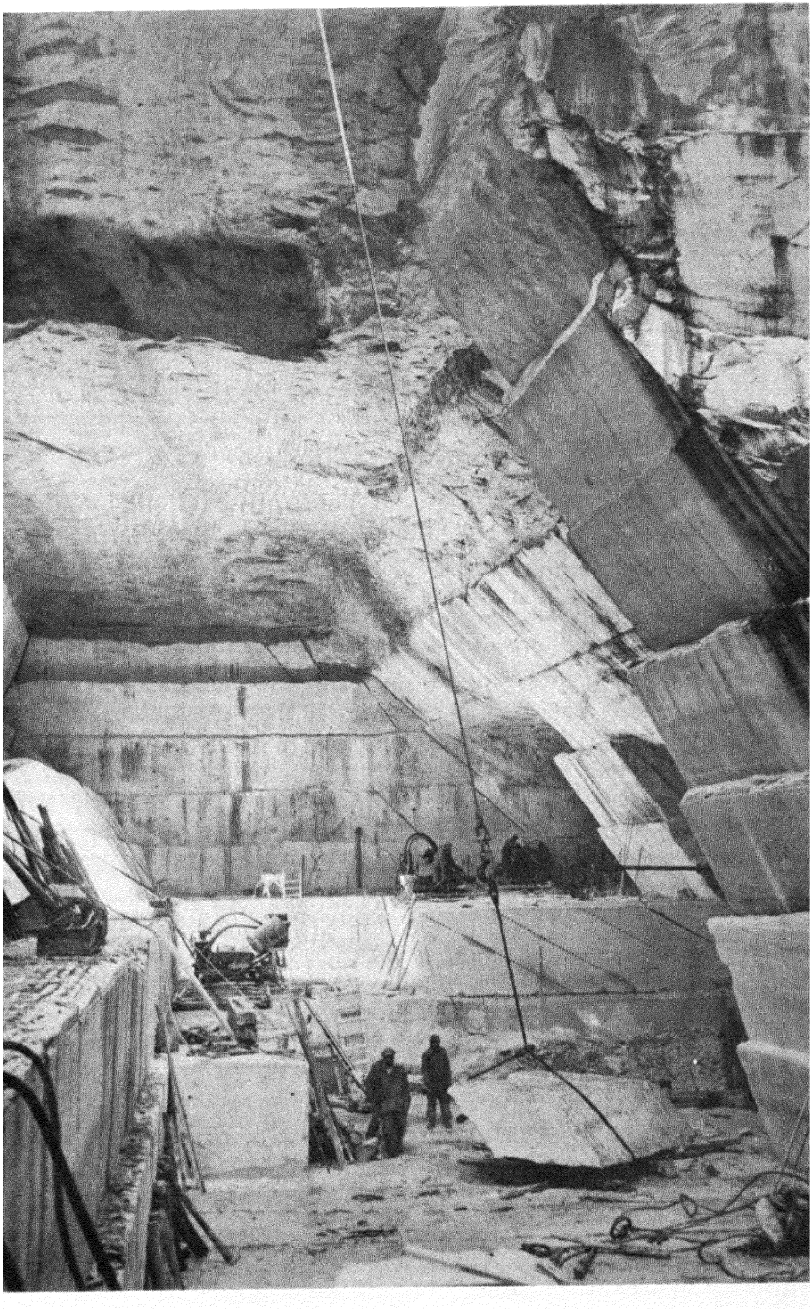


Figure 30–1 A marble quarry.

This reaction is an equilibrium system and proceeds to the right only as the carbon dioxide is removed. The heating is usually carried out in large furnaces or *kilns* at about 900°.

The product, if pure, is white in color and extremely porous. It is very stable toward heat (melting point 2572°). Its principal use is in the manufacture of slaked lime (see below), and it is also used in the preparation of bleaching powder and as a base in the neutralization of acid soils.

Calcium hydroxide When calcium oxide is added to water, a vigorout reaction ensues with liberation of considerable heat—enough to convert part of the water to steam. The white product is calcium hydroxide (*slaked lime*):

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

Calcium hydroxide, the cheapest of bases, is only slightly soluble in water. Because of its basic characteristics, it absorbs carbon dioxide from the atmosphere and is converted into calcium carbonate. After exposure to the atmosphere for some time it contains considerable calcium carbonate.

Although not very soluble in water, an aqueous solution of the hydroxide (lime water) may be used to test for carbon dioxide gas. If carbon dioxide gas is passed into lime water, the latter becomes turbid from precipitation of calcium carbonate:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

If excess carbon dioxide is added, the precipitate dissolves to form calcium bicarbonate, which is soluble:

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

Slaked lime has many uses, chiefly the preparation of mortar and plaster. *Mortar* consists of a mixture of sand and slaked lime with enough water to form a paste. As mortar sets, some water evaporates, and the $Ca(OH)_2 \cdot xH_2O$ solidifies to a firm gel which includes sand particles. After years of time, the outer one-eighth inch or so of mortar is converted to a calcium carbonate-sand mixture as CO_2 from the air is slowly absorbed. Plaster is identical with mortar except that hair may be added to help hold the mass together. Plaster of Paris, the formula for which is $CaSO_4 \cdot \frac{1}{2} H_2O$, may be added to give a smoother plaster in the finishing coat.

Other uses of slaked lime are for milk of lime, which is a suspension of calcium hydroxide in water; preparation of bleaching powder; and whitewash.

Cement Over a century ago, Joseph Aspdin found that if he applied high heat to some rock occurring naturally near his home in Portland, England, and pulverized the product, he had a powder that, with water, would set to a strong mass. The rock became known as Portland stone and eventually as "Portland cement." Portland cement is now prepared from a mixture of limestone and clay. In some cases, natural rock formations contain these ingredients in suitable proportions and may be used directly for cement manufacture. The mixture, after being ground to a fine powder, is heated in rotary kilns until the mass just begins to fuse. During the heating, CO_2 is lost from the limestone which then combines with silica and alumina from the clay to form calcium silicates and calcium aluminate:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O + 3\,CaO \rightarrow Ca(AlO_2)_2 + 2\,CaSiO_3 + 2\,H_2O$$

The resulting mass, known as "clinker," is ground finely, and a small amount of gypsum is added to retard the rate of setting. When a paste of cement and water is allowed to stand, the material sets to a hard, durable, rocklike mass. This process occurs even if the material is under water, because of insolubility of the constituents. Mechanism of the setting process is somewhat obscure, but it is known that hydration of the constituents takes place so that the mass is securely bound together by interlacing crystals of hydrates formed.

Cement is never used alone but is mixed with sand and gravel; the resulting set mixture is called *concrete.* Concrete that is to be subject to considerable strain may be reinforced with steel rods or wire netting.

Other calcium compounds Another natural calcium compound is *gypsum,* $CaSO_4 \cdot 2\,H_2O$, formed from evaporation of sea water or ground waters containing calcium and sulfate ions. Since calcium sulfate is relatively insoluble, the salt is one of the first to crystallize from solution. In some instances the anhydrous salt, $CaSO_4$, may deposit; it is known as "anhydrite."

When gypsum is heated carefully below 125°, it loses three-fourths of its water of hydration and forms the hemihydrate of calcium sulfate, often written $CaSO_4 \cdot \frac{1}{2}\,H_2O$, and commonly known as plaster of Paris:

$$2\,CaSO_4 \cdot 2\,H_2O \rightarrow (CaSO_4)_2 \cdot H_2O + 3\,H_2O$$

When the hemihydrate is mixed with water to form a paste, this reaction is reversed and, on setting, a hard mass of interlacing crystals of gypsum is formed. It is used in making plaster casts for holding broken bones and in making statuary casts. If the gypsum is heated too strongly, the anhydrous salt, which hydrates only slowly, is formed. The anhydrous salt is useless as plaster because of this property.

Gypsum is used as fireproofing for building materials, as a soil fertilizer, and for many other purposes. About two per cent gypsum is added to Portland cement to retard and regulate the setting process.

In an important process of manufacturing pulp from wood, a water solution of calcium acid sulfite, $Ca(HSO_3)_2$, is used. Wood chips are largely composed of cellulose, lignin, and resins, and $Ca(HSO_3)_2$ solution dissolves lignin and resin from the cellulose pulp. The solution of lignin and resins issuing from pulp mills is called "waste sulfite liquor." The calcium bisulfite solution is made as follows:

$$S + O_2 \rightarrow SO_2$$
$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + CO_2 + H_2O$$
$$CaSO_3 + H_2SO_3 \rightarrow Ca(HSO_3)_2$$

In some mills $Mg(HSO_3)_2$ or NH_4HSO_3 is used instead of $Ca(HSO_3)_2$.

Other important compounds of calcium are given in Table 30–1.

TABLE 30–1 Other Compounds of Calcium

SALT	FORMULA	SOURCE	USES
Calcium chloride	$CaCl_2$	By-product of Solvay soda process	Drying agent; lay dust on roads
Calcium cyanamide	$CaNCN$	Calcium carbide + nitrogen	Prep. of ammonia; fertilizer
Bleaching powder	$CaOCl_2$	Lime and chlorine	Bleaching
Calcium carbide	CaC_2	Lime and carbon	Source of acetylene
Calcium phosphate	$Ca_3(PO_4)_2$	Occurs as phosphate rock	Making fertilizer
Superphosphate	$Ca(H_2PO_4)_2 + 2\ CaSO_4$	Rock phosphate + H_2SO_4	Fertilizer
Calcium silicate	$CaSiO_3$	Limestone, sand	In glass along with Na_2SiO_3

Hard waters Most natural waters with the exception of rain water contain dissolved mineral matter. This mineral matter is derived from the rocks and soil and contains calcium, magnesium, or iron salts as chlorides, sulfates, or bicarbonates. Waters containing any of these salts are objectionable for certain household and industrial uses and are termed *hard waters*. If soap is added to hard water, a precipitate forms before a lather can be obtained. This residue may stain the cloth with which it comes in contact, and of course the soap is wasted. Soap is a sodium or potassium salt of complex organic acids—stearic, palmitic, or oleic acids. We may represent the formula for soap as NaSt, in which

St stands for the stearate acid radical. If calcium ions are present in water, the reaction with soap is as follows:

$$Ca^{++} + 2\ NaSt \rightarrow Ca(St)_2 \downarrow + 2\ Na^+$$

Temporary water hardness Waters containing bicarbonates of calcium, magnesium, or iron are said to possess *temporary hardness,* since the hardness may be removed simply by boiling the water. Thus, when calcium bicarbonate is heated, the following reaction takes place:

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

Calcium carbonate precipitates and since the calcium ions are removed, the water will no longer act with soap. Such a water from which the ions responsible for the precipitation of soap are removed is termed *soft* water. Decomposition of bicarbonates is the cause of scale in tea kettles in which considerable water has been boiled. Water containing bicarbonates is also objectionable for industrial uses, as it will form boiler-scale deposits (carbonates of calcium or magnesium) on the inside of boiler pipes. Since the scale is a poor conductor of heat, boiler efficiency is reduced.

Temporary hardness may be removed by adding the proper amount of slaked lime, $Ca(OH)_2$, or household ammonia, NH_4OH:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 \downarrow + 2\ H_2O$$
$$Ca(HCO_3)_2 + 2\ NH_4OH \rightarrow CaCO_3 \downarrow + (NH_4)_2CO_3 + 2\ H_2O$$

Permanent hardness Permanent hardness in water results from chlorides or sulfates of metals such as calcium or magnesium. Boiling does not remove these salts; a substance called a *water softener* must be added to the water to form a precipitate with these salts. Common water softeners are soda, Na_2CO_3, and borax, $Na_2B_4O_7$. Either of these will precipitate calcium or magnesium carbonate or borate from solution as an insoluble substance. Typical reactions of these water softeners are as follows:

$$Ca^{++} + CO_3^{--} \rightarrow CaCO_3 \downarrow$$
$$Mg^{++} + B_4O_7^{--} \rightarrow MgB_4O_7 \downarrow$$

In some cases, both soda and slaked lime are used to soften water, the slaked lime to remove temporary hardness and the soda to remove permanent hardness.

Zeolites Another method of softening water utilizes *zeolites,* minerals that contain sodium aluminum silicate. If water is allowed to filter through this coarse-grained material, sodium ions are displaced by calcium and magnesium ions (this is called *ion exchange*):

$$Na_2Zeolite + Ca^{++} \rightarrow Ca\ Zeolite + 2\ Na^+$$

Sodium ions left in solution are not objectionable, since they do not make the water hard. In this process, the sodium zeolite may be regenerated with a concentrated sodium chloride solution. By mass action, the above reaction is reversed and the original zeolite re-formed:

$$\text{Ca Zeolite} + 2\ \text{NaCl} \rightarrow \text{CaCl}_2 + \text{Na}_2\text{Zeolite}$$

An artificial zeolite called Permutit is also effective as a water softener. Figure 30–2 shows the arrangement of a typical system using Permutit.

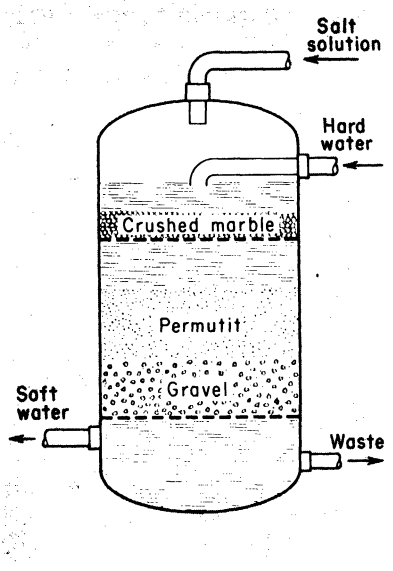


Figure 30–2 Permutit water softener.

STRONTIUM AND BARIUM

Little discussion of strontium and barium is necessary, since they resemble calcium very closely in both chemical and physical properties. Both metals are somewhat more active than calcium; barium is the most active of the alkaline earth family except for radium. Barium oxidizes readily in moist air and reacts vigorously with water. Strontium and barium are much less abundant than calcium, and strontium is less abundant than barium. Because of their activity, they are not found in the free state. Both metals occur naturally as carbonates and sulfates; strontium as *strontianite,* $SrCO_3$, found near Strontian, Scotland, and *celestite,* $SrSO_4$; barium as *witherite,* $BaCO_3$, and *barite* or *heavy spar,* $BaSO_4$. In the United States, strontium deposits are found in Arizona, Washington, and Texas, barium deposits in Tennessee and Georgia.

Both strontium and barium metals may be prepared by electrolysis of the fused chlorides; however, there is very little demand for the metals. A limited use of barium is in the removal of the last traces of gases from vacuum tubes and as a constituent of certain bearing metals.

Strontium compounds give a deep carmine color to a flame and have some use in making "red fire" for flares, fireworks, and signal lights. For this purpose, the carbonate is usually converted to the nitrate before use.

Some strontium salts are used to facilitate crystallization of sugar from molasses residues and in removal of iron from commercial caustic soda.

Barium sulfate, the most insoluble sulfate of the group, is used as a filler for rubber goods and as an ingredient of lithopone, a paint pigment. Barium salts are prepared from the sulfate, which is first reduced with carbon to barium sulfide.

$$BaSO_4 + 4\,C \rightarrow BaS + 4\,CO$$

Barium sulfide treated with the appropriate acid forms soluble barium salts which may be crystallized from solution. Barium salts produce a light green color in the flame and, like strontium salts, are used in making flares and signal lights

MAGNESIUM

History and occurrence Like other members of the alkaline earth group, compounds of magnesium have been known and used for some time, although the metal itself was not isolated until 1808 by Davy. Magnesium sulfate was extracted from mineral water in Epsom, England, in 1695 by Grew; hence the name, *Epsom salts.*

Since magnesium is a very active metal, it is not found free in nature. Its compounds are widely distributed, however; magnesium stands eighth in abundance among the elements present in the earth's crust. Many complex silicates, some of importance commercially, are found in nature: *asbestos*, $Mg_3Ca(SiO_3)_4$; *meerschaum*, $Mg_2Si_3O_8 \cdot 2\,H_2O$; *talc*, $H_2Mg_3(SiO_3)_4$; *olivine*, Mg_2SiO_4. As a source of metallic magnesium, the more important natural compounds are *magnesite*, $MgCO_3$, large deposits of which are found in Washington and California, and *magnesium chloride*, $MgCl_2 \cdot 6H_2O$, obtained from salt brines and sea water The most abundant mineral of magnesium is *dolomite*, $CaCO_3 \cdot MgCO_3$.

Preparation Magnesium metal may be produced by electrolysis of the fused chloride obtained from salt brines by a complex series of recrystallizations. The cell for the electrolysis consists of an iron container which acts as the cathode, and carbon rods as anodes. Some other chloride (sodium or calcium chloride) is added to lower the melting point of magnesium chloride. Magnesium metal is less dense than the bath and collects on the surface of the electrolyte; a salt covering prevents its oxidation. Heat for the cell to keep the electrolyte molten is supplied from the outside

A second method used extensively in Germany for the preparation of the metal is similar in principle to the Hall electrolytic process for making aluminum. Magnesium oxide is dissolved in a molten mixture of

fluorides of magnesium, barium, and sodium; an iron cathode and carbon anode are used.

Properties and uses Magnesium is silvery white, tough, and strong, and the lightest of the rigid metals. It is malleable and ductile and may be rolled into sheets or drawn into wire. Magnesium is high in the activity series, though somewhat less active than calcium which appears just above it in the series. It reacts with hot water slowly to liberate hydrogen and reacts readily with acids (except hydrofluoric) to produce hydrogen. It is stable in dry air but corrodes slowly in moist air to form a basic carbonate. In a finely divided state or in the form of a thin ribbon, the metal burns vigorously in air to form both magnesium oxide and magnesium nitride. During combustion, a bright white light rich in short wave lengths of light is produced; thus, the metal, mixed with an oxidizing agent such as potassium chlorate, is used in photographic flash powders. It is also used in military pyrotechnics for signals, flares, and incendiaries. In large pieces, the metal does not ignite readily and may be forged and worked at high temperatures.

Alloyed with aluminum, magnesium forms a light, strong, durable metal for aircraft construction. The alloys with aluminum are easily machined and worked and are resistant to corrosion. Because of its many advantages for aircraft construction, production of magnesium has increased tremendously in the past few years. *Magnalium,* an alloy of aluminum containing 5 to 30 per cent magnesium, and *duralumin* (Mg 5 per cent, Cu 3 to 5 per cent, and Al) are the more important alloys.

COMPOUNDS OF MAGNESIUM

Magnesium chloride $MgCl_2 \cdot 6\ H_2O$, the principal direct source of magnesium metal, is obtained from salt brines in Michigan, from sea water, and from the Stassfurt salt deposits in Germany. It may also be obtained from solution of magnesium metal or of the carbonate in hydrochloric acid, and subsequent crystallization. Magnesium chloride often occurs in impure 'table salt and is responsible for its caking in moist weather. A type of cement is made by mixing magnesium oxide and a solution of magnesium chloride; the mass hardens on drying, probably because of formation of a complex addition compound.

Magnesite $MgCO_3$, in a nearly pure form, is found in large amounts in the northeastern part of the state of Washington. When the carbonate is heated, it breaks down to form the oxide and carbon dioxide. This occurs at a somewhat lower temperature than does the decomposition of limestone. MgO thus produced may be used in electrothermal production of Mg. A basic carbonate, $MgCO_3 \cdot Mg(OH)_2$, formed by the

addition of a soluble carbonate to a solution of magnesium ions, is used as a filler and as a component of certain toothpastes and polishing powders. Like $CaCO_3$, magnesium carbonate is soluble in water containing dissolved carbon dioxide, because of the soluble bicarbonate formation, $Mg(HCO_3)_2$.

Magnesium oxide A product of the heating of magnesite, magnesium oxide is slightly soluble in water to form *magnesium hydroxide* Since only a few hydroxyl ions are formed in solution, a suspension of magnesium hydroxide, known as *milk of magnesia*, is used as a mildly alkaline substance for treatment of hyperacidity and as a mild laxative. The oxide is very resistant to action of heat and thus is used as a refractory for lining furnaces

Magnesium sulfate $MgSO_4 \cdot 7\ H_2O$, or Epsom salts, is found in many springs and mineral waters It is very soluble in water and has a very bitter and unpleasant taste In medicine, it is used as a purgative. Other uses are as a fireproofing agent and in weighting cotton

Magnesium ammonium phosphate This white crystalline insoluble salt is precipitated from solutions of magnesium ion by addition of disodium phosphate and ammonium hydroxide

$$Mg^{++} + NH_4OH + Na_2HPO_4 \rightarrow MgNH_4PO_4 \downarrow + 2\ Na^+ + H_2O$$

This crystalline precipitate is actually a hexahydrate, $MgNH_4PO_4 \cdot 6\ H_2O$, and is the final identifying substance for magnesium in most qualitative analysis procedures It is the substance formed in the quantitative estimation of the magnesium content of a sample. When ignited, the compound is converted to *magnesium pyrophosphate*, $Mg_2P_2O_7$, which is weighed as such

BERYLLIUM

The element beryllium is present in many natural silicates, most important of which is *beryl*, an aluminum silicate with the composition $(BeO)_3 \cdot Al_2O_3 \cdot 6\ SiO_2$. *Emerald* is a green transparent form of beryl containing traces of chromium. Beryllium may be obtained by electrolytic methods, but this is difficult because of the high melting point (1280°). Thus, the price of beryllium has remained high (several dollars a pound). It alloys readily with aluminum to which it adds strength and resistance to corrosion, these alloys offer considerable promise in aircraft construction. Beryllium is only slightly denser than magnesium, so that if it could be prepared cheaply it might find extensive use as a light alloy for structural purposes.

EXERCISES

1 Point out similarities and differences in properties of members of the alkaline earth family. Contrast the general properties of the group with those of the alkali group.

2 Calculate the quantity of soda ash necessary to soften 1000 gallons of water (sp. gr. = 1) containing 10 mg. $Ca(HCO_3)_2$ and 15 mg. $MgSO_4$ per liter. Ans. 75 g.

3 In exercise 2 above, if $Ca(OH)_2$ is added to remove the temporary hardness and Na_2CO_3 the permanent hardness, calculate the quantities of $Ca(OH)_2$ and Na_2CO_3 required.

4 A rock is 74 per cent $SrCO_3$; the rest of the rock is not acted on by acid. What weight of 40 per cent HNO_3 is needed to act on 1 ton of the rock to convert the $SrCO_3$ to $Sr(NO_3)_2$? Ans. 3160 lb.

5 A seller of superphosphate fertilizer $Ca(H_2PO_4)_2 + 2\ CaSO_4$ was suspected of diluting his product with fine sand. Analysis of a one-gram sample of the product yielded 0.4 g. $Mg_2P_2O_7$. This weight of $Mg_2P_2O_7$ represents what per cent phosphorus in the sample? Had the dealer markedly diluted his product? Ans. No; product is more than 90 per cent superphosphate.

6 By equations, show how you would prepare:

(*a*) $Ba(NO_3)_2$ from $BaCl_2$
(*b*) $MgSO_4$ from metallic Mg
(*c*) $Ca(HCO_3)_2$ from $Ca(OH)_2$
(*d*) $MgNH_4PO_4$ from $MgCO_3$

7 How could you distinguish between the four white solids: $CaCO_3$; $BaSO_4$; $MgCl_2$; $Sr(NO_3)_2$?

8 The following are ionic radii of the paired alkali–alkaline earth metals: Na 0.95, Mg 0.65; K 1.33, Ca 0.99; Cs 1.69, Ba 1.35. What does this suggest in regard to the greater activity of the alkali metal in each pair?

9 List the raw materials used in the production of each of the following: cement, mortar, glass, superphosphate.

10 List as many industrial operations as you can which use limestone as a raw material.

11 An egg weighing 32 g. was oxidized so that all the sulfur was converted to Na_2SO_4. Addition of $BaCl_2$ precipitated 0.466 g. of $BaSO_4$. What was the percentage of sulfur in the egg?

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thirty-one

RADIOACTIVITY AND NUCLEAR CHANGES

Ancient scientists philosophized that all matter is made up of minute particles called atoms. This theory is today accepted as fact, and the number of atoms that make up a given weight of an element is known with a percentage of accuracy equal to that for the population of New York City. A constant number (Avogadro's number) of the atoms of any element gives its gram atomic weight, thus

6.02×10^{23} atoms of hydrogen weigh	1.008 g.
6.02×10^{23} atoms of copper weigh	63.57 g.
6.02×10^{23} atoms of silver weigh	107.88 g.

The reason for listing silver here is that 4 silver dollars (8 fifty-cent pieces) weigh about 108 grams and are thus composed of about 6.02×10^{23} atoms of Ag. Suppose you had 4 silver dollars, were philanthropically inclined, and had the capability of a genie to distribute these atoms of silver equally to everyone on this earth; yes, even to the estimated 45,000,000,000 people who had lived on this earth in the past 35,000 years. By dividing 6.02×10^{23} by 45,000,000,000 we obtain 13,000,000,000,000, or the number of silver atoms that would be the share of each individual, alive or dead, from the atoms in 4 silver dollars. This calculation can hardly fail to impress you as to the minute size of an atom.

Small as are the atoms, there are reasons for thinking that atoms are not the ultimate division of matter but are themselves composed of smaller particles. Among the reasons for believing atoms to be complex rather than indivisible unit particles are: (1) The discovery of cathode rays (electron beams) and of positive rays (pages 29, 31) gave

definite evidence of subatomic particles. (2) It is a fact that 43 of 90 elements have an atomic weight within 0.1 of being a whole number. Is this a random happening? If a person at the seashore picked up at random 90 pebbles of varying size and then weighed the lightest one, what chance is there that the 90 pebbles will conform to a weight sequence between 1 and 238, with 43 of the 90 pebbles having a weight within 0.1 of a multiple of the weight of the lightest one? The chance of this happening is but 1 in 131 million. It is evident, then, since 43 of 90 elements are nearly whole numbers when compared to $\frac{1}{16}$ the atomic weight of oxygen as a standard, that this is not a random relationship. This logic supported Prout's hypothesis of 1815 that all atoms were composed of hydrogen atoms. This thinking is now modified to the belief that all atoms are composed of the same units. (3) The most conclusive evidence of atomic complexity is the phenomenon of radioactivity, which will now be discussed.

Radioactivity In 1896, Henry Becquerel discovered that a photographic plate was sensitive to the presence of uranium minerals, even though the plate was wrapped in black paper which is opaque to ordinary light. This unknown radiation was similar in action to X rays, which had been discovered nearly a year earlier by Roentgen. Furthermore, uranium salts rendered the air a good conductor of electricity as was evidenced by the discharge of an electroscope. This new phenomenon, the spontaneous emission of radiation by an element, was termed *radioactivity,* and those elements responsible for the radiation were termed *radioactive elements.*

Madame Curie and her husband, Pierre, began the investigation of the new phenomenon and found that *pitchblende,* an ore of uranium, consisting largely of U_3O_8, exhibited an activity greater than could be accounted for on the basis of the uranium present. Then began a long series of tedious and painstaking experiments in the separation and analysis of this uranium mineral. After several months of work, Madame Curie announced the separation of an element more active than uranium, which she named *polonium* after her native country, Poland. The work continued, and in 1898 the Curies announced the discovery of *radium* which showed an activity a million times as great as uranium itself.

Radium is an element similar to barium; and, like $BaSO_4$, the compound $RaSO_4$ is very insoluble, even in acid solution. Use is made of this fact in concentrating radium from other metals with which it occurs. (Only about 0.2 gram of radium is contained in a ton of high grade uranium ore.) The element itself was isolated by Madame Curie in 1910 by the electrolysis of radium chloride.

During the studies with uranium minerals, Madame Curie found that all uranium minerals are radioactive, and that the activity of a sample depends upon the amount of uranium present. As a result of her studies, Madame Curie concluded that radioactivity is a specific property of the atom and is not affected by the nature of the chemical combination in which the atom exists; nor is it affected by physical conditions.

Radioactive rays By means of an electric field, Rutherford was able to identify three types of radiation from radioactive substances. A bit of radioactive substance was placed in a depression in a block of lead (Figure 31–1). All rays except those moving directly upward were absorbed by the lead. Electrodes and a photographic plate to record the emitted radiation were placed above the block of lead. This experiment shows that the radiation may be resolved into three kinds: one kind unaffected by the electrodes, the other two kinds showing opposite charges as evidenced by the bending of the rays in opposite directions. From the extent and the direction of bending, it is possible to calculate the masses and charge of the radiations. The three types of radiation were named *alpha* (α), *beta* (β), and *gamma* (γ) rays.

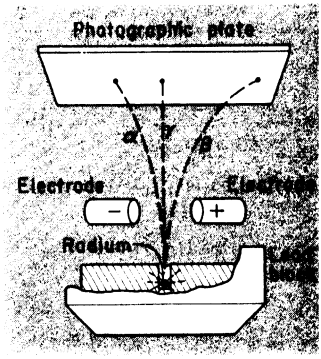


Figure 31–1 Three kinds of rays produced from the radioactive disintegration of radium.

Alpha rays, positively charged particles with a mass four times that of the hydrogen atom, have been shown by spectral studies to be nuclei of helium atoms, each particle consisting of 2 neutrons and 2 protons. These particles are expelled from radioactive substances at moderate velocities (10,000 to 12,000 miles per second) and have a low penetrating power since they may be stopped by thin sheets of paper. Air through which alpha particles pass becomes ionized due to electrons knocked out of molecules in the air on impact with these relatively heavy particles. If this ionized air is saturated with water vapor and suddenly cooled, the ionized particles in the air act as nuclei for the condensation of small droplets of water, and these particles are rendered visible as a fog. C. T. R. Wilson was able to follow the path of an alpha particle by photographing the fog tracks thus produced.

The expulsion of alpha particles from radioactive material may also be observed with the aid of a *spinthariscope,* a device consisting of a nar-

row tube which is fitted at one end with a lens and at the other end with a screen coated with zinc sulfide (Figure 31–2). If a piece of radium is placed in front of the screen and the screen is observed through the lens, flashes of light may be seen as a result of alpha particles colliding with zinc sulfide particles.

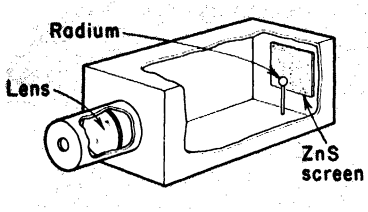


Figure 31–2 Spinthariscope.

Beta rays are negatively charged particles and are identical with electrons. They are sometimes referred to as "high speed electrons," since their speed sometimes approaches that of light (186,000 miles per second). These rays are somewhat more penetrating than alpha particles, passing through thin layers of metals.

Gamma rays are of high frequency and are identical with X rays of very short wave length. They possess relatively high penetrating power and like alpha and beta rays affect a photographic plate. They carry no charge. Gamma rays constitute the portion of radioactive emission which affected the photographic plate of Becquerel even though the plate had been wrapped in several layers of black paper.

Disintegration of atoms In 1902, Rutherford suggested that elements may spontaneously change into other elements or break down into simpler elements. The idea was revolutionary, since elements were supposed to be permanent. However, Rutherford's theory has been completely confirmed by experimental evidence, and today there is no doubt that elements may be broken down into simpler elements. When radium disintegrates, an alpha particle is expelled from the nucleus of the radium atom, leaving an atom of mass number that is four mass units less than radium. The change may be represented thus, *p* standing for proton and *n* for neutron (only the nucleus is shown):

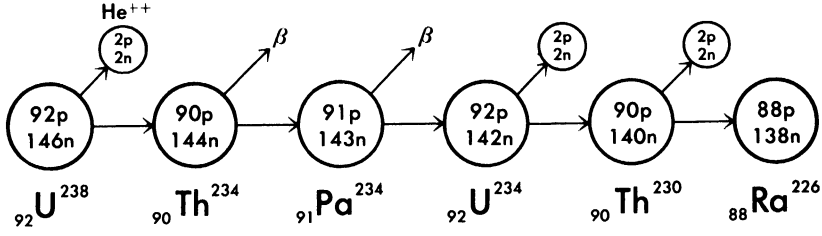


Rutherford was able to collect an inert gas from the disintegration of radium and named it niton, now called *radon*. Ramsey studied this "radium emanation," and found its atomic weight to be 222, which is what we should expect from theoretical considerations.

During the disintegration of radioactive substances, not all three types

of rays are emitted at the same time. A pure sample of uranium emits only α rays at first, but after a time β rays are also emitted. That both α and β rays are obtained after a time is explained by the formation, during the disintegration process, of other radioactive substances which do emit β particles. Uranium itself emits only α particles, but thorium, which is formed in the first step, gives off β particles. Gamma rays are light rays, not discrete particles; they accompany all types of radioactive decay but do not necessarily appear in every particular case. An entire series of disintegration products of $_{92}U^{238}$ has been discovered, and the successive changes are represented in Table 31–1 on page 402.

The expulsion of an alpha particle results in a decrease of 2 in atomic number (loss of 2 protons) and a decrease of 4 in mass number (2 protons and 2 neutrons). The emission of a β particle[1] results in no change in mass number (electrons have almost negligible weight) but an increase of 1 in atomic number (number of protons). A part of the uranium disintegration series is shown below.



Half-life periods The time required for the decomposition of one-half of any given amount of radioactive element is termed its half-life period. The half-life of radium is 1622 years, which means that during this time one-half of any given sample of radium will decompose; during the next 1622 years half of that remaining will decompose; and so on. Half-life periods vary from .00016 second for $_{84}Po^{214}$ to 4,500,000,000 years for $_{92}U^{238}$.

Properties of radium Radium appears in Group II*A* of the periodic table, and, except for its radioactive properties, is not unlike the other elements in this group—calcium, strontium, and barium. Although not as active as members of the alkali group, it is the most chemically active member of Group II and will decompose water with the formation of hydrogen. Radium has distinct metallic properties and forms the

[1] We should differentiate very carefully between the loss of electrons from the nucleus of an atom (radioactivity) and the loss of electrons from the valence orbits of an atom (ionization). As an electron is emitted from a nucleus, some such change as conversion of a neutron into a proton and an electron must take place; for example, $n \rightarrow p^+ + e^-$. In writing equations, electrons or beta rays will be represented by e.

TABLE 31–1 Disintegration Products of Uranium

ELEMENT	ISOTOPE*	HALF-LIFE
Uranium	$_{92}U^{238}$	4.5×10^9 years
↓ ↘ α		
Thorium	$_{90}Th^{234}$	24.1 days
↓ ↘ β		
Protactinium	$_{91}Pa^{234}$	1.18 minutes
↓ ↘ β		
Uranium	$_{92}U^{234}$	2.5×10^5 years
↓ ↘ α		
Thorium	$_{90}Th^{230}$	8.0×10^4 years
↓ ↘ α		
Radium	$_{88}Ra^{226}$	1622 years
↓ ↘ α		
Radon	$_{86}Rn^{222}$	3.8 days
↓ ↘ α		
Polonium	$_{84}Po^{218}$	2.05 minutes
↓ ↘ α		
Lead	$_{82}Pb^{214}$	26.8 minutes
↓ ↘ β		
Bismuth	$_{83}Bi^{214}$	19.7 minutes
↓ ↘ β		
Polonium	$_{84}Po^{214}$	1.6×10^{-4} seconds
↓ ↘ α		
Lead	$_{82}Pb^{210}$	19.4 years
↓ ↘ β		
Bismuth	$_{83}Bi^{210}$	5.0 days
↓ ↘ β		
Polonium	$_{84}Po^{210}$	138 days
↓ ↘ α		
Lead	$_{82}Pb^{206}$	stable

* Subscripts represent atomic numbers; superscripts represent mass numbers.

strong base, radium hydroxide, $Ra(OH)_2$. Its compounds are very similar to those of the other alkaline earth elements.

Radioactivity is a distinctive property of radium. Radium atoms are spontaneously and continuously disintegrating at a constant rate,

whether the element is free or combined with other elements. Furthermore, there seems to be nothing that the chemist can do to accelerate or retard this rate.

Rays from radium have a powerful effect on living tissues and produce severe and painful sores if allowed to come in contact with the skin for any length of time. Fortunately, the effect is greater on diseased than on healthy tissue; if it is very carefully controlled, radium may be used in the treatment of cancerous tissue and other malignant growths. Its principal application is in the treatment of surface cancer. Since the rays of radium are so penetrating, it is stored in heavy lead containers to prevent injury to persons working around it.

One of the principal sources of radium, the mineral pitchblende, U_3O_8, is found in the Belgian Congo and northern Canada. As we mentioned previously, purest deposits of pitchblende yield about 0.2 gram of radium per ton of ore. Deposits of *carnotite,* a low-grade uranium ore, are found in Utah and Colorado.

The unit of radioactivity: the curie The uses of radioactive substances are based principally on the effect of their alpha, beta, and gamma ray emission. The intensity or quantity of the emission is measured in *curies.* A curie is the quantity of a substance which gives the same number of disintegrations as one gram of radium. Since the curie represents a very large amount of radioactivity (it represents the disintegration of 3.70×10^{10} atoms of radioactive substance per second), the *millicurie* (.001 curie) and the *microcurie* (.000001 curie) are frequently used.

Radioactive and stable atomic nuclei The nuclear structure of atoms was discussed briefly in Chapter 3, in which it was pointed out that the nuclei of all atoms contain protons and neutrons. The nuclei of the *lighter stable atoms contain about an equal number of neutrons and protons;* in fact, many contain an equal number of neutrons and protons; for example, ${}_2He^4$, ${}_6C^{12}$, ${}_7N^{14}$, ${}_8O^{16}$, ${}_{16}S^{32}$, ${}_{20}Ca^{40}$. Atoms heavier than calcium lose the tendency to have about an equal neutron-proton ratio; there is a tendency for *neutrons to exceed protons as atomic weight increases;* for example, ${}_{24}Cr^{52}$, ${}_{42}Mo^{96}$, ${}_{92}U^{238}$. However, for each of the elements having atomic numbers 1 through 83, there is apparently a *narrow range of stability insofar as the neutron-proton ratio is concerned.* This range of stability for a given element is an index of the number of stable isotopes for that element (see Figure 31–3). As long as the neutron-proton ratio is within this range for a particular element, the isotopes will be stable; but if the ratio falls outside this range, an unstable isotope subject to radioactive disintegration results. To illustrate, three stable isotopes of oxygen are known (${}_8O^{16}$, ${}_8O^{17}$, and ${}_8O^{18}$) which indicates that the range of stability in neutron-proton ratio is from 8:8 to 10:8. Atoms of oxygen

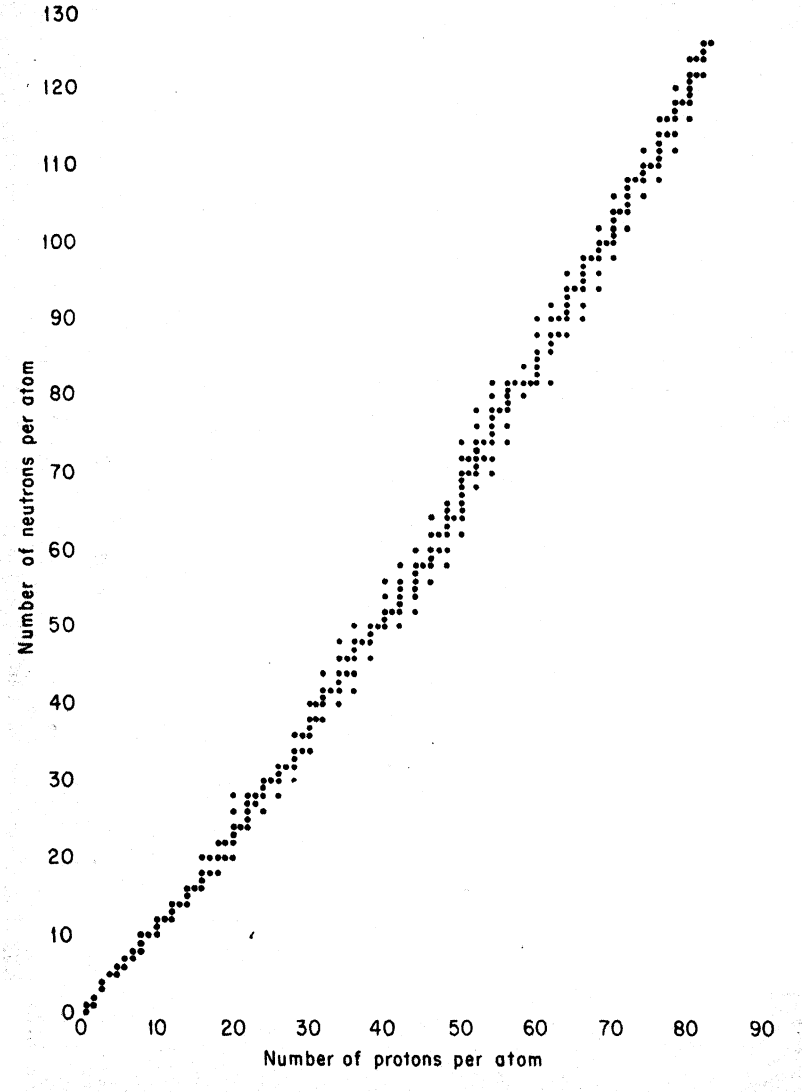


Figure 31–3 Neutron and proton content of stable nuclei. Neutron-proton ratio of the lighter elements is near one to one. Hydrogen is unique with no neutrons; deuterium, however, has a neutron-proton ratio equal to one. Heavier elements have an excess of neutrons over protons. Elements of atomic number above 83 are radioactive.

such as ${}_8O^{13}$ or ${}_8O^{20}$ must be too unstable to exist. The range of stability for most of the heavier elements appears to be wider than for the lighter elements, hence more stable isotopes are possible (see Table 3–2, page 46).

Both naturally occurring and man-made elements having atomic numbers greater than 83 are characterized by radioactivity; the nuclei of these heaviest atoms are subject to alpha- or beta-particle emission. When an atom loses an alpha particle, which means the loss of 2 protons and 2 neutrons from the nucleus, the residual atom will be two less in atomic number and four less in mass number. When an atom loses a beta particle (an electron) from the nucleus, there must be disintegration of a nuclear neutron into a proton and the ejected electron. At any rate, the residual atom gains in atomic number while the mass number remains the same. The newly formed nucleus may be stable or radioactive. A radioactive series ends with an atom which has a stable neutron-proton ratio.

Isotopes of lead Radioactivity of U^{238} ceases with the formation of lead having a mass number of 206. In the series of changes between uranium and lead, a total of 8 α particles are lost per atom; which means a decrease of 32 (8×4) units of mass. Since the mass number of uranium is 238, we should expect a mass number of 206 for lead ($238 - 32$). Careful determinations of the mass number of lead from radioactive sources by T. W. Richards yield a value about 206. The usual atomic weight of lead is given as 207.2; this value is for lead not associated with radioactive changes. This difference between the atomic weight of lead from radioactive sources and that of usual lead is factual evidence confirming the radioactive disintegration series which yields Pb^{206} rather than the usual isotopic mixture of atomic weight 207.21.

The age of the earth In nature, when Pb^{206} is found associated with U^{238}, it is quite certain that this lead isotope has been formed as a result of the radioactive decay of uranium. By analysis of the amount of lead in ratio to the uranium, and with application of half-life information in the radioactive series U^{238} to Pb^{206}, it is possible to calculate the time required to reach the uranium-to-lead ratio found in the mineral deposit. It is assumed that the original pure uranium was formed as the earth formed. Accordingly, calculation of the age of the mineral gives a minimum age for the earth. This "radioactive clock" shows that some of these minerals were formed three or four billions of years ago.

Radioactivity and subatomic particles Radioactivity has contributed immeasurably to the modern concept of atomic structure. The spontaneous disintegration of atoms at once alters Dalton's theory that atoms are compact, indivisible particles. Since definite particles of

matter are expelled during radioactive changes, it is natural to assume that very probably these same particles were units in the structure of the atom from which they were expelled. These considerations have led to the present-day ideas regarding atomic structure in which the fundamental units that compose an atom—namely, protons, electrons, and neutrons—are regarded as common to the atoms of all the chemical elements.

The present situation regarding the fundamental particles of matter is both unprecedented and exciting. Unsuspected new particles are being found, and new properties of old ones are being ascertained; see Table 31-2. Experimentation has pushed far ahead of theory, and scientists are faced with a composite of facts about subatomic particles that gives rise to a sense of frustration. Some fundamental organization must underlie the information at hand, but no comprehensive theory has been advanced as yet. How simple it was to consider that atoms were the ultimate particles of matter instead of having to think about the many subatomic particles discovered in recent research.

TABLE 31-2 Fundamental Particles of Matter

SUBATOMIC PARTICLES	ELECTRIC CHARGE	RELATIVE MASS
Nucleon { proton	+1	1836
Nucleon { neutron	0	1839
Electron, positron	−1, +1	1
Leptons (of diverse energy; such as photons and neutrinos)	0	0
π-mesons (pions)	−1, 0, +1	264–273
μ-mesons (muons)	−1, +1	207
K-mesons (several are known)		Masses between pions and nucleons
Hyperons (several are known)		Masses greater than nucleons

Protons and neutrons—often called *nucleons*—along with electrons are thought to be the major particles in atom building. A *positron* is almost equal in mass with, but opposite in charge to, an electron. This knowledge of the existence of particles having like mass and other like physical characteristics but with opposite electrical charge seems to hold for many of the minute particles that make up matter. There are now known to be positive and negative *μ-mesons* (muons) and positive and negative *π-mesons* (pions) that weigh more than two hundred times as much as electrons. A variety of *K-mesons* have been detected in some

radioactive decay processes, and these have a weight of about 966 electrons. *Hyperons* are particles heavier than protons. *Leptons* is the generic name given to a group of zero-mass units which are questionably called particles; these include *photons* and *neutrinos.* A photon is at times referred to as a *light quantum.* In summation, it should be honestly stated that scientists do not know in any detailed certainty what part all these particles play in the matter-energy aspects of the universe or even of a small part of the earth.

Artificial transmutation of elements The facts of radioactivity immediately bring to mind the questions: (1) Can the atoms of those elements which are not radioactive be broken down by artificial means into atoms of simpler elements? (2) Can atoms of the simpler elements be built up into more complex atoms? In either case, a transmutation of the element would result, a problem at which the alchemists worked vainly for centuries. Radioactivity proves to us that if we can alter the nuclei of atoms, new elements must result. Some success in transmutation has been achieved by bombarding atoms with high-speed particles such as protons or neutrons. Since atoms somewhat resemble a solar system in that their volume is largely open space with a nucleus of exceedingly small diameter as compared to the diameter of the atom, the problem of hitting the minute positively charged nucleus to effect nuclear change is difficult. A particle for nuclear bombardment must necessarily be smaller than the atom in order to penetrate the electron orbital atmosphere. If a properly directed positive particle is to hit the positive nucleus, it must have sufficient speed to overcome the repelling force of the positively charged nucleus. Rutherford reasoned correctly that alpha particles from naturally radioactive elements would have sufficient speed and mass to disrupt an atomic nucleus.

In 1919 Rutherford allowed a beam of alpha particles from a radioactive substance to pass through nitrogen gas. Some of the high speed alpha particles, on collision with the nuclei of nitrogen atoms, effected a change as represented by the following equation (α particles are helium nuclei)[2]:

$$_{7}N^{14} + {}_{2}He^{4} \rightarrow {}_{8}O^{17} + {}_{1}H^{1}$$

In this particular case an isotope of oxygen (mass number 17, atomic number 8) and a proton were obtained from the nitrogen and helium. Only a few alpha particles were effective in bringing about a change, since atoms have so much nothingness of space in their volume that only a few of the alpha particles actually collided with a nucleus. In

[2] In equations representing artificial transmutation of elements, $_{2}He^{4}$ stands for an alpha particle; $_{1}H^{1}$ is a proton; $_{1}T^{3}$ is tritium; and $_{1}D^{2}$ is deuterium.

fact, only about one alpha particle in 50,000 made an effective collision; but nevertheless this marked the first accomplishment of artificial transmutation.

Many further experiments in bombarding atoms with alpha particles resulted in small-scale transmutations. Examples are:

$$_{13}Al^{27} + {}_{2}He^{4} \rightarrow {}_{15}P^{30} + {}_{0}n^{1}$$
$$_{5}B^{11} + {}_{2}He^{4} \rightarrow {}_{7}N^{14} + {}_{0}n^{1}$$
$$_{4}Be^{9} + {}_{2}He^{4} \rightarrow {}_{6}C^{12} + {}_{0}n^{1}$$

This last equation denotes the way in which Chadwick discovered the neutron, ${}_{0}n^{1}$ (see page 32). Because of their neutral character, neutrons should make good nuclear bombardment particles; but man-made electrical machines cannot accelerate neutrons. Slow neutrons, however, have been effective in instigating certain nuclear changes. To accelerate a beam of any nuclear particle such as a helium ion, a proton, or a deutron (heavy hydrogen nucleus), E. O. Lawrence of the University of California invented the *cyclotron*. In this machine the particles are accelerated in a strong magnetic field between electrodes which change their charge at intervals equal to the time of half a revolution of the particles. These accelerated particles have been effective in many transmutations. A second accelerating machine is the *betatron*. The betatron throws off high-energy electrons which are used to produce high-energy gamma rays, and these in turn instigate many nuclear changes. The *synchrotron* is a third and newer type electrical machine which gives increased kinetic energy to electrons and is also applicable to positive ions. The cosmotron at Brookhaven National Laboratory is an example of a synchrotron.

Further examples of artificial transmutations are[3]:

$$_{3}Li^{6} + {}_{0}n^{1} \rightarrow {}_{2}He^{4} + {}_{1}T^{3}$$
$$_{7}N^{14} + {}_{0}n^{1} \rightarrow {}_{6}C^{14} + {}_{1}H^{1}$$
$$_{14}Si^{28} + {}_{1}D^{2} \rightarrow {}_{15}P^{29} + {}_{0}n^{1}$$
$$_{11}Na^{23} + {}_{1}D^{2} \rightarrow {}_{11}Na^{24} + {}_{1}H^{1}$$
$$_{19}K^{39} + {}_{1}H^{1} \rightarrow {}_{20}Ca^{39} + {}_{0}n^{1}$$
$$_{15}P^{31} + {}_{0}n^{1} \rightarrow {}_{15}P^{32} + \gamma$$
$$_{77}Ir^{191} + {}_{2}He^{4} \rightarrow {}_{79}Au^{194} + {}_{0}n^{1}$$
$$_{25}Mn^{55} + {}_{1}H^{1} \rightarrow {}_{26}Fe^{55} + {}_{0}n^{1}$$

The above examples of nuclear changes may be designated respectively as types (n, t), (n, p), (d, n), (d, p), (p, n), (n, γ) (α, n), (p, n) as the bombarding and emission unit are listed. These pairs are often referred to

[3] The understood release of energy, which might be designated as γ (gamma), is not added on the right side of most of these equations.

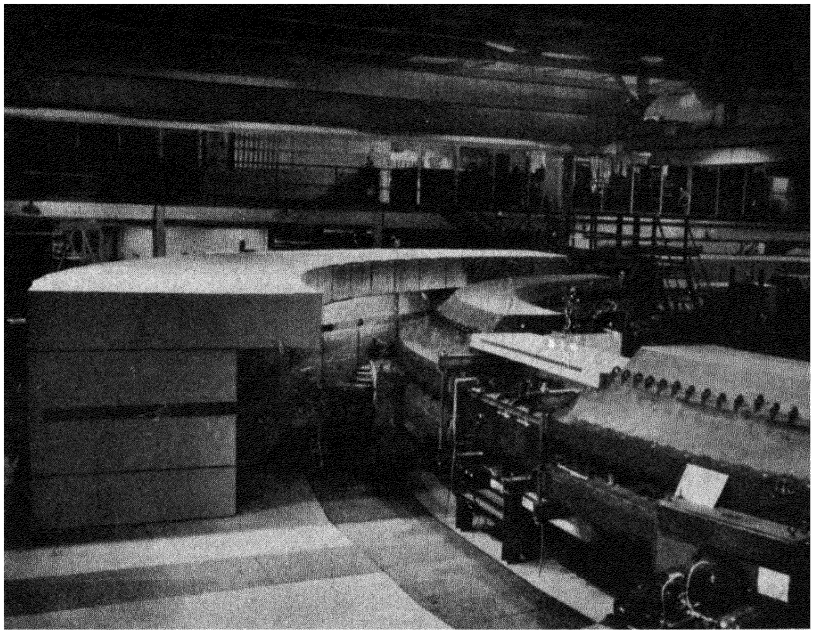


Figure 31–4 The cosmotron.

as the "in" and "out" particles. Nuclear changes of the above types are among the most common.

Note that the sum of the subscripts on the left side of each equation is equal to the sum on the right. Likewise, the superscripts, which represent mass number, must give the same total on both sides of the equation. To illustrate an abbreviated form of writing nuclear equations in which the "in" and "out" particles are shown in parentheses, the first three equations may be rewritten as:

$$_3\mathrm{Li}^6\ (n,\ t)\ {}_2\mathrm{He}^4$$
$$_7\mathrm{N}^{14}\ (n,\ p)\ {}_6\mathrm{C}^{14}$$
$$_{14}\mathrm{Si}^{28}\ (d,\ n)\ {}_{15}\mathrm{P}^{29}$$

Artificial radioactivity It has been found that the bombardment of nuclei of several of the lighter elements results in the formation of isotopes of elements which disintegrate spontaneously, very much in the manner of the heavier radioactive elements. For example, when aluminum is bombarded with alpha particles, an isotope of phosphorus is formed:

$$_{13}\mathrm{Al}^{27} + {}_2\mathrm{He}^4 \rightarrow {}_{15}\mathrm{P}^{30} + {}_0n^1$$

This isotope of phosphorus is radioactive and decomposes spontaneously:

$$_{15}P^{30} \rightarrow {}_{14}Si^{30} + e^{+}$$

In this reaction, e^{+} is a *positron,* a unit of matter having about the same mass as an electron but with a positive charge. This isotope of phosphorus, with a half-life of 2.5 minutes, is said to be artificially radioactive, since it has been produced by artificial means. Other artificially radioactive elements have been produced, and they offer promise as therapeutic agents to share the place of naturally radioactive elements like radium. In general, these radioactive isotopes have short half-life periods, and this offers certain advantages in treatment of disease. Additional examples are:

$$_{53}I^{127} + {}_{0}n^{1} \rightarrow {}_{53}I^{128} + \gamma$$
$$_{53}I^{128} \text{ (half-life 25 min.)} \rightarrow {}_{54}Xe^{128} + e$$
$$_{17}Cl^{35} + {}_{0}n^{1} \rightarrow {}_{16}S^{35} + {}_{1}H^{1}$$
$$_{16}S^{35} \text{ (half-life 87 days)} \rightarrow {}_{17}Cl^{35} + e$$

The discovery of these radioactive elements may lead to very significant new discoveries in the metabolism of plants and animals. For example. the passage of radioactive phosphorus and calcium may be followed through the body of an animal by means of a very sensitive instrument called a Geiger counter.

As a result of research in the past twenty years, radioactive isotopes of every known element have been artificially prepared. Elements 43, 61, 85, and 87 were for years blank spaces in the periodic table. After much unsuccessful research to find them, scientists began to realize that if these elements existed in nature at all it was in exceedingly small amounts. These elements have now been prepared in small (or trace) amounts by nuclear reactions or have been identified as branch elements in radioactive decay series.

Experiments with small-scale artificial transmutations resulting in stable or radioactive new atoms gave rise to the idea that atoms heavier than uranium might be produced. Research on the small-scale production of transuranium atoms was successful, and in the work the phenomenon of nuclear fission was discovered.

ATOMIC ENERGY AND THE ATOMIC BOMB

In early August of 1945 came the startling announcement that a bomb of unprecedented explosive violence had been dropped on the Japanese city of Hiroshima. The war with Japan came to an end a few days later. It was then revealed that scientists since early in the war had been con-

centrating their attentions on the release of atomic energy, and an atomic bomb was the result. Preliminary experiments had been carried out with the bomb near Los Alamos, New Mexico. Four huge plants for the manufacture of the essential ingredients of the bomb had been erected, three in Tennessee and one on the Columbia River in the state of Washington.

Although the details of the construction of the atomic bomb are still secret, the underlying scientific principles have been fairly well known for some time. A detailed examination of these principles is beyond the scope of this text; for the curious reader, several references are provided at the end of this chapter. A brief discussion of some of the principles underlying the release of atomic energy follows.

Chemical energy and atomic energy In ordinary chemical changes, atoms of the elements may undergo rearrangement, but the identity of the atom is retained. Electrons in the valence orbit may be transferred or shared, but the remainder of the atom is unchanged. If carbon is burned in oxygen, the carbon atom is not changed basically but appears as such in carbon dioxide, the product of combustion. Likewise, the oxygen atoms entering into the combination appear as such in the carbon dioxide. The combination takes place as a result of the sharing of outer electrons between the two kinds of atoms:

$$C + O_2 \rightarrow CO_2$$

This reaction provides the basis of most of the energy developed for industrial uses; coal is essentially carbon, and various fuel oils are carbon-containing compounds. In their combustion, carbon dioxide is produced. These reactions are exothermic; that is, energy is evolved in the form of heat. The heat energy is said to be derived from the chemical or potential energy of the reacting substances. Energy associated with the electrons of the atoms is considered the basic factor of chemical energy.

Atomic energy is associated with *changes in the nuclei* of atoms; as a result, the basic nature of the atom is changed; the product atoms are not the same as the reacting atoms. An example of a nuclear change that results in release of much energy is:

$$_3Li^7 + {}_1H^1 \rightarrow 2\ {}_2He^4$$

In contrast to the 4.1 electron volts (abbreviation, ev) of energy produced from the combustion of one atom of carbon, 17,000,000 electron volts are produced from the nuclear reaction of one atom of lithium with one atom of hydrogen. It is evident, then, that the energy produced in nuclear reactions is many million times greater than that produced as a result of ordinary chemical change. What is the source of this tre-

mendous amount of energy? The energy is now known to be associated with a very small mass loss; for example,

$$_3Li^{7\ 01818} + {}_1H^{1\ 00813} \rightarrow 2\ {}_2He^{4\ 00380}$$
$$8\ 02631 \text{ units of mass} \rightarrow 8\ 00778 \text{ units of mass}$$

In this transformation, a loss of mass equal to 8.02631 − 8.00778, or 0.01853, units of mass takes place. This disappearance of mass accounts for the resulting energy. Einstein in 1905 stated the law of equivalence of mass and energy, which says in effect that matter may be converted into energy, and vice versa. By using the Einstein equation

$$\text{Energy} = \text{mass} \times (\text{velocity of light})^2$$

and proper physical units, the energy evaluation associated with a given loss of mass can be calculated.

Mass-energy relationship[1] The units of mass or energy used depend on whether we are considering gram (or larger) amounts of substances in chemical or nuclear change, or merely the basic atoms or particles involved. Accordingly, following is a brief summary of mass and energy units

If $\frac{1}{16}$ of the weight of a single O^{16} atom is taken as a fundamental unit, such a unit may be called an *atomic mass unit* or *amu* (An amu is 1 00000 on the physical atomic weight scale) Since Avogadro's number of hydrogen atoms is required to weigh one gram (see page 115), a close approximation is

$$6\ 02 \times 10^{-24} \text{ atomic mass units (amu)} = 1 \text{ gram}$$

The erg is a unit of energy, but it is too large for use in considering a single atomic phenomenon An *electron volt* is the energy necessary to raise an electron through a potential difference of one volt This basic unit of energy is so small that a *million electron volts* (abbreviated *mev*) is the commonly used unit, it equates to the erg and calorie as follows

$$6.24 \times 10^5 \text{ mev} = 1 \text{ erg}$$
$$26\ 11 \times 10^{12} \text{ mev} = 4\ 184 \times 10^7 \text{ erg} = 1 \text{ calorie}$$
$$56\ 16 \times 10^{25} \text{ mev} = 9 \times 10^{20} \text{ ergs} = 2.15 \times 10^{13} \text{ calories}$$

Now, substituting units in Einstein's equation

$$\text{Energy (ergs)} = \text{mass (grams)} \times [\text{velocity of light (cm /sec)}]^2$$
$$= 1 \times [3 \times 10^{10}]^2$$
$$= 9 \times 10^{20}$$

In interpretation, one gram of mass equates to 9×10^{20} ergs of energy

From the above relationships

$$6\ 02 \times 10^{23} \text{ amu} = 1 \text{ gram}$$
$$= 9 \times 10^{20} \text{ ergs}$$
$$= 56\ 16 \times 10^{25} \text{ mev}$$

Therefore, $$1\ 0 \text{ amu} = 931 \text{ mev}$$

[1] Weights used in this discussion are physical atomic weights based on the main oxygen isotope as 16 rather than chemical atomic weights which are based on the weight of natural oxygen (a mixture of O^{16}, O^{17}, O^{18}) as 16

Once the atomic mass unit (amu) relationship to 931 million electron volts (mev) of energy is established, other mass-to-energy or energy-to-mass calculations can be made. Returning to a consideration of the lithium atom plus hydrogen to give two helium atoms in nuclear change, in which 0.01853 amu is lost, we may now solve the proportion:

$$\frac{1 \text{ amu}}{0.01853 \text{ amu}} = \frac{931 \text{ mev}}{x \text{ mev}}$$

$$x = 17 \text{ mev (17,000,000 electron volts)}$$

Thus, we have calculated the energy release (see page 412) as a single lithium atom combines with a single hydrogen atom. If Avogadro's number of atoms of lithium (7.01818 grams) and of hydrogen (1.00813 grams) forms helium with a 0.01853 gram loss, the energy release is

$$17 \text{ mev} \times 6.02 \times 10^{23} = 102.34 \times 10^{23} \text{ mev} = 4 \times 10^{11} \text{ calories.}$$

The energy release in chemical change involving electron transfer can now be more understandingly contrasted with the nuclear change which takes place with loss of mass:

12 grams of $C + O_2 \rightarrow CO_2 + 7{,}900$ calories (chemical change)

7.0181 grams of ${}_3Li^7 + {}_1H^1 \rightarrow 2\ {}_2He^4 + 400{,}000{,}000{,}000$ calories (nuclear change)

One gallon of octane (gasoline) on complete burning yields about 43,000,000 calories. It would take 9,300 gallons of gasoline on complete burning to equal the 400,000,000,000 calories of heat resulting from the nuclear reaction of about 7 grams of lithium.

Chain reactions Why are not nuclear reactions with the evolution of these tremendous amounts of energy taking place about us in everyday life much the same as ordinary chemical changes are taking place? The answer seems to be that whereas most chemical changes are self-maintaining, nuclear changes are not. In a chemical reaction, once the action is started, it proceeds until the reactants are used up. A piece of wood or coal ignited in the air continues to burn until used up. However, in nuclear changes the nuclear "fire" usually goes out soon after it is started. If some way were available to keep a nuclear "fire" burning, nuclear changes would proceed as easily as ordinary chemical changes; a so-called *chain reaction,* in which the action, once started, would pass from one atom to another as in the links of a chain, appears to be necessary for a self-maintaining nuclear reaction. Before 1939, many nuclear reactions were known and had been carried out on a very small scale; but more energy was used in maintaining the reactions than was obtained as a result of them.

Atomic fission The transmutation of many elements has already been described (pages 407–408). In general, in these atom-smashing experiments, only small fragments of matter such as protons, electrons, or helium ions were knocked out of a nucleus or added to it. As a result,

the product atom had an atomic number very near that of the bombarded atom.

Researchers in Germany in 1939 discovered a new and potentially most important type of nuclear change. By bombarding uranium with neutrons traveling at moderate speeds, they split the atom into two fragments of approximately equal size. Actually, it was only the U^{235} isotope in natural uranium that was subject to this change. This process, now referred to as *fission,* was accompanied by the evolution of a tremendous amount of energy. Furthermore, in the fission process—in addition to the relatively large fragments produced—several neutrons were released in the fission of each atom. The implications of the neutron release were at once clear—these product neutrons might be used to bombard another parent atom, the fission of which in turn would produce more neutrons; thus, a self-maintaining, or chain, reaction seemed to be a definite possibility. The important point, of course, was that a chain reaction would be self-maintaining only if a neutron from each fission produced fission in at least one other atom. We may illustrate a nuclear fission by the following equations (see also Figure 31–5):

$$_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{38}Sr^{94} + {}_{54}Xe^{139} + 3\,{}_{0}n^{1} + \underset{\text{(about 200 mev)}}{\text{energy}}$$

or

$$\rightarrow {}_{56}Ba^{145} + {}_{36}Kr^{88} + 3\,{}_{0}n^{1}$$

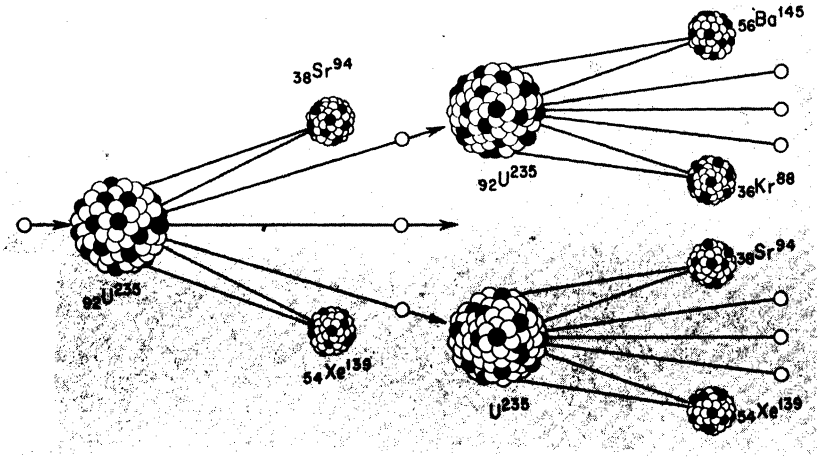


Figure 31–5 Fission of uranium and the chain reaction. In this diagram, the small white circles represent neutrons.

In these equations, strontium plus xenon, or barium plus krypton, are shown as the two large fragments in the fission. However, it should not be assumed that these elements always constitute the major fragments of a fission, since many other elements near the middle of the periodic table have been identified as products (see Figure 31-6) The mass of all the products of the fission is not quite equal to the mass of the reactants; the loss in mass is responsible for the very large amounts of energy evolved in these nuclear fissions; that is, mass is converted into energy.

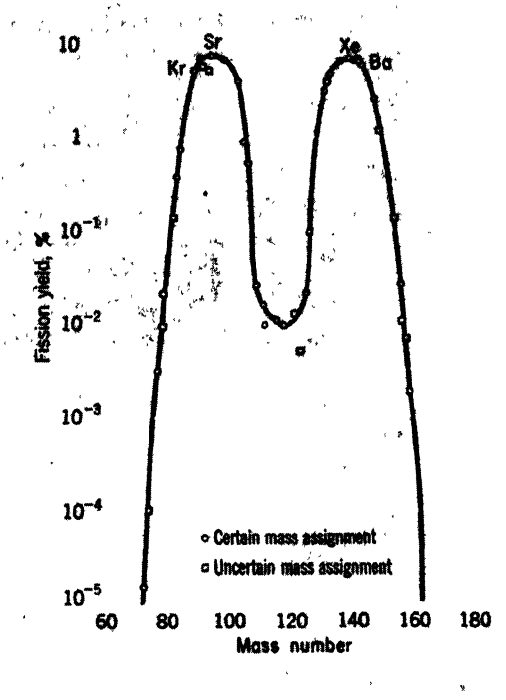


Figure 31-6 Yields of U^{235} fission products as a function of mass.

No whole units of mass are lost in a fission; note in the two fission equations given on page 414 that the sum of the atomic numbers on the left is equal to that on the right, and that the sums of the mass numbers on the left and right sides of the equations are equal. The energy is derived from only a fractional part of one unit of mass. Note also that the ${}_{38}Sr^{94}$ plus ${}_{54}Xe^{139}$, and ${}_{56}Ba^{145}$ plus ${}_{36}Kr^{88}$ are isotopes of these elements having high neutron-proton ratios. It is the radioactive decomposition of such atoms that accounts for the intense radiation associated with fission—radiation mainly of beta and gamma rays. For example:

$$ {}_{56}Ba^{145} \rightarrow {}_{57}La^{145} + e + \gamma \rightarrow {}_{58}Ce^{145} + e + \gamma \text{ etc} $$
$$ {}_{54}Xe^{139} \rightarrow {}_{55}Cs^{139} + e + \gamma \rightarrow {}_{56}Ba^{139} + e + \gamma \text{ etc} $$

U^{235} is not the only atom subject to fission. Slow neutrons also produce fission of U^{233} and Pu^{239}; in addition, fast neutrons produce fission

of Th^{232}, Pa^{231}, U^{238}, and Np^{237}. The isotopes U^{233} and Pu^{239} (page 419), which do not occur in nature, are obtained from the relatively abundant isotopes Th^{232} and U^{238}, respectively, by interaction with intermediate-energy neutrons. For example:

$$
\begin{aligned}
{}_{90}\mathrm{Th}^{232} + {}_{0}n^{1} &\rightarrow {}_{90}\mathrm{Th}^{233} + \gamma \\
{}_{90}\mathrm{Th}^{233} &\rightarrow {}_{91}\mathrm{Pa}^{233} + e \\
{}_{91}\mathrm{Pa}^{233} &\rightarrow {}_{92}\mathrm{U}^{233} + e
\end{aligned}
$$

Other elements of fissionable importance will probably be discovered. There is a considerable amount of experimentation going on with bombardment particles other than neutrons for producing fission of fissionable elements. Among such other particles are protons, deuterons, and alpha particles, and similar experiments have been made with gamma rays as bombardment particles.

Controlled fissions It is evident that if the neutrons liberated in the fission of uranium were utilized in producing more fissions, a rapid and violent reaction might take place; a piece of uranium, once the reaction was started, would explode. Although a violently explosive substance was the immediate objective in producing an atomic bomb, many problems had to be solved before this objective was achieved. One of the first problems to confront scientists working on the atomic energy project was to find a means of controlling these atomic fissions. We may indicate in a general way how this was accomplished.

Ordinary uranium is composed of three isotopes, which occur in the following proportions: U^{238}, 99.276 per cent; U^{235}, 0.719 per cent; and U^{234}, 0.005 per cent. Thus, in ordinary uranium the ratio of the U^{235} isotope (which is the isotope fissionable by slow neutrons) to U^{238} is about 1 to 140. For a fission chain to be set up, neutrons liberated by the fission of one U^{235} atom must hit another U^{235} atom, and so on. But neutrons resulting from fission are moving so fast that many of them are captured by U^{238} atoms, though not in a fission-yielding process. Also, if the piece of uranium is small, many or most of the fast neutrons may escape through the surface of the metal before being absorbed by other nuclei. The uranium isotope U^{238} is particularly effective in capturing neutrons. Although this process lessens the chance for absorption of neutrons to produce fission in U^{235} atoms, it is of utmost importance in other considerations, as will be pointed out later.

It is evident that at least one neutron from each fission must be effective in bringing about another fission; otherwise, the chain is broken, and reaction ceases. U^{235} atoms seem able to capture slow neutrons in competition with the more numerous U^{238} atoms, but U^{238} atoms cap-

ture most of the high-energy neutrons. In order to increase the probability of capture of neutrons by U^{235} and the subsequent fission, it is necessary to slow down the liberated neutrons. This may be accomplished with a "moderator"—graphite, for example—which absorbs a part of the energy of the neutron and slows it down. With a lattice-work arrangement of U^{235}-enriched uranium lumps imbedded in graphite (called a "pile" and larger than a so-called "critical size") neutrons which might ordinarily be lost from the surface will diffuse back and forth through the lattice work until they have lost sufficient energy to be captured by a U^{235} nucleus. The capture results in fission with liberation of more neutrons, and the chain reaction is set up. The first pile was constructed at the University of Chicago in 1942 with about six tons of ordinary uranium and many tons of graphite. Since the fission process is exothermic, it is obvious that the pile would heat up as the fission process continues to take place more and more rapidly and would eventually reach a temperature high enough to cause an explosion. However, the pile may be controlled by providing passageways through which rods of neutron-absorbing material such as boron steel or cadmium metal may be inserted. Neutrons are absorbed by the boron steel or cadmium rods or plates, and the chain reaction is regulated. Proper adjustment of the controls will allow the reaction to proceed at only a given rate or power level. To raise the power level, the rods would be partially withdrawn; to lower it, the rods would be pushed in farther. Such a controlled pile provides a means for producing low-temperature heat energy from atomic energy; this source of energy is being increasingly used in nuclear-powered electric generating plants.

Nuclear power plants Figure 31–7 shows the necessary sections for a

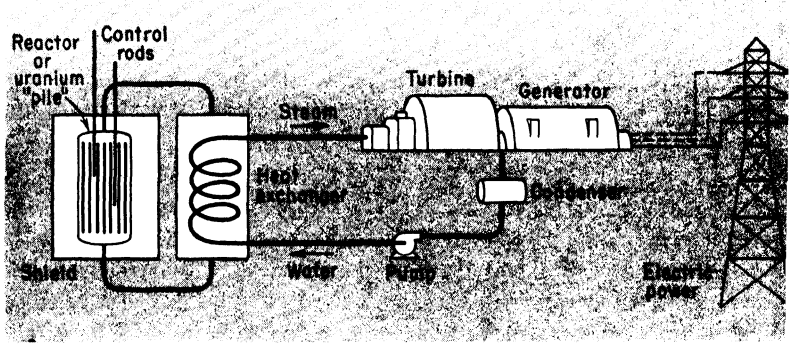


Figure 31–7 A nuclear-powered electric generating plant.

nuclear power plant, which consists of a "pile" as described above, a heat exchanger, and an electrical generating installation. A so-called breeder reactor is included to produce more fissionable material than is consumed. The splitting of a single fissionable atom produces an average of $2\frac{1}{2}$ neutrons, only 1 of which is required to continue the chain reaction. The other $1\frac{1}{2}$ neutrons per split atom may bombard nonfissionable U^{238} or thorium and so convert these to fissionable material. Argonne National Laboratory has already constructed one such reactor (it was fueled by U^{235}), the first to produce power and at least as much fissionable material as it consumed. Argonne's second breeder will be fueled by plutonium, with the fuel elements surrounded by a blanket of U^{238} which will be converted to plutonium.

Separation of uranium isotopes Since U^{235} undergoes fission by slow-moving neutrons whereas U^{238} does not, an important wartime project was to separate the two isotopes from the naturally occurring mixture of 0.7 per cent U^{235} and 99.3 per cent U^{238}. Experimental research on the separation in quantity was indeed a big problem. Three methods of separation of the uranium isotopes will be briefly described.

Small-scale testing of the separation of uranium isotopes by *thermal effusion* was sufficiently promising that a massive plant for this purpose was built at Oak Ridge, Tennessee. In actual operation, a compound of uranium which contains both isotopes is fed into a thermal effusion plant which consists essentially of thousands of units of concentric pipes (Figure 31–8). Steam passes through the innermost pipe, and the uranium compounds in liquid form are in the outer pipe. The lighter uranium isotope tends to travel to the hot inner wall of the unit and to rise. The heavier isotope is to some extent left in more concentrated form at the outer cold wall. By draining solution from near the center and top and also from the outside and bottom of the pipe and repeating the cycle thousands of times, a product much higher in percentage of U^{235} is obtained.

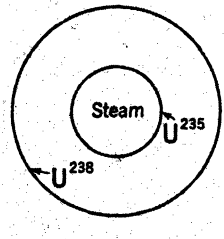


Figure 31–8 Cross section of concentric pipes for thermal effusion separation of uranium isotopes.

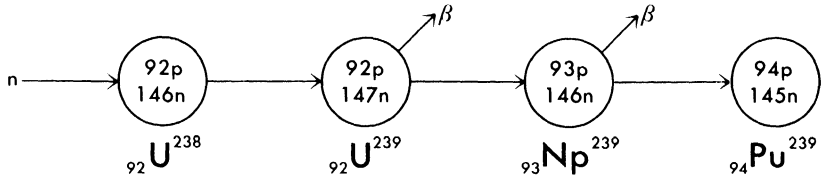
The thermal effusion plant had such large and costly steam requirements that a *gaseous effusion* method for separation of the isotopes soon took its place. If naturally occurring uranium is converted to gaseous UF_6, the compound containing the lighter isotope will effuse a little faster through a porous barrier. One passage of the isotopic gas mixture, of course, does not effect complete separation, so an enormous amount of gas recycling is necessary. Much as in frac-

tional distillation, an eventual concentration of U^{235} is effected by fractional gas effusion.

The *electromagnetic separation* process is based upon the use of the mass spectrograph (page 47). A uranium compound in vapor form is ionized by an electron beam. The ions produced are accelerated and passed through a narrow slit into a large evacuated region where electromagnetic forces act on them. Since the lighter isotopic ions have less weight though the same charge, they are deflected into a smaller semicircular path than the heavier ions. Slits are placed at the terminals of the semicircular ionic beams so that the respective isotopic ions are collected separately.

Separation of the two principal isotopes of uranium by any of these methods is very costly and requires large plant installations.

Plutonium As previously stated, ordinary uranium tends to absorb neutrons and thus to slow down the chain reaction, if not actually to break it. This absorption of neutrons by U^{238} turned out to be extremely important, since the absorption leads to the formation of a new element, plutonium (Pu, atomic number 94) which, like U^{235}, may undergo fission with the release of more neutrons. The changes taking place in the formation of Pu from U^{238} may be represented diagrammatically:



U^{238} absorbs a neutron to form U^{239} which then emits a beta particle, resulting in the formation of *neptunium*, Np, a new element of atomic number 93. Neptunium then emits a beta particle which results in the formation of plutonium, Pu.

The "piles" referred to previously were actually constructed for the purpose of manufacturing plutonium. The large amounts of heat energy evolved in the operation of the piles were not used. A large plant for plutonium manufacture was constructed at Hanford, Washington, in 1943. Several piles were set in operation; the heat from the reactions was dissipated into the Columbia River by pumping river water through the piles.

The atomic bomb With the discovery of Pu, two substances, U^{235} and Pu ^{239}, were available for the manufacture of atomic bombs. Plutonium manufacture possesses certain definite advantages over the recovery of U^{235} from ordinary uranium. The separation of U^{235} from U^{238} is ex-

ceedingly difficult, since *physical means,* which take advantage of the relatively small differences in the mass of the two isotopes, must be employed. Thermal effusion, gaseous effusion, and electromagnetic methods have been used to effect the separation, but many stages of purification are necessary. Plutonium, when produced in a uranium pile, can be separated from unconverted uranium by *chemical means,* since Pu is a different element and as such exhibits a different set of chemical properties.

Relatively little information has been released regarding the construction of the atom bomb itself. It was known early in the studies of this project, however, that a certain "critical size" of material was necessary for a chain reaction to be self-perpetuating and for an explosion to take place. In a small piece of U^{235} or Pu^{239}, in which the ratio of surface area to volume is large, too many neutrons escape through the surface, and consequently a chain reaction is not maintained. As the size of the piece is increased, the ratio of surface area to volume decreases, and there is more chance that neutrons will be captured before escaping through the surface. In producing an atomic bomb, it seems logical that pieces of subcritical size might be brought together rapidly, possibly by using one or more pieces as projectiles and another as a target in a firing mechanism. Just how pieces of subcritical size are brought together to form an effective fissionable mass in a bomb is still a secret.

In the explosion of an atomic bomb, a very high temperature is attained; desert sand was sintered at some distance from actual bomb tests at Los Alamos, New Mexico. Written accounts tell of vaporization of the metal of the tower holding the test bomb. Just how high a temperature is reached is difficult to estimate, as man has not heretofore attained temperatures above about 4000° C. Temperatures in the order of millions of degrees are known to be reached. This excessively high temperature consideration leads us to some understanding as to the nature of possible temperature effects in an atomic bomb explosion. Probably no large mass of material in an atomic bomb blast is heated as high as the internal part of the sun, though certainly some very high temperature is reached locally. The atomic bomb explodes and causes such air expansion—and later contraction on cooling—that cyclonic wind or blast effects are produced. The radioactive fragments, clinging to dust, are very dangerous.

The elements that are products of fission are commonly isotopes of quite high atomic weight for the given elements. In reverting to stable isotopes, intense beta and gamma ray activity is involved. This is the marked after-effect so dangerous to biological tissue. Radioactive strontium and cobalt isotopes have been publicized as particularly dangerous products of a fission bomb.

Binding energy, mass defect, packing fraction Variations in atomic weights from whole numbers may be explained by the following factors:

1 Isotopes;
2 Weight of electrons (can become a second decimal point factor);
3 Neither protons or neutrons have unit mass, and atoms have varied neutron-proton ratios;
4 A small amount of mass is converted to what is called *binding energy* as atoms are formed from their nucleons.

Recent and exacting work with the mass spectrograph shows that *atomic masses are always less than the additive weights of their particle content.* For example, we may compute the mass loss as helium is formed from two protons and two neutrons:

$$2\,{}_1H^1 + 2\,{}_0n^1 \rightarrow {}_2He^4 + \text{binding energy}$$
$$2 \times 1.00812 + 2 \times 1.00893 \rightarrow 4.00390 + 0.03020 \text{ mass units}$$

Similarly, for all atoms a fractionally small mass loss exists in atomic mass as compared to the total of nuclear particle masses. There is variation in the amount of binding energy per nuclear particle as diverse-sized atoms are built up. To further describe this extremely important relationship, the terms *mass defect* and *packing fraction* have been carefully designated as follows:

$$\text{Mass defect} = \text{atomic mass} - \text{mass number}$$

For helium: $\text{Mass defect} = 4.00390 - 4 = .00390$

$$\text{Packing fraction} = \frac{\text{mass defect}}{\text{mass number}}$$

For helium: $\text{Packing fraction} = \frac{.00390}{4} = .00975$

Consider the packing fraction curve which is shown in Figure 31-9. Note that a low in the curve exists near iron of mass number 56. This means the mass defect for iron is small as related to its mass number. *The low mass defect is an index of high binding energy, since much of the excess mass of the neutron and proton nuclear content has been dissipated to energy.* Iron would seem to be about the most stable atom from this concept. Some evidence indicates that the earth's core consists largely of iron and nickel, and meteorites have a high iron and nickel content. Perhaps this is related to the nuclear stability of these elements.

Note that the packing-fraction curve (Figure 31-9) gradually rises from iron to uranium and the transuranium elements (elements above uranium in atomic number). These larger-mass-number elements of higher-packing fraction and large mass defect have mass to be converted into energy in any fission of them into more stable elements in the middle range of mass numbers. This accounts for the very large amounts of energy accompanying atomic fission.

Consider the high packing fraction of the lighter elements as shown in Figure 31-9. These elements, which have comparatively large mass defect compared to atomic number, present distinct possibilities for conversion of mass to energy. The nuclear reactions—hydrogen plus neutrons to helium with energy emission, and lithium plus hydrogen to two helium atoms—have been developed (see page 412).

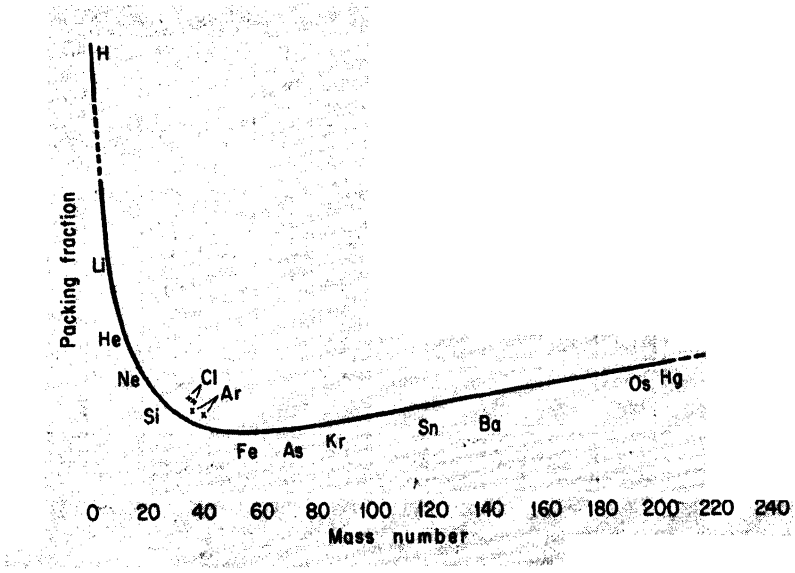


Figure 31–9 Packing fraction curve for the elements.

Atomic fusion It is evident from the foregoing that there exists another potential source of nuclear energy in a *fusion* process, in which the very lightest nuclei might be made to combine to give somewhat heavier, more stable nuclei, with an attendant release of energy. Fundamentally, this is the idea behind the much-discussed hydrogen bomb. Fusion of nucleons is believed to be the source of the sun's energy. Man probably will be able to control fusion processes someday as he has learned to control atomic fission processes.

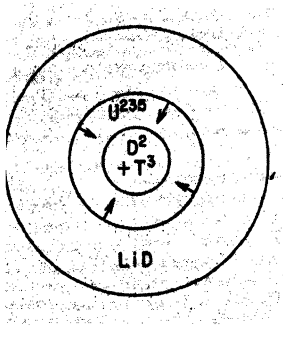


Figure 31–10 Arrangement of ingredients of an H bomb.

The hydrogen bomb Fusion of light elements requires temperatures of the order of millions of degrees. Such high temperatures may be obtained in "fission" bombs, and it is likely that the latter are used as detonators for "fusion" bombs. One possible arrangement of the ingredients in a hydrogen or fusion bomb may be such as that pictured in Figure 31–10. The core of the device contains the two hydrogen isotopes, deuterium and tritium. Around the core is a layer of fissionable matter

such as U^{235} which, when set off, "detonates" the interior. By implosion, the following reaction between the hydrogen isotopes in the core is initiated:

$$_1D^2 + {}_1T^3 \rightarrow {}_2He^4 + {}_0n^1$$

This reaction releases a flood of energy and further raises the temperature which is then sufficiently high to explode the outer layer of the bomb, which consists of lithium deuteride, $_3Li^6{}_1D^2$. The following sequences of nuclear reactions would give a self-maintaining chain process:

$$_3Li^6 + {}_0n^1 \rightarrow {}_2He^4 + {}_1T^3$$
$$_1D^2 + {}_1T^3 \rightarrow {}_2He^4 + {}_0n^1; \text{ and so on.}$$

In this arrangement, the mixture of the isotopes of hydrogen acts as a booster to increase the temperature.

The isotopes Li^6 of lithium and D^2 of hydrogen are fairly easily produced. However, tritium is very difficult to prepare in sizeable quantity, and this is an obvious drawback to the arrangement described here. Perhaps some substitute has already been found for the booster process, if indeed such a process is necessary at all. There is a great deal of speculation regarding the construction of "super" bombs, and the

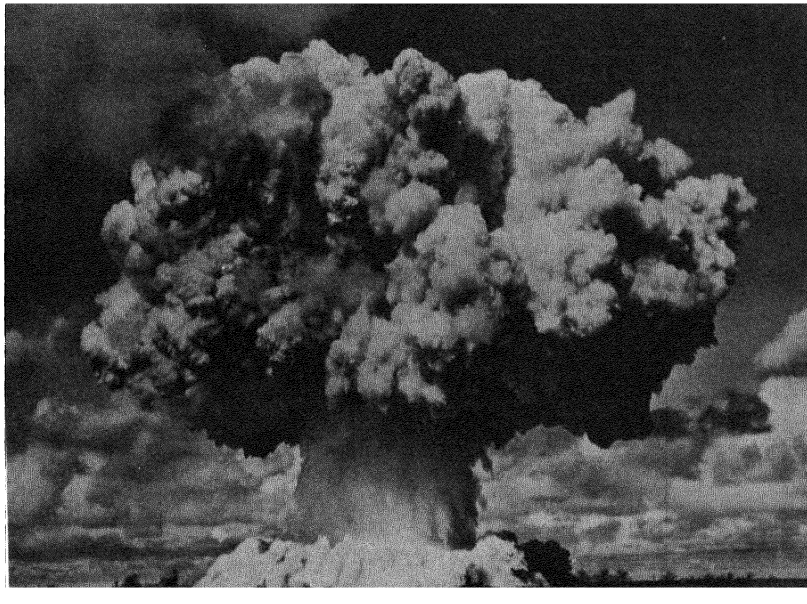


Figure 31–11 Aftercloud following underwater atomic explosion.

prospects become terrifying to civilized peoples. One pound of lithium deuteride, if completely utilized, produces the energy equivalent of about 2300 tons of TNT. The implications of the indiscriminate use of such energy potentials are clear to all.

Peacetime uses of atomic energy Vast new fields which have been opened by the advent of atomic energy are only just beginning to be explored. The heat released by an atomic pile constitutes a potent source of energy. Already at Harwell, England, an eighty-office building is being heated by a nearby atomic pile. The atomic-powered U. S. submarines *Nautilus* and *Sea Wolf* have completed thousands of miles of travel. A few nuclear power plants are in use and more are in construction.

In the publication *American Scientist,* Dr. Blabha is quoted concerning world power requirements. Taking the unit Q, equal to 10^{18} BTU of energy (approximately the energy given by burning 33 billion tons of coal), it is stated that only ½ Q of energy was used by man up to the year 1850. In 1950, the energy consumption by man was up to 10 Q per century; and it is increasing in rate by four per cent each year. Less than 100 Q are still available as coal and oil. In estimated mineable uranium and thorium, about 1700 Q may be available. A practically unlimited supply of energy would be available in the deuterium of sea water if a means of handling a controlled fusion-thermonuclear reaction were to be found, but the technical difficulties are formidable.

The use of atomic piles has made possible the preparation of artificial radioactive isotopes in amounts hitherto unimagined. A pile at the Oak Ridge National Laboratory is now given over to this exclusive purpose. The isotopes are derived from two sources: (1) direct uranium fission products, separated and chemically purified, and (2) neutron irradiation in the pile of various target materials. The latter source is by far the most important at present. Thousands of isotope shipments have been made from Oak Ridge, and the rate is constantly increasing.

These isotopes are finding application as "tracers" in medicine, scientific research, industrial research, and industrial control. The iodine isotope, I^{131}, is being used very extensively in the medical treatment of hyperthyroidism. Radioactive iodine administered to the patient tends to concentrate in the thyroid gland and provides radiation therapy right at the location of the trouble by virtue of its high-energy gamma rays. Cobalt-60, also a gamma emitter, with a half-life of 5.3 years, is currently being much used as an exceedingly cheaper substitute for radium, both in medicine and industry. Cobalt sources equivalent to many grams of radium may be used for radiation therapy or in industry for "X-raying" metal castings to check for flaws.

Representative of the extensive use of tracers in scientific research is the application of C^{14}, an isotope of carbon with a half-life of 5570

years, to the study of photosynthesis. You will recall that photosynthesis (see page 284) is the process by which green plants utilize the energy of sunlight to convert CO_2 (from the air) and H_2O into living material. The mechanism of this process has long baffled scientists. By allowing plants to photosynthesize for a time in an atmosphere containing C^{14} and O_2 and then carrying out chemical separations on the plant material, it is possible to find which compounds contain radiocarbon, to ascertain the chemical nature of the various initial compounds formed, and thus to discover the individual chemical steps in the photosynthetic process. In experiments of this sort, it was early shown that no radioactive formaldehyde, HCHO, was formed; therefore formaldehyde is not a primary photosynthetic product, as was once thought.

Biochemists are using C^{14} and P^{32} in the study of body chemistry. The use of isotopes in industry is only just getting started; it will unquestionably increase tremendously in the years ahead.

TRANSURANIUM ELEMENTS

Neptunium, ${}_{93}Np^{239}$, and plutonium, ${}_{94}Pu^{239}$, are artificially produced elements above uranium in atomic number. Several isotopes of each of these elements have now been prepared. These elements were discovered in connection with neutron capture by uranium and subsequent beta emissions (see diagram, page 419).

$$\begin{array}{l} {}_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} \\ \qquad\qquad\quad \downarrow \\ \qquad\qquad\quad {}_{93}Np^{239} + e \\ \qquad\qquad\quad \downarrow \\ \qquad\qquad\quad {}_{94}Pu^{239} + e \end{array}$$

${}_{93}Np^{239}$ has a half-life of but 2.3 days and on its beta-particle ejection forms ${}_{94}Pu^{239}$, which is quite stable with a half-life of 2.4×10^4 years. An isotope of neptunium of much longer half-life may be prepared:

$$ {}_{92}U^{238} + {}_{1}D^{2} \rightarrow {}_{93}Np^{237} + 3\,{}_{0}n^{1} $$

Neptunium shows oxidation numbers of +3, +4, +5, and +6.

The chemical properties of plutonium were originally studied by *tracer techniques*. To explain the nature of tracer techniques, assume that a very small quantity of plutonium ions is mixed with several other metal ions in solution. A quantitative scheme of analysis involving precipitations and separations is carried out. The minute amount of plutonium may be followed through the various chemical separations because of its radioactivity, and its chemistry is then likened to that of the metal ions it follows. Solutions of plutonium ion as dilute as 10^{-8} *M* may be treated by such tracer techniques, and in this manner much

of the chemistry of the element has been worked out. Since plutonium is now available in pound quantities for current investigations, tracer techniques or *microchemistry* are not so important for plutonium as for some other scarce elements or isotopes. Plutonium may exhibit oxidation numbers of +3, +4, +5, and +6 in various compounds.

Experimental endeavor to make still higher atomic-number atoms has met with some success. Bombardment of U^{238} and Pu^{239} with very high-energy helium ions in the cyclotron has produced isotopes of elements of atomic numbers 95 (americium, symbol Am) and 96 (curium, symbol Cm).

$$_{92}U^{238} + {}_{2}He^{4} \rightarrow {}_{94}Pu^{241} + {}_{0}n^{1}$$

$$_{94}Pu^{241} \rightarrow e + {}_{95}Am^{241} \text{ (500 year half-life)}$$

$$_{94}Pu^{239} + {}_{2}He^{4} \rightarrow {}_{0}n^{1} + {}_{96}Cm^{242} \text{ (5 month half-life)}$$

Researchers at the University of California, under the leadership of Professor G. T. Seaborg, have contributed markedly to knowledge of transuranium elements. Trace quantities of the new elements berkelium, $_{97}Bk^{245}$, and californium, $_{98}Cf^{246}$, have been produced, and a few properties of them and of their compounds established. Further, there has been discovery of einsteinium (99), fermium (100) and mendelevium (101). Element 102 is reported to have been made by bombarding $_{96}Cm$ with $_{6}C^{13}$; the name nobelium is proposed for it. These are in the realm of very radioactive elements. Still higher-atomic-weight atoms may be developed, but these larger nuclei are so unstable with such short half-lives that progress toward heavier atoms is not expected to go on indefinitely.

The chemistry of all these transuranium elements is being studied by tracer techniques, and the following speculation may be made. In considering atomic structure and periodic-table placement of elements, it is noted that the "rare earths" which follow lanthanum, atomic number 57, are part of a transition group of elements in which the fourth orbit is building up from 18 to 32 electrons (see page 58). It follows, by analogy, that beginning with actinium, atomic number 89, a second instance may occur of a group of elements filling up (in whole or part) an inner orbit; namely, orbit 5. There is definite experimental evidence that transuranium elements have a characteristic valence of 3 and thus are a part of what may be called a "rare rare-earth" group, or *actinide* series.

ENERGY OF THE SUN

The source of the energy that the sun has dissipated over many many millions of years, and the source of the heat to maintain its estimated

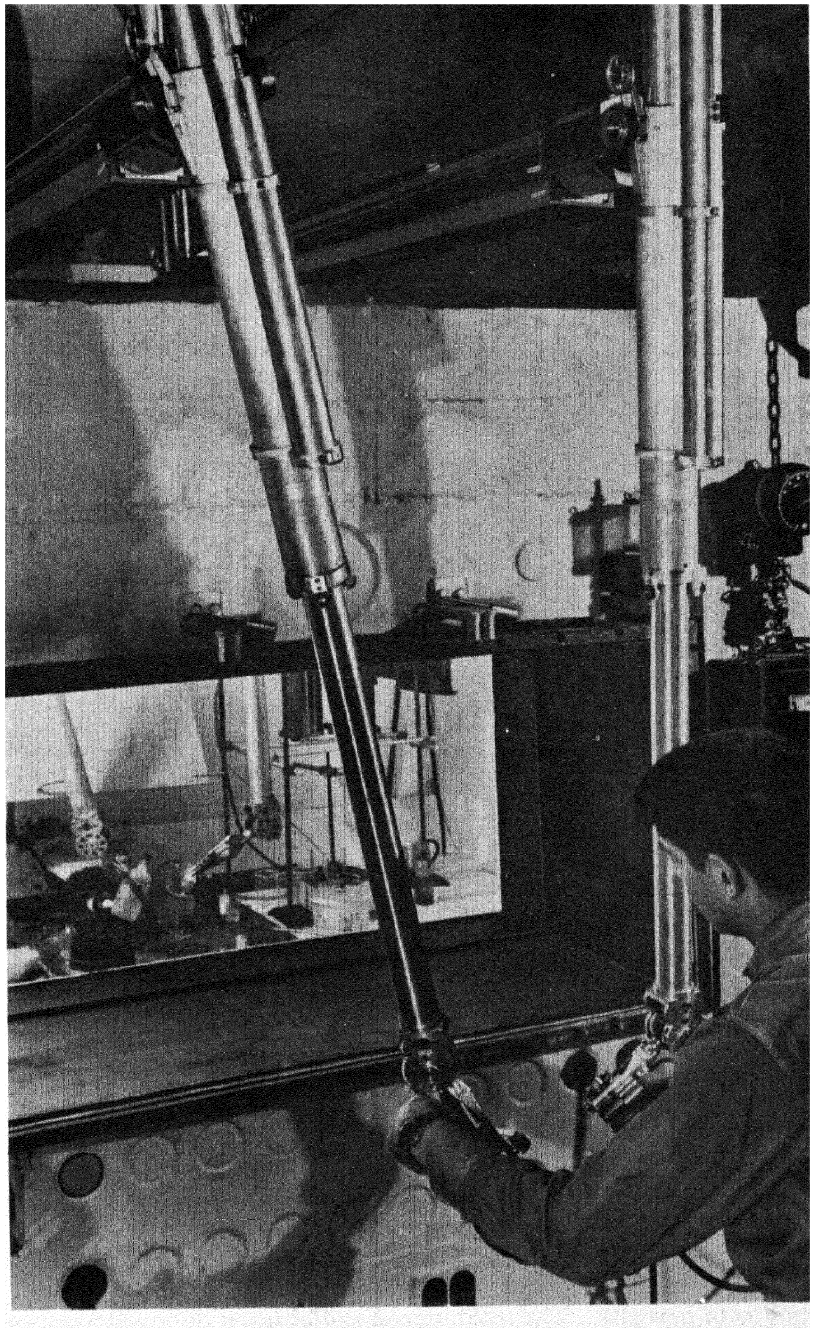


Figure 31–12 Manipulating dangerously radioactive materials.

millions of degrees of internal temperature, have long been subjects of conjecture. Chemical changes, involving mere electron interchange, cannot account for solar energy. It has been postulated that some hydrogen-to-helium nuclear reaction produces the sun's energy. Much as the mechanism of catalysis is sometimes explained by intermediate-compound formation and step-chemical changes, it has been a speculation that the following chain of nuclear changes may be involved in hydrogen-to-helium formation in which C^{12} acts as a catalyst:

$$
\begin{aligned}
{}_6C^{12} + {}_1H^1 &\rightarrow {}_7N^{13} + \text{energy} \\
{}_7N^{13} &\rightarrow {}_6C^{13} + e^+ + \text{neutrino} \\
{}_6C^{13} + {}_1H^1 &\rightarrow {}_7N^{14} + \text{radiation} \\
{}_7N^{14} + {}_1H^1 &\rightarrow {}_8O^{15} + \text{radiation} \\
{}_8O^{15} &\rightarrow {}_7N^{15} + e^+ + \text{neutrino} \\
{}_7N^{15} + {}_1H^1 &\rightarrow {}_6C^{12} + {}_2He^4
\end{aligned}
$$

Summing and canceling leaves

$$4\ {}_1H^1 \rightarrow {}_2He^4 + \text{energy equal to 29 mev.}$$

The matter of possible nuclear changes in steps and with some atom acting as a catalyst may have significance in man's endeavor to carry out nuclear fusions and thus increase his energy sources.

Astronomical evidence indicates that protons are much more abundant than any other nuclear particle in stars. A part of the energy of the sun is ascribed to proton union to form deuterons:

$${}_1H^1 + {}_1H^1 \rightarrow {}_1D^2 + e^+$$

Radiocarbon dating The mysterious cosmic rays which come to this earth cause some nuclear changes within the realm of their penetration. In the upper atmosphere, some neutrons resulting from disintegration of nuclei by cosmic rays produce radioactive carbon in the following way:

$${}_0n^1 + {}_7N^{14} \rightarrow {}_6C^{14} + {}_1H^1$$

The C^{14} atoms become well mixed with normal C^{12} atoms in the CO_2 content of air. A quite constant ratio of the two isotopes of carbon exists in the CO_2 of the air, and this same ratio continues into new plant and animal life. When plant and animal life dies and is covered with soil, it leaves the zone of the atmospheric CO_2-photosynthesis process, in which the definite ${}_6C^{14}$-to-${}_6C^{12}$ ratio is known. The nonliving carbonaceous material is subject to slow decrease in the amount of ${}_6C^{14}$ present, as these atoms, in accord with their half-life, radioactively emit beta particles. The technique of radiocarbon dating, developed

by W. F. Libby at the University of Chicago, can now be used by the geologist, archeologist, and historian to trace events which took place thousands of years ago:

$$_6C^{14} \rightarrow + {}_7N^{14} + e$$

By measuring the radioactivity which remains in a given carbonaceous specimen, the age since its death can be determined.

The half-life of $_6C^{14}$ is 5,570 years. Electronic-counting equipment now available, if carefully used, is sensitive enough to measure back through several half-life times. Fossil materials may be dated back to about 30,000 years ago.

EXERCISES

1 What is the essential difference between the loss of an electron from a radioactive substance and loss of an electron by ionization?

2 Diagram the changes taking place in the nucleus of the uranium atom in its series of disintegrations which finally produce lead

3 How does artificial radioactivity differ from natural radioactivity?

4 With reference to the discovery of the fission of U^{235}, discuss

(*a*) Implications of the discovery.
(*b*) Difference between "fission" and "atom-smashing experiments before 1939"
(*c*) The basic principle involved in the release of atomic energy.
(*d*) Subsequent discovery of fissionable materials.
(*e*) Possible peacetime applications

5 Discuss as briefly as you can the structural design of the uranium pile Include necessary components and the function of each Explain briefly how the pile operates

6 Consider the radioactive decay of $_{90}Th^{234}$ This isotope loses a β particle to produce element X, which in turn loses a β particle to produce element Y, which then loses an α particle to produce element Z. Complete the table.

ELEMENT	MASS NUMBER	ATOMIC NUMBER
Th	234	90
$\downarrow \beta$		
X	____	____
$\downarrow \beta$		
Y	____	____
$\downarrow \alpha$		
Z	____	____

7 An isotope has a half-life of 1 year. Starting with 96 grams, how much will be present at the end of the sixth year? Ans. 1.5 g.

8 An element is found to have a half-life of 80 years. How many years would be required for an 80 g. sample to decay to 5 g?

9 Considering the neutron-proton ratio for each of the following pairs of isotopes, select the member of each pair you would expect to be stable (*a*) $_{10}Ne^{20}$, $_{10}Ne^{30}$; (*b*) $_4B^9$, $_4B^5$; (*c*) $_{80}Hg^{200}$, $_{80}Hg^{160}$.

10 A radioactive isotope has a half-life of 1 day Starting with 6400 atoms, how many atoms of the original would be left after 1 week? Ans 50

11 Suppose a man had stored away 4.52 g of radium in the year 1960 Assuming the half-life of radium to be 1622 years, what weight of radium would be left in the year 3582?

12 Calculate in mev (million electron volts) the energy which would be released in the following process.

$$_1H^1 \rightarrow {}_2He^4 + \text{energy}$$

A decrease in mass of 1 0000 atomic mass unit corresponds to an energy release of 931 million electron volts Consider the masses involved as $_1H^1 = 1.008123$ and $_2He^4 = 4.00390$

13 Complete the following equations for radioactive decay processes

(*a*) $_6C^{11} \rightarrow {}_5B^{11} + \text{——}$
(*b*) $_{11}Na^{24} \rightarrow \text{——} + e$
(*c*) $_{90}Th^{232} \rightarrow {}_{88}Ra^{228} + \text{——}$
(*d*) $_{16}S^{35} \rightarrow {}_{17}Cl^{35} + \text{——}$
(*e*) $_8O^{15} \rightarrow \text{——} + e^+$
(*f*) $_{94}Pu^{239} \rightarrow \text{——} + \alpha$

14 Complete the following equations for nuclear bombardment reactions

(*a*) $_7N^{14} + {}_0n^1 \rightarrow {}_6C^{14} + \text{——}$
(*b*) $_{17}Cl^{37} + {}_0n^1 \rightarrow \text{——} + \gamma$
(*c*) $_{15}P^{31} + {}_1H^2 \rightarrow {}_{14}P^{32} + \text{——}$
(*d*) $_{24}Cr^{50} + {}_1H^2 \rightarrow \text{——} + {}_0n^1$
(*e*) $_{25}Mn^{55} + {}_0n^1 \rightarrow \text{——} + 2\ {}_0n^1$
(*f*) $_{29}Cu^{63} + {}_2He^4 \rightarrow {}_{31}Ga^{66} + \text{——}$
(*g*) $_{94}Pu^{239} + {}_2He_4 \rightarrow {}_{96}Cm^{241} + \text{——}$
(*h*) $_{92}U^{238} + {}_0n^1 \rightarrow {}_{57}La^{143} + \text{——} + 3\ {}_0n^1$

15 The half-life of $_{15}P^{30}$ is 3 minutes If one starts with 1 mg of this radioactive isotope, how much would remain after 15 minutes? Ans 0 03125 mg

16 In the fission of $_{92}U^{235}$ into two new nuclei, loss of about 0 2 mass units occurs, with concomitant energy emission Since 931 mev equates to one mass unit, the $_{92}U^{235}$ fission yields how many mev per initial nuclear unit? A gram atomic weight of $_{92}U^{235}$ (which is about $\frac{1}{4}$ pound) on fission will yield how many mev? How many calories? (Use the energy calculation associated with $_3Li^7 + {}_1H^1$, as explained on page 412, as an example)

Ans. Almost $4\ 4 \times 10^{12}$ calories.

17 Draw atomic-structure diagrams of $_{15}P^{30}$, $_{15}P^{31}$, $_{15}P^{32}$, $_{82}Pb^{206}$, $_{82}Pb^{210}$, $_{82}Pb^{214}$

18 On the physical atomic-weight scale, the mass of O^{16} is taken as the standard and assigned the value of exactly 16 00000 On this scale, ordinary oxygen—which is a mixture of O^{16}, O^{17}, and O^{18}—has a physical atomic weight of 16 004352 This mass, then, is the standard for chemical atomic weights Calculate the factor for converting physical to chemical atomic weights

Ans 1 000272

19 If $C^{12}H_4$ could be converted into O^{16}, a loss of 0.0363 mass units would occur (*a*) If one mass unit equals 931 mev, how many mev would be involved per atom of O^{16} formed? (*b*) If a mole of CH_4 changed to O^{16}, how many mev and how many calories would be produced?

Ans. (*a*) 33 8 mev (*b*) 203×10^{23} mev; 7×10^{11} cal

20 Use the following information to plot the curve of radioactive-ray emission for C^{14} The vertical axis of the graph will show radioactive emission in per cents. Using suitable unit divisions on this axis, mark a scale from 0% (radioactive

emission of carbonaceous materials buried for an infinitely long time) to 100% (radioactive emission from recently living carbonaceous material). The horizontal axis of the graph will show time in years. Since 5600 years is the half-life of C^{14}, use suitable divisions on the horizontal axis to show 5600; 11,200; 16,800; and 22,400 years. Plot points on a curve showing that the residual radiation from C^{14} at these periods of time will be 50%, 25%, 12.5%, and 6.25%, respectively. Use the graph to give estimates for the following:

(*a*) The age of charcoal from fire in a cave of prehistoric man if radioactive emission is 30% that of present-day new charcoal.

(*b*) The age of parchment paper sealed in jars in a cave and giving 70% emission compared to present-day paper.

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thirty-two

ELECTRO-CHEMISTRY

Electrochemistry is that division of chemistry dealing with (1) use of an electric current to cause chemical changes and (2) generation of an electric current by chemical change. Applied electrochemistry is important in the manufacture of many industrial products; thus, hydrogen and oxygen may be produced by electrolysis of water; electrolysis of an aqueous solution of sodium chloride yields hydrogen, sodium hydroxide, and chlorine; many metals are purified by electrodeposition; aluminum and the alkaline earth metals are produced by electrolysis of nonaqueous solutions of their respective compounds.

Conduction of the electric current The electric current may be carried by either of two types of conductors: (1) a metallic conductor such as a piece of copper wire, or (2) a solution of an electrolyte, for example, a solution of sodium chloride in water. (1) is called a conductor of the *first class,* and (2) a conductor of the *second class.* In a conductor of the first class, electricity is carried simply by a movement of electrons through the metal, while in a conductor of the second class, the current is carried by the ions in solution moving toward the electrodes of opposite charge. In the latter case since an ion is a charged particle of matter, the passage of current involves the transport of matter, which is an essential difference from conduction in metals.

Electrolysis This consists of passing a direct current through a solution of an electrolyte between two electrodes where chemical changes take place. In electrolysis of aqueous hydrogen chloride (hydrochloric acid), principal ions in the solution are H_3O^+ and Cl^-. Chloride ions (anions) move toward the anode, where they give up their electrons. These electrons move through the metallic conductor and through the battery or generator of the electric current to the cathode, where hydronium ions (cations) are discharged by taking up these electrons. The battery or generator is simply a device for moving electrons from one electrode

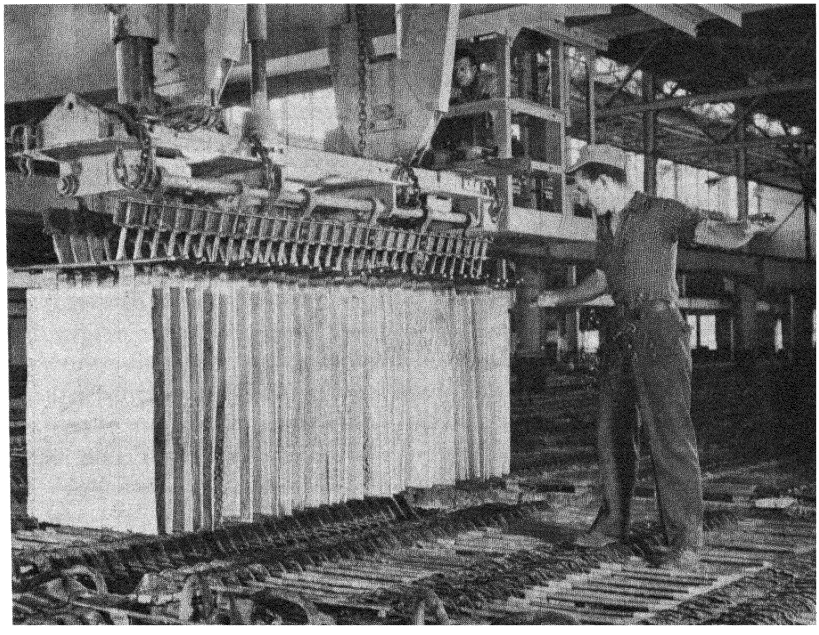


Figure 32–1 Tank room in an electrolytic refinery.

to the other. Since this process involves transfer of electrons, the chemical change occurring must be oxidation-reduction. At the anode, electrons are given up by anions; hence *oxidation takes place at the anode;* at the cathode, electrons are taken up by cations; hence *reduction takes place at the cathode.*

Electrical units When a current passes through a conductor (first or second class) a certain *resistance* to its passage is offered, which depends on the nature of the conductor. The greater the resistance of a conductor, the poorer the conductance; thus, water offers a high resistance to passage and is a poor conductor, but hydrochloric acid has low resistance and is a good conductor. The unit of electrical resistance is the *ohm,* defined as the resistance of a column of mercury 106.3 cm. long, weighing 14.4521 g. and of uniform cross section. The unit of current is the *ampere,* defined as that current necessary to deposit .001118 g. of silver in one second from a solution containing silver ions. The unit quantity of electricity is the *coulomb,* defined as a current of one ampere flowing for one second (an ampere-second).

For a current to pass from one point to another through a conductor, a *difference of potential* or *electromotive force* must exist. Just as water will

flow only from a higher to a lower level, so electricity will pass only from a region of high potential to one of lower potential. The unit of electrical potential or electromotive force is the *volt*, defined as that potential which will drive a current of one ampere through a resistance of one ohm.

Faraday's laws In 1833, Michael Faraday, an English scientist, discovered that during electrolysis (1) *the quantities of substances produced at the electrodes are directly proportional to the quantity of electricity passing through the solution*, and (2) when a given quantity of electricity is passed through solutions of several electrolytes, *the weights of substances formed at the electrodes are directly proportional to their equivalent weights* (atomic weight divided by valence). The quantity of electricity required to liberate one equivalent of an element was found to be 96,500 coulombs, called a *faraday*. If one faraday is passed through a series of solutions as shown in Figure 32–2, one equivalent of substance is liberated at each electrode—that is, 1.008 g. of hydrogen, 107.88 g. of silver, and $\frac{63.57}{2} = 31.78$ g. of copper.

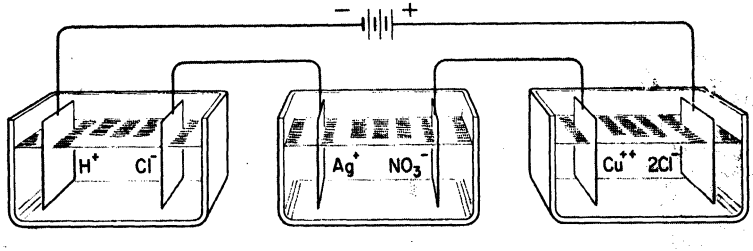


Figure 32–2 One equivalent of an element is deposited for each faraday of electricity passed through the solution.

Voltaic cells Since an electric current may cause a chemical change, can the process be reversed—can a current be generated from a chemical reaction? The answer is yes, if certain conditions are followed.

Chemical changes are always attended by energy changes, usually in the form of heat and light. To produce an electrical current, chemical energy must be transformed to electrical energy instead of to heat and light energy. As in electrolysis, electrons must be transferred; thus, the reaction must be one of oxidation-reduction. If a strip of metallic zinc is dipped into a solution of cupric sulfate, zinc goes into solution as zinc ion (zinc is more active than copper), and metallic copper is formed. This may be represented by:

$$Cu^{++} + Zn \rightarrow Cu + Zn^{++}$$

or by the two-half reactions

$$Zn \rightarrow Zn^{++} + 2e \text{ (oxidation)}$$
$$Cu^{++} + 2e \rightarrow Cu \text{ (reduction)}$$

Electrons are transferred directly from zinc to copper ions. The action is exothermic; the heat energy released is absorbed by the solution and container. No electric current has been generated in this case, but if the oxidation and reduction reactions could be made to take place at *different points* in the solution and the transfer of electrons was made through a metallic conductor, then at least a part of the chemical energy would be transformed into electrical energy. Thus, if we set up an arrangement as shown in Figure 32–3 in which metallic zinc is in contact with its ions, and at another point a strip of copper is in contact with copper ions, an electric current is generated by the flow of electrons through the wire which connects the two metals outside the solution. This will be indicated by a deflection of the needle of the voltmeter connected in series between the two electrodes. A porous diaphragm serves to prevent mixing of the solutions of zinc and copper ions but allows the passage of the SO_4^{--} under the influence of the current. To generate an electric current, the reaction must be one of *oxidation-reduction,* and *these two processes must be made to take place at different points in a solution.*

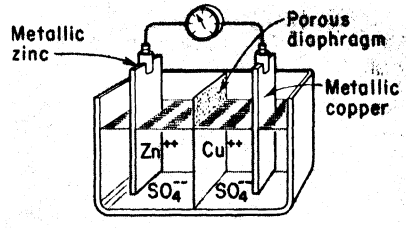


Figure 32–3 The Daniell cell. Electrons flow from the Zn electrode to the Cu electrode, thus generating an electric current.

Electrode potentials When a metal is placed in contact with water, the metal shows a tendency to pass into solution to produce ions of the metal and consequent liberation of electrons to the metal surface. This tendency of a metal to lose electrons sets up an electrical potential difference between the metal and the solution, and the resulting voltage is termed the *electrode potential* for that particular metal. As ions of the metal are formed, the reverse of the process—that is, deposition of metal from ions—occurs; eventually, an equilibrium exists between the metal and its ions.

If a metal is placed in contact with its ions and the tendency of the ions to deposit out is greater than the tendency of the metal to pass into solution, then the ions will deposit out until equilibrium between

metal and ions has been established. The potential difference between a metal and a solution of its ions at a concentration of 1 molar is termed the *standard electrode potential* and is designated as E^0. The tendency for different metals to form ions and give electrons varies widely; therefore, the electrode potentials of metals vary greatly. In the cell described above, if the concentrations of Zn^{++} and Cu^{++} are fixed at 1 molar, zinc shows a much greater tendency than copper to produce ions in solution; thus, electrons flow through the wire from the zinc electrode to the copper electrode where copper ions are actually deposited from solution by taking up these electrons. The potential difference between the zinc and copper electrodes will depend upon the facility with which electrons are transferred from one electrode to the other and therefore depends upon the difference in electrode potentials of the two metals. The difference in the electrode potentials of copper and zinc is 1.1068 volts; consequently, that is the voltage of the cell.

Absolute electrode potentials are not readily determined as the potential difference between a metal and a solution of its ions cannot be recorded on a voltmeter directly. However, if the metal and its solution are made one half of a cell in which the other half is likewise made up of a metal and a solution of its ions, then the potential difference of the two half cells can be measured and a relative value or relative potential may be assigned. Thus, in the zinc and copper cell, while we do not know the absolute potential difference of either of the half cells, or *couples*—that is, $Zn \rightarrow Zn^{++}$ and $Cu \rightarrow Cu^{++}$—the relative potential of one to the other can be said to be 1.1068 volts.

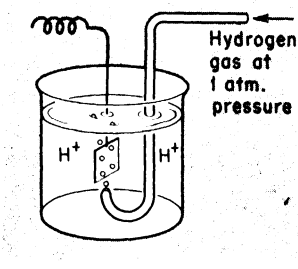


Figure 32–4 The hydrogen electrode.

In order to arrive at a working system of electrode potentials, all values are referred to a standard electrode—the hydrogen electrode, which has been assigned the arbitrary value of zero potential. The electrode (Figure 32–4) consists of a piece of platinum foil which has been coated with a spongy deposit of platinum black in contact with a solution containing hydrogen ions of a concentration of 1 molar. Hydrogen gas at one atmosphere pressure is bubbled over the platinum electrode, setting up the equilibrium:

$$H_2 \rightleftharpoons 2\,H^+ + 2\,e \qquad E^0 = 0$$

By using this hydrogen half cell in conjunction with a half cell composed of a metal and its ions at a concentration of 1 molar, the poten-

tial of the metal compared to the standard can be measured. Thus, if the cell indicated in Figure 32–5 is set up, the voltage is .762, and since zinc gives up electrons more easily than does hydrogen, the standard potential of the $Zn–Zn^{++}$ electrode is recorded as $+.762$. The electrode potential of $Cu–Cu^{++}$ may be determined in a similar manner. Since, in the cell reaction, hydrogen gives up electrons to form H^+, and Cu^{++} takes up these electrons, copper gives up electrons less readily than hydrogen, and the voltage of the $Cu–Cu^{++}$ couple is recorded as $-.3448$.

By combining the two half cells $Zn–Zn^{++}$ and $Cu–Cu^{++}$, it is evident that the potential difference of such a cell should be $.762 - (-.3448) = 1.1068$ volts

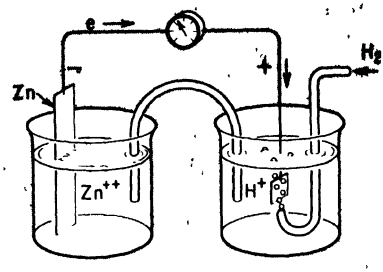


Figure 32–5 The voltage of the cell if .762 volt. Since *E* for the hydrogen electrode is arbitrarily taken as 0, the *E* for the zinc electrode is taken as +.762.

Standard electrode potentials of several of the common metals are given in Table 32–1.

TABLE 32–1 Standard Electrode Potentials

HALF-CELL REACTION	E°
$K \rightleftarrows K^+ + e$	+2 92
$Ba \rightleftarrows Ba^{++} + 2e$	+2 90
$Ca \rightleftarrows Ca^{++} + 2e$	+2 87
$Na \rightleftarrows Na^+ + e$	+2 71
$Mg \rightleftarrows Mg^{++} + 2e$	+2 34
$Al \rightleftarrows Al^{+++} + 3e$	+1 67
$Zn \rightleftarrows Zn^{++} + 2e$	+0 762
$Fe \rightleftarrows Fe^{++} + 2e$	+0 44
$Sn \rightleftarrows Sn^{++} + 2e$	+0 14
$Pb \rightleftarrows Pb^{++} + 2e$	+0 13
$H_2 \rightleftarrows 2H^+ + 2e$	0 0
$Cu \rightleftarrows Cu^{++} + 2e$	−0 3448
$Ag \rightleftarrows Ag^+ + e$	−0 7995
$Pt \rightleftarrows Pt^{++} + 2e$	−1 2
$Au \rightleftarrows Au^{+++} + 3e$	−1 42

The metals in this electromotive series are in the same order as in the activity series (see page 93). Thus, the activity of a metal is a measure of its ability to lose electrons. Table 32–1 shows that the half reactions, when written to give up electrons, are oxidation reactions. The elec-

trode potentials are sometimes referred to as *oxidation potentials.* If the half reaction is written as a reduction (electrons taken up), then the potential may be termed a reduction potential. It will have the same value as the oxidation potential, but with the sign reversed. The magnitude of the positive oxidation potential is a measure of the ease with which a given metal is oxidized; that is, a measure of the reducing capacity of the metal. Thus, of the metals listed in Table 32–1, potassium is the best reducing agent, and K^+ is the poorest oxidizing agent; Au^{+++} is the best oxidizing agent and Au is the poorest reducing agent. Reducing ability decreases on the left side and oxidizing ability increases on the right side (for the ions) in going from top to bottom of the table. Thus, any metallic ion in the table should oxidize any of the metals appearing above it in the series—Zn^{++} should oxidize Mg but not Cu; Cu^{++} will oxidize Zn but not Ag.

This information also can be derived by combining couples, writing down the cell reaction, and considering the voltage of the cell. If the cell potential is positive, then the reaction (cell reaction) will proceed as written. Consider the reaction

$$Pb^{++} + Zn \rightarrow Pb + Zn^{++}$$

involving the couples $Zn \rightarrow Zn^{++}$ and $Pb^{++} \rightarrow Pb$. The potential of the first couple is .762; that of the second is .126. Since in the above reaction Pb^{++} accepts electrons (reduction), the sign of the potential will be reversed and given the value $-.126$.

$$\begin{aligned} Zn &\rightarrow Zn^{++} + 2\,e \quad & E^0 &= \quad .762 \text{ (oxidation)} \\ 2\,e + Pb^{++} &\rightarrow Pb & E^0 &= -.126 \text{ (reduction)} \end{aligned}$$

Adding the two steps to obtain the cell reaction:

$$Zn + Pb^{++} \rightarrow Zn^{++} + Pb \quad E_{cell} = +.636$$

Since the potential for the cell is positive, the reaction will proceed as written—that is, Pb^{++} will oxidize Zn.

Consider a second example: Will Ag^+ oxidize Au? In other words, will the following reaction occur?

$$Au + 3\,Ag^+ \rightarrow Au^{+++} + 3\,Ag$$

Setting up the two half reactions (one oxidation, one reduction):

$$\begin{aligned} Au &\rightarrow Au^{+++} + 3\,e \quad & E^0 &= -1.42 \quad \text{(oxidation)} \\ 3\,e + 3\,Ag^+ &\rightarrow 3\,Ag & E^0 &= \quad .7995 \text{ (reduction)} \end{aligned}$$

The latter potential is positive because the step is reduction (the table gives oxidation potentials). The fact that 3 electrons are involved in

balancing does not change the potential. Adding the two steps, we obtain

$$Au + 3\,Ag^{+} \rightarrow Au^{+++} + 3\,Ag \qquad E_{cell} = -0.6205$$

The negative value for the voltage of the cell indicates that the reaction will *not* proceed as written. The reverse change will take place.

A further discussion of oxidation potentials is beyond the scope of this book. However, oxidation potentials may be determined for most oxidation processes; see Appendix, page 568, for a brief table of other oxidation potentials. This information is invaluable in predicting the possibility of a given reaction. The process outlined above may be employed. If the potential of a cell (which may be a hypothetical one) is positive, the reaction will proceed as written. Of course, concentration effects are important factors in determination of oxidation potentials; in some cases when the oxidation potentials are nearly the same, concentration effects may serve to reverse the reaction that might be predicted from the standard electrode potentials (which are for 1 molar solutions of ions).

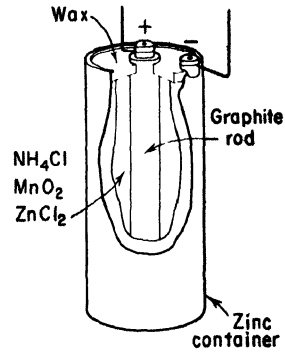


Figure 32-6 The dry cell.

The dry cell For small intermittent currents such as for flashlights and door bells the dry cell is convenient and effective (see Figure 32-6). The cell consists of a zinc container which acts as the negative electrode; a graphite rod as the positive electrode, and a paste of ammonium chloride, zinc chloride, manganese dioxide, and water as the electrolyte. Although the substances are present in a semisolid (paste) state, the cell is not really dry, and a wax seal on the top of the cell is used to prevent evaporation of water. At the negative electrode, Zn passes into solution as Zn^{++}, giving up electrons to the electrode.

$$Zn \rightarrow Zn^{++} + 2e$$

At the carbon electrode (positive pole), ammonium ion is converted into ammonia and hydrogen by taking up electrons:

$$2e + 2\,NH_4^{+} \rightarrow 2\,NH_3 + H_2$$

The products of this reaction are gases which must be removed, since their accumulation would result in a swelling and eventual bursting of the cell. Ammonia gas is absorbed by the zinc ions present, forming the complex $Zn(NH_3)_4^{++}$ ion:

$$Zn^{++} + 4\,NH_3 \rightarrow Zn(NH_3)_4^{++}$$

Hydrogen gas formed at the carbon electrode tends to remain in contact with the electrode. An accumulation of the gas forms an insulating layer which increases the resistance of the cell, thereby reducing the voltage of the cell. Such a cell is said to be *polarized* The manganese dioxide functions as a *depolarizer* since it oxidizes the hydrogen to water by the reaction:

$$MnO_2 + H_2 \rightarrow MnO + H_2O$$

If current is drawn from a dry cell continuously, the voltage soon drops because of accumulation of hydrogen on the carbon electrode. After a brief period of disuse, the hydrogen is slowly oxidized by the manganese dioxide, and the voltage of the cell rises to 1.5 volts, the normal value

The storage battery The storage battery is a cell which, after discharge, can be restored to its original state by passage of a direct electric current through the cell from an outside source. Theoretically, the reaction which takes place in any cell producing an electric current may be reversed by passing an electric current through the cell in the opposite direction. Practically, this cannot be done with most cells; a storage cell is one in which a cell reaction may be carried out *reversibly.*

The lead storage battery is the most common of this type. The electrodes consist of plates or grids arranged in pairs; the negative electrode is a sheet of pure lead and the positive pole a framework of lead in which lead dioxide has been deposited. The electrolyte is sulfuric acid. When the cell is discharging—producing an electric current—lead from the negative electrode produces lead ions which immediately combine with sulfate ions from the sulfuric acid to precipitate insoluble lead sulfate:

$$Pb \rightarrow Pb^{++} + 2e$$
$$Pb^{++} + SO_4^{--} \rightarrow PbSO_4 \downarrow$$

Adding these reactions, the net reaction at the negative pole is:

$$Pb + SO_4^{--} \rightarrow PbSO_4 \downarrow + 2e$$

At the positive pole of the battery, lead dioxide is reduced to Pb^{++} by taking up electrons according to the equation

$$2e + PbO_2 + 4\,H^+ \rightarrow Pb^{++} + 2\,H_2O$$

Lead ion immediately combines with sulfate ion to precipitate lead sulfate:

$$Pb^{++} + SO_4^{--} \rightarrow PbSO_4 \downarrow$$

The net reaction at the positive pole is then:

$$2e + PbO_2 + 4\,H^+ + SO_4^{--} \rightarrow PbSO_4 \downarrow + 2\,H_2O$$

The sum of the reactions taking place at the two electrodes gives as the over-all reaction occurring during *discharge* of the battery:

$$Pb + PbO_2 + 2\ H_2SO_4 \rightarrow 2\ PbSO_4 \downarrow + 2\ H_2O$$

During *charge* of the battery this reaction is reversed:

$$2\ PbSO_4 + 2\ H_2O \rightarrow Pb + PbO_2 + 2\ H_2SO_4$$

It is evident that during discharge the concentration of sulfuric acid in the cell decreases; during charge the sulfuric acid is regenerated and its concentration in the cell thus increased. The state of charge of a battery may be approximately determined by means of a hydrometer which gives the specific gravity of the acid. In a fully charged battery the specific gravity of the acid is about 1.30. The voltage of the lead storage cell is about two volts. For automobile batteries, several cells are used in series to give a total potential of six or twelve volts.

Electroplating Very often, in order to prevent a metal from corroding or to give it a more pleasing appearance, a second metal may be coated over it. This is most effectively accomplished electrolytically. The metal object which is to be coated or plated is made the cathode in an electrolytic cell (Figure 32–7). The anode usually consists of a strip of the plating metal dipping into the electrolyte. As the current is passed through the cell, the plating metal dissolves at the anode and the ions thus produced migrate to the cathode where they are discharged and plated out upon the object. Any desired thickness of deposit may be obtained. If one metal does not adhere well to another, a series of platings may be necessary; for example, an auto bumper may be first plated with copper, then with nickel, and finally with chromium.

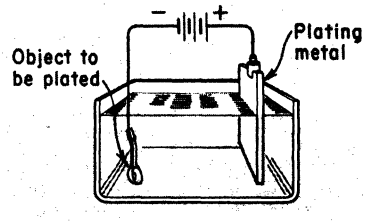


Figure 32–7 A spoon may be silver plated by making it the cathode in a cell in which a bar of pure silver acts as anode. A $NaAg(CN)_2$ solution makes a good electrolyte.

EXERCISES

1 What is the difference between conductors of the first and second classes?

2 Calculate the quantity of electricity in coulombs necessary to deposit 15.89 g. of copper from a solution of $CuSO_4$. Ans. 48,250 coulombs.

3 What are the necessary conditions which must be fulfilled to obtain electrical energy from chemical energy?

4 From the table of standard electrode potentials (page 437), determine the electromotive force of the following cells:

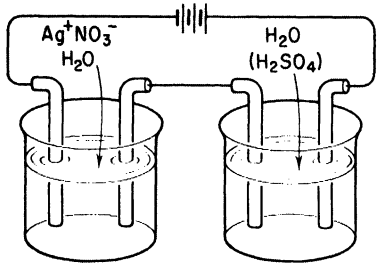
(*a*) Zn, Zn^{++} and Pb^{++}, Pb (*c*) Al, Al^{+++} and Fe^{++}, Fe
(*b*) Cu, Cu^{++} and Ag^{+}, Ag (*d*) H_2, H^{+} and Mg^{++}, Mg

5 Define the terms: ohm, volt, coulomb, ampere, faraday, depolarizer.

6 Write equations for reactions taking place at the electrodes during
(*a*) Electrolysis of a solution of copper sulfate with copper electrodes.
(*b*) Discharge of a dry cell.
(*c*) Discharge of a lead storage cell.
(*d*) Electrolysis of aqueous sodium bromide solution.

7 What weight of copper would be deposited from a solution of $CuSO_4$ by the passage of a current of 0.5 ampere for two hours? Ans. 1.19 g.

8 The two electrolytic cells below are connected in series:



Only a few drops of H_2SO_4 are added to the water in the second cell. When a sufficient quantity of electricity is passed through the solutions to deposit 107.9 g. of silver on the cathode of the first cell, what volumes of hydrogen and oxygen at standard conditions would be produced in the second cell? Ans. 11.2 l.; 5.6 l.

9 According to Faraday's laws, 96,500 coulombs of electricity if passed through suitably constructed electrolytic cells would produce what weight of each of the following (atomic weights are in parenthesis): (*a*) hydrogen (1), (*b*) silver (107.9), (*c*) copper (63.5), (*d*) aluminum (27)?

10 The same amount of electricity which deposits 0.415 g. of silver will deposit 0.254 g. of gold from a solution. What is the equivalent weight of gold? Ans. 65.7.

11 How long must a current of 10 amperes be passed through a bath of molten $CaCl_2$ in order to liberate .04 g. of metallic calcium at the cathode?

12 In the electrolysis of aqueous NaCl, a sufficient quantity of electricity is used to liberate 7.1 g. of chlorine gas at the anode. What volume of hydrogen (at standard conditions) would be liberated at the cathode? Ans. 2.24 l.

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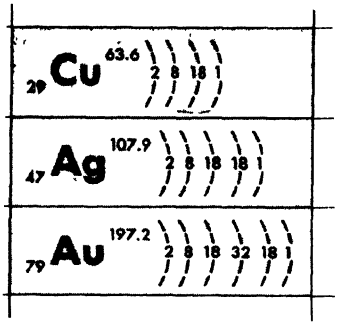
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thirty-three

COPPER, SILVER, GOLD

METAL	SYMBOL	SP GR	MELTING POINT	BOILING POINT	OXIDATION STATES
Copper	Cu	8.9	1083	2340	+1, +2
Silver	Ag	10.5	961	1950	+1
Gold	Au	19.3	1063	2600	+1, +3

These three metals are transition elements of Group I*B* of the periodic table. A marked contrast in properties is to be observed between the members of divisions *A* and *B* in this group. Metals of division *A* (alkali metals) are very active chemically, but the metals of division *B* are very resistant to chemical action and are near the bottom of the activity series. However, copper, silver, and gold have one electron in the outer structure of their atoms and therefore exhibit a characteristic oxidation state of +1. Copper and gold also exhibit higher oxidation states, which may be attributed to the transfer of one or more electrons from an inner to the valence orbit.

COPPER

The use of copper is older than written history. References to it are made in early writings, and objects of copper and bronze have been

found dating back to three or four thousand years before the Christian era. Because of its relative inactivity and resistance to corrosion, copper is used extensively in the preparation of a wide variety of articles.

Occurrence Copper ores are widely distributed over the earth's surface. Large deposits of native copper are found in the Lake Superior region of Michigan, on the island of Cyprus, and in Bolivia. However, the metal usually occurs in the combined state as sulfides, oxides, or carbonates. Most of the copper produced in this country comes from sulfide minerals, chief of which is *chalcopyrite,* $CuFeS_2$. Another important sulfide mineral is *chalcocite,* Cu_2S. In general, sulfide ores are of low grade, the copper content usually running from 1 to 10 per cent. Oxide and carbonate ores have been formed as a result of the action of dissolved oxygen and carbon dioxide in ground water. *Cuprite,* Cu_2O, a reddish mineral, and *malachite,* $CuCO_3 \cdot Cu(OH)_2$, a green mineral, are important so-called oxidized copper minerals. Principal copper-producing localities in the United States are Montana, Arizona, and Utah. South America and central Africa have large producing copper mines.

Copper in fairly high percentage has been found in the feathers of certain birds of brilliant plumage. It is interesting that the touraco bird of Africa has quite a high copper content in its feathers, which have the red color of cuprite and the green color of malachite. Traces of copper are found in several sea plants and marine animals. In oysters, it appears that a copper compound is substituted for an iron compound as an oxygen carrier in the hemoglobin of the blood. There is some evidence to indicate that copper in minute amounts may play a vital role in the health and well-being of man and animals. For example, a healthy cow's liver contains between 40 and 200 parts per million of copper.

Metallurgy In general, the metallurgy of copper is quite complex, and the method of treatment depends upon several factors including the type of ore and the facilities for treatment. We shall outline here only the principal types of treatment. Native copper ores require the simplest of the metallurgical processes. The ore, which consists of copper pellets dispersed in silica and rock, is crushed and heated to a temperature sufficient to melt the metal. The metal is heavier than the rock or gangue with which it is associated and settles to the botom and may be separated. In some cases separation is effected by mechanical means; the lighter particles of silicate rock are floated away by washing the ore with large quantities of water.

Oxide and carbonate ores may be reduced with carbon or mixed with sulfide ores and smelted with the latter. Low grade oxide ores are often

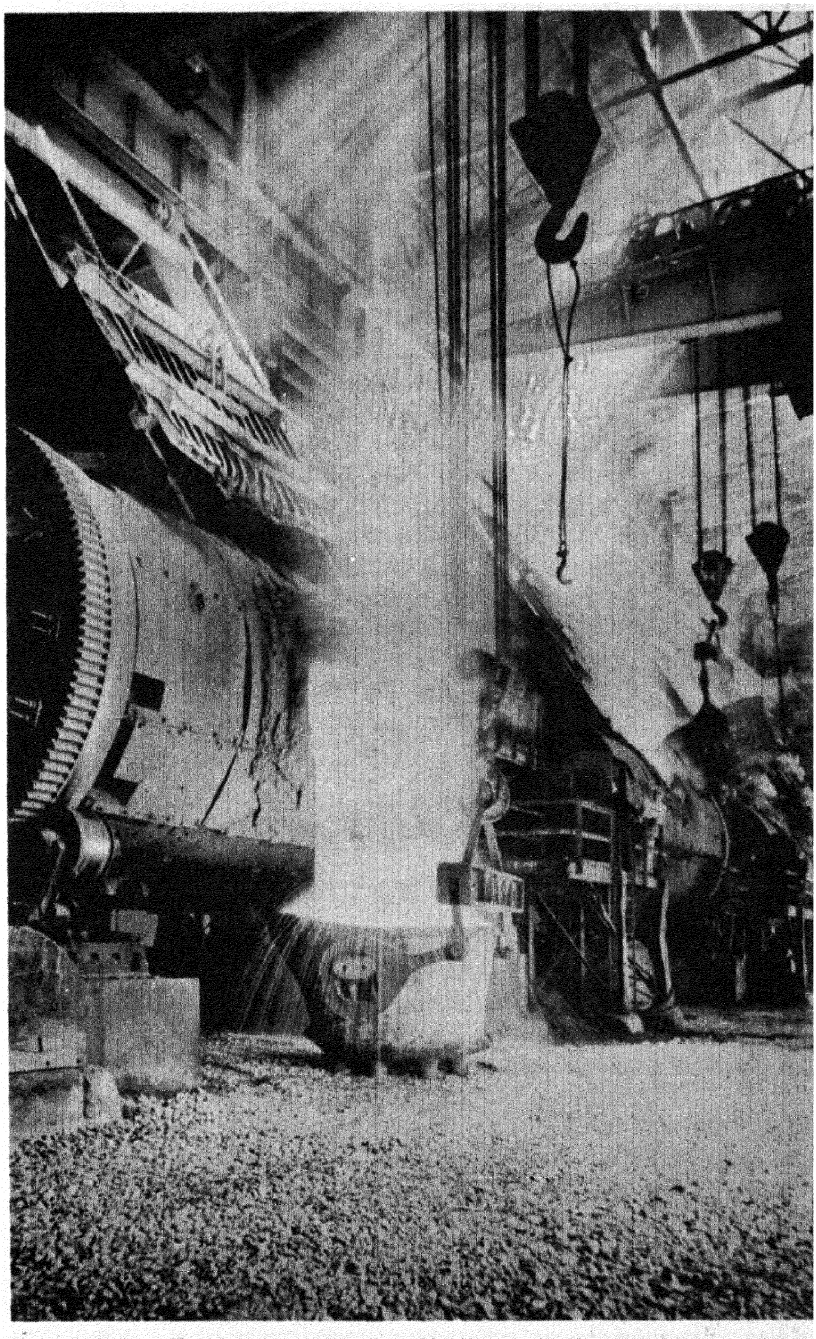


Figure 33–1 Copper converters.

leached with sulfuric acid, after which the copper sulfate solution is electrolyzed and the copper plated out.

Eighty per cent of the copper produced in this country comes from sulfide ores, most of which are low grade and associated with large quantities of iron pyrites and silica. After the ore is crushed, it is concentrated by gravity and flotation processes (see page 366). The ore concentrate, which contains 20 to 50 per cent copper, is roasted to remove some of the sulfur. Following the roasting process, the ore is smelted in special reverberatory furnaces with arching roofs to reflect the heat down to the charge. Limestone, which combines with the silica to form a slag of calcium silicate, is added as a flux. Some ferrous oxide also combines with silica to form ferrous silicate. A heavy molten layer of a mixture of iron and copper sulfides called "copper matte" remains under the liquid slag. After drawing off the slag, the liquid copper matte is charged into a converter made of steel plates and lined with magnesia. The converter, quite similar to the Bessemer converter used for the production of steel, is equipped in such a way that a blast of air may be blown through the charge from small holes in the bottom of the converter. The blast of air oxidizes the iron sulfide to the oxide:

$$2\ FeS + 3\ O_2 \rightarrow 2\ FeO + 2\ SO_2 \uparrow$$

This action takes place before the sulfides of copper are converted to oxide, since iron sulfide is more easily oxidized than copper sulfide. The oxidation process produces enough heat to keep the mass molten and no fuel is necessary. Silica is added to form a slag of ferrous silicate with the iron oxide:

$$FeO + SiO_2 \rightarrow FeSiO_3$$

The charge in the converter is approximately 65 tons. Removal of the iron requires approximately three hours. The slag is removed at intervals by tilting the converter until oxidation of iron sulfide is complete. The air blast is continued for approximately two hours more and the sulfide of copper is slowly oxidized:

$$2\ Cu_2S + 3\ O_2 \rightarrow 2\ Cu_2O + 2\ SO_2 \uparrow$$

The oxide thus formed reacts with the sulfide present to form metallic copper:

$$2\ Cu_2O + Cu_2S \rightarrow 6\ Cu + SO_2$$

In order to remove the slag completely, the metal is treated in a small reverberatory furnace which permits a careful control and skimming off of slag. Traces of copper oxide are removed by stirring the charge with

poles made from green saplings. These poles act as reducing agents to change oxide to metallic copper. The product, called "blister copper" because of blisters formed on the surface by the escape of gas, is cast into large blocks or plates for electrolytic refining.

Electrolytic refining of copper Blister copper is approximately 99 per cent copper, the remaining 1 per cent being made up of gold, silver, arsenic, bismuth, iron, and zinc. Nearly all of the gold and silver present in the original ore is retained by the blister copper, and their recovery from the refining process furnishes approximately one-fourth of the silver and about one-seventh of the gold used for commercial purposes. Arsenic is a particularly objectionable element in copper as it very appreciably lowers the conductivity of the metal, and since large quantities of copper wire are used in the transmission of electric power, it is necessary that arsenic be absent in the finished product. Bismuth and iron in the copper make for brittleness.

Blister copper is refined electrolytically. Reference to Figure 33-2 will make the operation of the process clear. The copper anode consists of a block of blister copper approximately three feet square and two inches thick, and a thin sheet of pure copper is used as the cathode. The electrolyte consists of an aqueous solution of copper sulfate, sulfuric acid, and sodium chloride. On passage of the current, copper dissolves at the anode by giving up two electrons per atom. The resulting copper ions migrate toward the cathode where they are deposited; as a result the copper cathode gradually increases in size as the anode decreases in size. Iron and zinc ions also pass into solution along with the copper at the anode, but by proper regulation of the voltage, these ions are not deposited at the cathode. Silver ions, which are also produced at the anode, are immediately precipitated by chloride ions from the sodium chloride, and the precipitated silver chloride settles to the bottom of the electrolytic tank. Gold, platinum, and arsenic do not go into solution and drop to the bottom of the tank in the form of a sludge called "anode mud," which is later refined and the valuable metals recovered. The value of the gold and silver obtained from this sludge is sufficient to pay for the entire cost of the electrolytic refining. The copper plated out on the cathode is 99.95 per cent pure. The cathode copper is remelted and cast into bars for wire rolling mills.

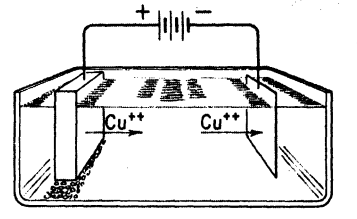


Figure 33-2 Electrolytic refining of copper.

Properties Copper is a soft metal with a melting point of 1083° and a boiling point of about 2300°. By reflected light it appears red in color and by transmitted light in thin sheets its color is green. The metal is very ductile and malleable, and, while not as tough as iron, it may be used for many structural purposes. It does not respond to heat treatment as does steel, but the addition of small quantities of alloying elements such as manganese and silicon yields a product which may be hardened by heating.

Copper lies low in the activity series and thus is quite resistant to corrosion. Dry air, water, and nonoxidizing acids do not attack the metal. However, long exposure to air and moisture gradually forms a tightly adhering coating of a green basic carbonate on the surface. Corrosion then ceases, in direct contrast to the rusting of iron, which in time changes the metal over completely to iron oxide. Hydrochloric acid does not act on copper unless oxygen is present, in which case it gradually dissolves according to the equation:

$$2\ Cu + 4\ HCl + O_2 \rightarrow 2\ CuCl_2 + 2\ H_2O$$

Nitric acid acts readily on the metal to form copper nitrate, but hydrogen is *not* liberated; instead the other products are oxides of nitrogen and water. Hot concentrated sulfuric acid dissolves the metal to form copper sulfate, sulfur dioxide, and water:

$$Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2\ H_2O$$

Copper is an excellent conductor of heat and is second only to silver as a conductor of electricity.

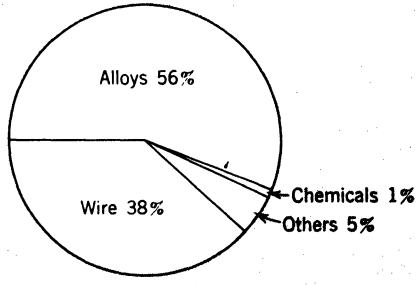


Figure 33–3 Uses of copper.

Uses Large quantities of copper are used for the fabrication of wire, cables, and bars for transmission of the electric current; smaller amounts are used in the construction of motors, generators, and other electrical devices. Because of its resistance to corrosion, copper may be used as a roofing material and for covering ships' bottoms. Cooking vessels used for cooking food in large quantities may be made of copper though, since copper salts are poisonous, it is necessary to clean these utensils frequently to prevent contamination of foods.

One of the principal uses for the metal is in the preparation of alloys. The two most common and important alloys are *brass,* which contains copper and zinc, and *bronze,* which contains copper and tin. Bronze or brass does not refer to alloys of a definite composition but rather to all alloys of copper with zinc and tin in varying percentages. There are many brasses, for example, all varying somewhat in percentage of zinc and other elements present. A small amount of copper is frequently alloyed with steel because the resistance of steel to corrosion is greatly increased by as little as 0.25 per cent copper. Copper is also alloyed with gold, silver, and nickel for coinage purposes.

Compounds of copper Copper forms two series of compounds, *cuprous* in which the valence of copper is 1, and *cupric* compounds in which the valence is 2. In general, the cupric compounds, because they are the more stable, are more commonly used.

Cuprous oxide, Cu_2O, occurs naturally as the mineral *cuprite.* The red oxide may also be obtained by careful oxidation of copper in air or by precipitation of cuprous ions from solutions with sodium or potassium hydroxide. Cuprous hydroxide is not known. Cuprous oxide is also obtained as a reduction product of *Fehling's solution,* a reagent used in the diagnosis of diabetes to test for the presence of reducing sugars in the urine.

Fehling's solution consists of an aqueous solution of copper sulfate, sodium hydroxide, and sodium potassium tartrate (Rochelle salt). The tartrate forms a complex with cupric ion; as a result, so few free cupric ions are left in solution that no precipitate of copper hydroxide is obtained when the sodium hydroxide is added. Reducing sugars reduce cupric ions to cuprous, and cuprous oxide separates as a reddish precipitate.

Black *cupric oxide* may be obtained by heating copper in air to a fairly high temperature, or by heating cupric hydroxide. The compound is used as an oxidizing agent in the analysis of organic compounds and is also used as a starting material in the preparation of many copper salts.

The addition of sodium hydroxide to a solution of cupric ions produces a light blue gelatinous precipitate of *cupric hydroxide.* The latter compound is very unstable toward heat, breaking down to cupric oxide. *Bordeaux mixture* consists of copper sulfate and calcium hydroxide; the mixture produces cupric hydroxide and is widely used as a spray and insecticide.

Copper sulfate, or *blue vitriol,* $CuSO_4 \cdot 5\,H_2O$, is the most important and widely used salt of copper. On heating, the salt slowly loses water to form first the trihydrate, $CuSO_4 \cdot 3\,H_2O$, then the monohydrate, $CuSO_4 \cdot H_2O$, and finally the white anhydrous salt. The anhydrous

salt is often used to test for the presence of water in organic liquids. For example, some of the anhydrous copper salt added to alcohol which contains water will turn blue because of the hydration of the salt.

Copper sulfate is used in electroplating and occasionally in lakes or other bodies of water to kill algae and other vegetative growths. Fishermen dip their nets into copper sulfate solution to inhibit the growth of organisms that play an important part in rotting the fabric.

When ammonium hydroxide is added to a solution of cupric ions, a greenish precipitate of cupric hydroxide or a basic cupric salt is formed, which dissolves as more ammonium hydroxide is added. The excess ammonia forms an ammoniated complex with the cupric ion of the composition, $Cu(NH_3)_4^{++}$:

$$Cu^{++} + 4\,NH_3 \rightarrow Cu(NH_3)_4^{++}$$

This ion is only slightly dissociated; hence in an ammoniacal solution very few cupric ions are present. Most insoluble copper compounds are dissolved by ammonium hydroxide though cupric sulfide is an exception. The formation of the cupric ammonia ion is often used as a test for cupric ion because of its deep and intense blue color.

Cupric ion is reduced by the addition of either sodium or potassium cyanide, forming cuprous cyanide and poisonous cyanogen gas:

$$2\,Cu^{++} + 4\,CN^- \rightarrow 2\,CuCN \downarrow + (CN)_2 \uparrow$$

Cuprous cyanide is soluble in an excess of the cyanide, since it forms a complex cyanide ion, $Cu(CN)_2^-$:

$$CuCN + CN^- \rightarrow Cu(CN)_2^-$$

Since $Cu(CN)_2^-$ is even less dissociated than the ammoniated complex, nearly all insoluble copper salts are soluble in excess alkali cyanides.

Cupric ferrocyanide, $Cu_2Fe(CN)_6$, is obtained as a reddish brown precipitate on the addition of a soluble ferrocyanide to a solution of cupric ions. The formation of this salt is sometimes used as a test for the presence of cupric ions. It is more delicate than the blue color formed with excess ammonia.

SILVER

History and occurrence Metallic silver has been known since prehistoric times. The symbol for silver, Ag, comes from the Latin, *argentum,* which means white. The alchemist associated silver with the moon and used a crescent as the symbol for the element.

In nature, silver occurs both free and combined. In the native state, it is sometimes found as nuggets but usually occurs in veins in rock

masses associated with copper and lead. Principal minerals of silver are *argentite,* Ag_2S, and *argyrite,* AgCl, also called *horn silver.* The element is nearly always present in copper and lead ores and follows these metals through the various metallurgical processes. The refining of copper and lead in which the silver is recovered constitutes one of the principal sources of silver produced; in the United States, approximately 80 per cent of the silver is obtained this way. About 70 per cent of the world's production comes from the western hemisphere, with Mexico the leading producer, followed by the United States, Canada, and Peru.

Metallurgy Since most of the silver produced in this country is a by-product of the refining of copper and lead, the treatment of these latter metals for recovery of silver is of primary interest. In the electrolytic refining of copper, the silver finds its way into the anode sludge or mud along with gold, platinum, bismuth, and arsenic. This sludge, after treatment with dilute sulfuric acid removes most of the base metals, is dried and mixed with sodium carbonate, sodium nitrate, and silica. The mixture is highly heated to oxidize and flux away the remainder of the base metals. Silver remains along with any gold or platinum originally present.

Silver is recovered from lead by the Parkes process, which depends upon the greater solubility of silver in zinc. About one per cent of zinc is added to molten lead and the mixture thoroughly stirred. The silver concentrates in the layer of zinc which is skimmed off. The zinc and silver are separated by distillation; zinc, being more volatile, passes into the distillate and may be used in treating subsequent batches of lead. The silver remaining usually contains gold and some lead and is refined by heating in a shallow hearth made of bone ash or other absorbent material. An oxidizing atmosphere is maintained which oxidizes and volatilizes some of the lead as oxide; the remainder of the liquid lead oxide is absorbed by the bone ash, leaving a silver-gold alloy. The process is called *cupellation.* The silver and gold are separated or *parted* by means of sulfuric or nitric acid which dissolves silver and other metals present but has no effect on the gold. The silver which passes into solution may be further refined by electrolysis.

Silver ores, after being crushed finely, may be leached with a dilute sodium or potassium cyanide solution in the presence of air. Metallic silver or its compounds are soluble because of the formation of a complex cyanide:

$$4\,Ag + 8\,CN^- + O_2 + 2\,H_2O \rightarrow 4\,Ag(CN)_2^- + 4\,OH^-$$

The metal is precipitated from the cyanide solution by the addition of zinc shavings:

$$2\,Ag(CN)_2^- + Zn \rightarrow Zn(CN)_4^{--} + 2\,Ag$$

Properties Silver is a white metal intermediate in hardness between copper and gold. It is ductile and malleable and the best conductor of heat and electricity known. Since silver lies low in the activity series, it is classed as an inactive metal. It is resistant to the action of air, water, alkalies, and the nonoxidizing acids. Sulfur and sulfur compounds attack silver, readily producing a black deposit of silver sulfide; this action is responsible for the tarnishing of the metal. Silver is also attacked by the halogens to form an adhering layer of halide salt which soon stops the action.

Uses Silver is used principally for ornaments, coins, jewelry, and various articles of silverware. Pure silver is too soft for these purposes and is usually alloyed with copper to increase its hardness and durability. *Sterling* is 92.5 per cent silver and 7.5 per cent copper; it is said to be 925 fine. American silver coinage is 900 fine, or 90 per cent silver and 10 per cent copper. Silver is often plated onto cheaper metals. Copper may be readily plated on iron and this in turn may be plated with silver—silver adheres much more readily to the copper than to iron. The plating bath is usually a solution of a complex silver cyanide. Silver may be precipitated on mirrors by reducing a silver salt with an organic reducing agent; the surface is then highly polished.

Compounds of silver *Silver nitrate,* sometimes called *lunar caustic,* is the most important salt of silver. It melts readily and may be cast into sticks for use by surgeons in cauterizing wounds. The salt is prepared by dissolving silver in nitric acid and evaporating the solution. The salt is the starting material for most of the compounds of silver, including the halides which are used in photography. The salt is readily reduced by organic reducing agents with the formation of a black deposit of finely divided silver; this action is responsible for black spots left on the fingers from the handling of the salt. Indelible marking inks and pencils take advantage of this property of silver nitrate.

The *halides* of silver, except the fluoride, are very insoluble compounds and may be precipitated by the addition of a solution of silver salt to a solution containing chloride, bromide, or iodide ions. Of the three halides, silver iodide is the most insoluble. This compound is yellow in color; silver bromide is pale yellow; silver chloride is white. Since all three salts are darkened on exposure to light, they are used in photography.

The addition of a strong base to a solution of a silver salt precipitates brown *silver oxide,* Ag_2O. Normally one might expect the hydroxide of silver to precipitate, but it seems likely that silver hydroxide is very unstable and breaks down into the oxide and water if, indeed, it is ever formed at all. However, since a solution of silver oxide is definitely basic, there must be hydroxyl ions present in solution.

Photography Photography is based upon the sensitivity of the silver halides to light. Of these, silver bromide is most commonly used. The salt is precipitated from silver nitrate and potassium bromide in the presence of gelatin, which acts as a protective colloid (page 353) to prevent the particles of silver bromide from becoming too coarse. The gelatin solution is spread as a thin coating onto glass or film made from cellulose nitrate. The fundamental operations in the preparation of a photograph are described below.

The film is *exposed* by opening the shutter of a camera for a moment. The image of the object being photographed is projected onto the film through the lens, and the light reflected from the object brings about a change in the silver bromide emulsion in direct proportion to the intensity of the light. Light parts of the object will reflect more light than the darker portions and thus effect a greater change on the film, though the change that takes place is somewhat obscure. The film is next *developed* by washing it in a solution of a mild reducing agent, such as hydroquinone or ferrous oxalate. The ease of reduction is a direct function of the intensity of light falling on the film during exposure. The light parts of the object appear as dark patches on the plate because of the reduction of the silver bromide probably to finely divided silver. The film is next *fixed* by washing in a solution of sodium thiosulfate (hypo) which dissolves away the unchanged silver bromide that has not been affected in the exposure stage. After being washed thoroughly with water, this "negative" is dried. *Printing* consists of allowing light to pass through the negative onto paper which is coated with silver bromide. The light and dark portions of the negative are again reversed, and the object now appears as a "positive." The process of developing and fixing the positive is essentially a repetition of the treatment of the negative. The photo may be toned by use of a solution of gold or platinum chloride, which to some extent replace silver to impart characteristic colors.

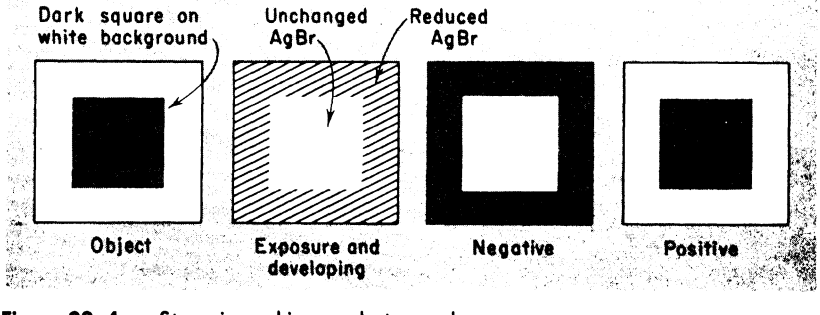


Figure 33–4 Steps in making a photograph.

GOLD

History and occurrence Without question, gold was one of the first metals known to man. History records the use of the metal for jewelry and ornamental purposes in very early times. The fact that the metal occurs free, is pleasing in appearance, and is easily worked would account for its early use. The symbol, Au, is derived from the Latin, *aurum*. Gold occupies a unique place in chemical history since the principal pursuit of the alchemists was to find a method for transmutation of the baser metals into gold.

Gold nearly always occurs in the native state, either in placer deposits in river sands or in veins disseminated in quartz. Native gold is occasionally found in the form of nuggets; one such nugget found in Australia weighed more than one hundred pounds and was worth $50,000. The only combined source of gold of any consequence is the telluride mineral, $AgAuTe_2$, small deposits of which are found in Colorado. Some gold is usually associated with copper and lead ores. While gold is widely distributed over the earth, relatively few deposits are worth working. A very small amount of gold is present in sea water —less than 0.00005 gram per ton of water. More than 50 per cent of the world's supply of gold comes from mines in South Africa.

Gold production The era of gold production that followed the discovery of America was in all probability the greatest the world had witnessed up to that time. The exploitation of mines by slave labor and the looting of palaces, temples, and graves in Central and South America resulted in an influx of gold that unbalanced the economic structure of Europe and disturbed its political structure. The history and romance of Spanish galleons carrying Inca gold as treasure leads us to wonder what were the bulk and value of this gold. From the discovery of America by Columbus in 1492 to 1600, over 8,000,000 ounces of gold came from South America, which was 35 per cent of the world production during this time. This amount of gold would have a bulk of an eight-foot cube and a value of $280,000,000. Contrary to usual belief it did not take many galleons to carry this bulk of gold—there were no large rooms filled with golden treasure. This amount of gold, which seemed of fabulous value to people of the fourteenth century, is small as compared to money values involved in twentieth century world finance. South American mines (especially Colombian mines) continued in the fifteenth and sixteenth centuries to furnish 61 and 80 per cent respectively of world gold production; 48,000,000 ounces were mined between 1700 and 1800. During the second era of intensive gold production, the 25 years following 1850, more gold was

produced in the world than in the 358 years immediately previous, chiefly because of discoveries of gold in California and Australia. A third marked increase in world gold recovery was in the period from 1890 to 1915, when gold discoveries in Alaska, in the Yukon, and on the Rand in the Transvaal were made. A big factor was the introduction of the cyanide process for recovery of gold from low grade ores and ores containing minute, particle size gold.

Throughout the years gold production has increased, until just prior to World War II the average yearly gold production was greater than production during 1493–1600 or 1600–1700. The 1936 world production, for example, was 32,960,158 ounces, having a value of $1,153,605,530 (at $35 an ounce). This amount of gold stacked as gold bricks would make a 13-foot cube. Postwar gold production has not quite reached the prewar level. Since most mined gold goes through counting houses and mints, a fairly accurate account of all gold mined since 1493 is recorded. The world production from 1493 to 1955 closely approximates 1,500,000,000 ounces, with a value (at $35 an ounce) of $52,500,000,000. This gold would have the bulk of a 50-foot cube, which is indeed a small volume of matter to have so influenced the toil and destiny of so many people.

Metallurgy *Placer mining* is based upon the high specific gravity of gold, which occurs usually as small particles mixed with sand and gravel. The sand may be washed in pans or long troughs called sluices, and since the particles of gold are heavier, they settle to the bottom and are retained behind cleats or riffles, while the lighter sand particles are washed away.

Gold ore obtained from hard rock vein deposits is crushed to a powdery condition, after which a water suspension of the ore is passed over copper plates covered with a coating of mercury. Mercury amalgamates (page 465) with the gold and at intervals the copper plates are scraped. The amalgam (Hg-Au) is heated and the mercury distilled away from the gold, which remains as a residue. The recovered mercury is used over and over again. The tailings from this treatment may be leached with cyanide solution, which removes more of the gold.

If a gold ore is "free milling" (gold not intimately associated with other metal sulfides) and if the gold is in the ore in a quite finely divided state, it may be treated with sodium cyanide solution after having first been ground to a porous granular mass. Like silver, gold is quite soluble in NaCN or KCN solution in the presence of air:

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O \rightarrow 4\,Au(CN)_2^- + 4\,OH^-$$

The gold may be recovered from the cyanide solution by adding zinc

dust or allowing the solution to flow over zinc shavings; the zinc replaces and precipitates the gold.

The recovery of gold and silver as by-products of the smelting of copper and lead ores has already been discussed.

An alloy of gold and silver may be treated with nitric acid and the silver dissolved away from the gold, provided the content of the gold in the alloy is not greater than 25 per cent. An alloy of greater gold content is not soluble in the acid. More silver may be added to lower the gold content below 25 per cent or the alloy may be refined by electrolysis. The impure gold is made the anode in a cell with gold chloride and hydrochloric acid as the electrolyte and a sheet of pure gold as the cathode. Passage of the current causes gold to pass into solution at the anode and pure gold is deposited on the cathode.

Properties Gold is a soft yellow metal with a specific gravity of 19.3. It is a good conductor of heat and electricity and is the most malleable and ductile of metals. The metal may be hammered into sheets only 0.00001 inch in thickness, and 1 gram of the metal may be drawn into a wire 3 kilometers in length (about 1.8 miles). Gold is resistant to the action of most chemicals; air, oxygen, and water have no effect, nor do the common acids attack the metal. However, a mixture of hydrochloric and nitric acids (aqua regia) dissolves the metal to form auric chloride or chloroauric acid. The action is probably due to free chlorine present in the aqua regia:

$$3\,HCl + HNO_3 \rightarrow NOCl + Cl_2 + 2\,H_2O$$
$$2\,Au + 3\,Cl_2 \rightarrow 2\,AuCl_3$$
$$AuCl_3 + HCl \rightarrow HAuCl_4$$

Chlorine and bromine attack the metal readily and it dissolves slowly in selenic acid.

Uses Principal uses of gold are for coinage and jewelry. Pure gold is too soft for these purposes and is usually alloyed with copper to increase its hardness. The purity or fineness of gold is measured in terms of "carats;" 24 carat gold is 100 per cent gold. Thus, 18 carat gold would be $\frac{18}{24}$ or 75 per cent gold, 12 carat gold would be 50 per cent; and so on. American gold coinage is 21.6 carats or 90 per cent; British coinage is 22 carats or 91.7 per cent. Many alloys containing varying percentages of gold are on the market, such as white gold (gold and silver) and green gold (gold and cadmium or silver). Various articles are electrolytically plated with a thin coating of gold.

Compounds of gold Because of its inactivity, gold forms relatively few compounds. Two series of compounds are known, monovalent and trivalent. Monovalent (aurous) compounds resemble silver compounds

(aurous chloride is water insoluble and light sensitive), while the higher valence (auric) compounds tend to form complexes. If gold is dissolved in aqua regia and the solution is evaporated, yellow crystals of *chloroauric* acid, $HAuCl_4 \cdot 4\,H_2O$, are obtained. On controlled heating of chloroauric acid, red crystals of *auric chloride* are formed. Further heating results in the decomposition of auric chloride into *aurous chloride* and finally into free gold. The complex cyanide, $KAu(CN)_2$, obtained by dissolving the metal in potassium cyanide solution in the presence of air, is the chief form in which gold is used for plating purposes.

EXERCISES

1 Contrast the differences in physical and chemical properties between the members of divisions *A* and *B* of Group I of the periodic table.

2 List formulas and mineral names of the more important ores of Cu, Ag, Au.

3 What is the principal property of members of this group which makes them useful for ornaments and jewelry?

4 List the principal steps in the recovery of pure copper from low-grade sulfide ores. What is the purpose of each step?

5 What weight of silver would be displaced from solution by 31.8 grams of copper. Ans. 107.8 g.

6 By means of chemical changes, how could you distinguish between:

(*a*) gold, silver, copper?
(*b*) silver, magnesium, aluminum?
(*c*) chlorides of silver, lead, and copper?
(*d*) sulfates of copper, silver, and magnesium?

7 Diagram an electrolytic cell in which a copper spoon could be plated with silver.

8 What is the weight in grams of a gold brick $5 \times 10 \times 20$ cm.? (The specific gravity of gold is 19.3.) What is its weight in kilograms? In pounds?

9 Outline the chemistry involved in the various steps from exposure to development of a photographic plate.

10 Complete and balance the equations:

(*a*) $Ag + HNO_3 \rightarrow NO_2 +$
(*b*) $Cu^{++} + NH_3 \rightarrow$
(*c*) $Cu(OH)_2 + H^+ \rightarrow$
(*d*) $Au + HNO_3 + HCl \rightarrow NOCl +$
(*e*) $Cu^{++} + Fe(CN)_6^{----} \rightarrow$

11 Diagram an electrolytic cell in which an object might be gold plated. Indicate the nature of the electrodes and the electrolyte.

12 Write equations for steps you would take in preparing reasonably pure samples of the following (reactions must be complete): AgCl from Ag; $Cu(NO_3)_2$ from $CuSO_4$; Ag_2SO_4 from $AgNO_3$; Cu from CuO; $CuCl_2$ from Cu.

13 A U. S. silver dollar weighs 26.5 g. With silver worth 77½¢ per troy ounce, what is a dollar really worth? (A troy ounce is 31.1 g.)

14 A counterfeit coin weighing 10 g. was dissolved in HNO_3. The addition of HCl precipitated 5.95 g. of AgCl. What was the percentage of silver in the coin?

15 A 16 carat gold ring weighs 4.5 g. At the legal rate of $35 a troy ounce, what is the value of the gold in the ring?

16 Write equations to indicate the manner of preparing copper arsenate from solid As_2O_5, solid $CuSO_4$, and water.

17 A piece of jewelry was analyzed for silver by dissolving in conc. HNO_3, followed by precipitation of the silver as AgCl. If a sample of the jewelry weighing 0.26 g. yielded 0.277 g. AgCl, what is the percentage of silver in the sample? Ans. 80.

18 How many grams of silver chloride will be precipitated by the action of excess HCl on 1000 ml of 0.5 N $AgNO_3$?

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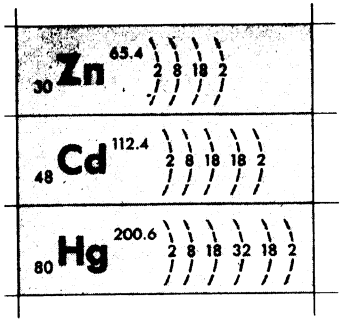
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thirty-four

ZINC, CADMIUM, AND MERCURY

METAL	SYMBOL	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Zinc	Zn	7.14	419	907	+2
Cadmium	Cd	8.65	321	770	+2
Mercury	Hg	13.60	−39	357	+1, +2

Zinc, cadmium, and mercury show greater differences in properties than the members of Group I*B* (copper, silver, gold). Zinc and cadmium are relatively high in the activity series; mercury is near the bottom. Zinc and cadmium react with steam to form hydrogen; mercury does not react with water at any temperature. The characteristic oxidation state for members of this group is +2, although mercury in some of its compounds exhibits also an oxidation state of +1.

ZINC

Brass, an alloy of zinc and copper, has been known since very early times. Pure zinc was probably not obtained until a good deal later; its identity as an element was not established until the latter part of the seventeenth century.

Occurrence Zinc does not occur in the free state, but its compounds

are widely scattered over the earth's crust. Principal naturally occurring compounds are ZnS, *zinc blende* or *sphalerite;* Zn_2SiO_4, *calamine;* $ZnCO_3$, *smithsonite;* and a complex mixture of the oxide with oxides of manganese and iron called *franklinite.*

Metallurgy Sulfide ores are ground and concentrated by the flotation process, after which they may be roasted to convert the sulfide to oxide:

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2 \uparrow$$

Carbonate ores are heated to convert to the oxide:

$$ZnCO_3 \rightarrow ZnO + CO_2 \uparrow$$

The oxide is next heated with carbon in a retort approximately five feet in length, where reduction to the metal takes place:

$$ZnO + C \rightarrow Zn + CO \uparrow$$

As the metal is produced, it is distilled off at a temperature of about 1200° and condensed in a receiver which is maintained at a temperature high enough to keep the zinc in a molten condition. If the temperature of the receiver drops below the melting point of zinc, 420°, the metal condenses as zinc dust. The metal cast into bars is called "spelter" and contains small amounts of iron, cadmium, and arsenic. The latter elements may be removed by redistillation of the spelter. However, most of the spelter is used for galvanizing purposes where the impurities present are not objectionable.

In a second metallurgical procedure, sulfide ores are roasted at a lower temperature which converts most of the sulfide to sulfate:

$$ZnS + 2\ O_2 \rightarrow ZnSO_4$$

The product is then leached with dilute sulfuric acid which dissolves any zinc oxide and oxides of other metals as well as the zinc sulfate. The addition of zinc dust to this solution causes the precipitation of the heavier metals and electrolysis of the filtered solution produces zinc of 99.9 per cent purity.

Properties of zinc Zinc is a crystalline, silver-white metal which is brittle at ordinary temperatures but may be rolled into sheets at a temperature of 120° to 150°. Above 200° it again becomes brittle. On contact with air an adherent film of basic carbonate forms on the surface of the metal which prevents further corrosion.

Zinc is fairly high in the activity series and therefore quite an active metal. It reacts readily with acids to produce hydrogen and displaces less active metals from their salts. The action of acids on impure zinc is much more rapid than on very pure zinc, since in the latter case



Figure 34–1 Drilling to obtain zinc ore.

bubbles of hydrogen gas collect on the surface of the metal and slow down the action. If another metal is present as an impurity, the hydrogen is liberated from the surface of the contaminating metal rather than from the zinc. An electric couple to facilitate the action is probably set up between the two metals.

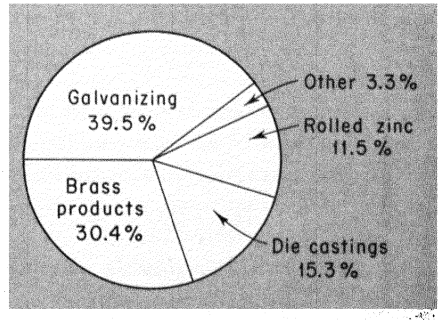


Figure 34–2 Uses of metallic zinc.

Uses of zinc Principal uses and distribution of zinc are shown in Figure 34–2. The chief use is in the manufacture of *galvanized iron.* A thoroughly cleaned iron sheet is dipped into molten zinc, and a thin layer of zinc forms on the surface of the iron. Galvanized iron is much more resistant to corrosion than plain iron, since the zinc forms a protective basic carbonate coating. In another process called *sherardizing,* zinc dust and zinc oxide are sprinkled on the surface of an

iron sheet and heated. A tightly adhering layer is thus formed. In *electrogalvanizing* of iron objects, the iron article to be coated is made the cathode in a cell and drawn slowly through the bath containing zinc ions. Although this method is more expensive than the others, it has the advantage of forming a layer of any desired thickness, and the layer is of uniform thickness and adheres more tightly to the iron. Because of its resistance to corrosion, galvanized iron is used for roofing, gutters, and cornices.

Galvanized iron has the advantage over tin plate (sheet iron coated with tin) of resisting corrosion longer after the surface is broken and the iron exposed. Since zinc is more active than iron, it corrodes first, thus protecting the iron. Once the surface of tin plate is broken, the iron corrodes first, since it is more active than tin. Important alloys of zinc are *brass* (Cu, Zn), *bearing metal* (Zn, Cu, Sn, Sb) and *German silver* (Cu, Zn, Ni).

Compounds of zinc Zinc oxide, ZnO, the widest used zinc compound, is a white powder at ordinary temperatures which changes to a yellow color on heating. When cooled, it again becomes white. Zinc oxide is obtained by burning zinc in air, by heating the basic carbonate, or by roasting the sulfide. Principal use of ZnO is in rubber manufacture as a filler, particularly in automobile tires. As a body for paints, it has the advantage over white lead of not darkening on exposure to an atmosphere containing hydrogen sulfide. Its covering power, however, is inferior to that of white lead. Thus, it is used primarily for interior paints. Because of its mild alkaline and antiseptic properties, zinc oxide is also used in ointments and medicinally as an antiseptic powder.

Zinc hydroxide, $Zn(OH)_2$, forms as a white precipitate when sodium or potassium hydroxide is added to a solution of a zinc salt:

$$Zn^{++} + 2\,OH^- \rightarrow Zn(OH)_2 \downarrow$$

The hydroxide is amphoteric and dissolves in both acids and bases. An excess of sodium hydroxide will redissolve the precipitated zinc hydroxide with the formation of zincate ions:

$$Zn(OH)_2 + 2\,OH^- \rightarrow Zn(OH)_4^{--} \text{ or } ZnO_2^{--} \cdot 2\,H_2O$$

The hydroxide is also soluble in ammonium hydroxide because of the formation of an ammonia complex:

$$Zn(OH)_2 + 4\,NH_3 \rightarrow Zn(NH_3)_4^{++} + 2\,OH^-$$

Zinc sulfide, ZnS, a white salt, is precipitated in neutral or alkaline solution with hydrogen sulfide:

$$Zn^{++} + H_2S + 2\,OH^- \rightarrow ZnS \downarrow + 2\,H_2O$$

Zinc sulfide is an ingredient of *lithopone,* a mixture of barium sulfate and zinc sulfide, used as a paint body and produced by the reaction:

$$BaS + ZnSO_4 \rightarrow BaSO_4 \downarrow + ZnS \downarrow$$

Zinc chloride, $ZnCl_2$, hydrolyzes readily in water to give an acid solution. The salt is highly poisonous and because of its antiseptic action is used as a wood preservative. It finds limited use as a cleaner for metals before soldering and mixed with zinc oxide produces a certain type of cement.

Zinc sulfate heptahydrate, $ZnSO_4 \cdot 7\ H_2O$, commonly called *white vitriol,* is prepared by action of sulfuric acid on the oxide or carbonate of zinc. It is used extensively in the preparation of lithopone.

CADMIUM

Occurrence and metallurgy Because of its close similarity to zinc, cadmium is a constituent of zinc ores in the proportion of about 1 part in 200. The mineral CdS (called *greenockite*) is also known but is relatively unimportant as a source of cadmium. Cadmium is obtained as a by-product in the smelting of zinc ores. After zinc sulfide ore is roasted, both cadmium and zinc are present as oxides. The cadmium oxide is more easily reduced than zinc oxide, and cadmium is more volatile than zinc; hence the greater portion of cadmium metal is found in the first portion of the distillate. By fractional distillation, highly pure cadmium is recovered.

Properties and uses Cadmium, a white metal more malleable than zinc, is very similar to zinc in chemical properties, appearing just below zinc in the activity series. Its compounds, like those of zinc, are all divalent. The addition of a strong base to a solution of a soluble salt produces a white precipitate of cadmium hydroxide. Unlike zinc hydroxide, cadmium hydroxide is not amphoteric; it will not dissolve in an excess of the base. However, the hydroxide is soluble in ammonium hydroxide because, like zinc, cadmium ions form a complex with ammonia, $Cd(NH_3)_4^{++}$.

Cadmium is becoming of increasing economic importance. Its principal uses are in low-melting alloys for fuses and automatic fire sprinklers, and in production of bearing metal. It offers promise as a plating material in place of zinc and tin. Alloyed with copper, it produces a product of durability, hardness, and tensile strength which is used for telegraphic and power transmission lines. An alloy of cadmium is used in making jewelry. Cadmium rods find use in atomic energy piles because the metal is a good neutron absorber (page 417).

Compounds of cadmium *Cadmium sulfide,* a yellow salt, is precipitated

from solutions of cadmium salts by hydrogen sulfide. It is less soluble in acid than zinc sulfide; separation of the two metals may be effected with H_2S if the hydrogen ion concentration of the solution is carefully regulated. This is the basis for separation of cadmium and zinc ions in qualitative analysis. Cadmium sulfide is used as a yellow pigment in paint manufacture.

Cadmium sulfate hydrate, $3\ CdSO_4 \cdot 8\ H_2O$, and metallic cadmium are used in making standard electric cells for scientific work.

MERCURY

Mercury was probably known in very early times, although it seems likely that its discovery came after silver, gold, copper, tin, and lead were known. Mercury played an important role in the early work of the alchemists, since it was regarded by many as one of the elements of which all matter is composed. Mercury was given the name quicksilver because of its liquid character and its silver-white appearance; the metal was diligently studied and efforts were made to fix it (solidify it), since it was believed by many that it would be changed to gold in the process. Mercury was not recognized as a true metal or its identity as an element established until the middle of the eighteenth century. Its Latin name, *hydrargyrum,* meaning liquid silver, is the source of the symbol Hg.

Occurrence Mercury is sometimes found in the native condition dispersed as small globules in rock masses, but by far the largest source of the metal is the mineral *cinnabar,* HgS.

Metallurgy Ore containing mercuric sulfide is heated or roasted in small furnaces or retorts. If oxide of mercury is formed in the roasting process, it quickly decomposes because of its instability toward heat, and metallic mercury is formed:

$$HgS + O_2 \rightarrow Hg + SO_2$$

Because of its volatile nature, the mercury is distilled from the impurities present and collected in iron flasks. Mercury may be further purified by filtering through chamois skin or by allowing the mercury to drop slowly through dilute nitric acid which oxidizes impurities more easily than it oxidizes the metal. Redistillation provides another means of purification. Mercury is stored in iron flasks having a capacity of 76 pounds.

Properties Mercury is a silver-white metal; it is the only common metal possessing the unique property of being a liquid at ordinary temperatures. Its melting point is $-39°$; boiling point, 357°; density, 13.6. Mercury is one of the "noble" metals; it appears near the bottom of the activity

series and is very inactive. It is not affected by oxygen of the air at ordinary temperatures but if heated to about 300° slowly combines with oxygen to form mercuric oxide. It does not dissolve in the nonoxidizing acids but dissolves readily in nitric acid to form either mercurous or mercuric nitrate, depending on whether mercury is present in excess:

$$3\,Hg + 8\,HNO_3 \rightarrow 3\,Hg(NO_3)_2 + 2\,NO + 4\,H_2O \text{ (excess } HNO_3)$$
$$6\,Hg + 8\,HNO_3 \rightarrow 3\,Hg_2(NO_3)_2 + 2\,NO + 4\,H_2O \text{ (excess Hg)}$$

Mercury vapor and its salts are poisonous although the free metal may be taken internally under certain conditions. Because of its relatively low boiling point and hence volatile nature, free mercury should never be allowed to stand in an open container in the laboratory. Evidence shows that inhalation of its vapors is distinctly injurious.

The metal alloys readily with most of the metals (except iron and platinum) to form *amalgams,* as any alloy of mercury is called.

Uses of mercury The principal use of mercury is in the preparation of its salts, many of which have important medicinal uses. Because of its convenient wide range between freezing and boiling points and its uniform expansion with rise in temperature, it finds extensive use in the manufacture of thermometers. Its high density, 13.6, makes it useful as a liquid in barometers. Some mercury is used in the preparation of dental amalgams of gold and silver for filling teeth. Because of its thermal properties, mercury is used in some modern boilers instead of water to attain higher heat efficiency. The distribution of uses of mercury is shown in Figure 34–3.

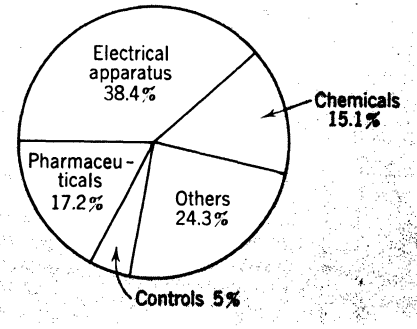


Figure 34–3 Uses of mercury.

Compounds of mercury Mercury forms two series of compounds, *mercurous* compounds in which the valence of mercury is one, and *mercuric* compounds in which the valence of the metal is two. The most important of the mercurous compounds is the chloride, Hg_2Cl_2, commonly called *calomel,* which is used medicinally as a liver stimulant and cathartic. It may be prepared by the reduction of mercuric chloride with metallic mercury:

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2 \downarrow$$

The reverse of this reaction may take place on exposure of the mercurous chloride to light, resulting in the formation of the more soluble and highly poisonous mercuric chloride; hence calomel should be stored in darkened bottles Mercurous chloride is insoluble; therefore, it is not readily absorbed by the body when given internally

Mercurous nitrate, $Hg_2(NO_3)_2$, is prepared from nitric acid and excess mercury and is one of the few soluble mercurous salts.

Mercuric chloride, $HgCl_2$, commonly called *corrosive sublimate*, is a white crystalline salt soluble in water. It may be prepared by direct combination of mercury and chlorine or by heating a mixture of sodium chloride and mercuric sulfate.

$$HgSO_4 + 2\ NaCl \rightarrow HgCl_2 + Na_2SO_4$$

The product is removed by sublimation. The chloride is very poisonous and is widely used in dilute solutions (about 1 per cent) as a germicide. If taken internally, its action on the kidneys is destructive and causes death. The albumen combines with the mercuric ions to form an insoluble white solid. The action of Hg^{++} on the protein, albumen, is like the action of heat on the white of an egg.

Mercuric ions are readily reduced by stannous ions, thus, the addition of stannous chloride to a solution containing mercuric ions results in the formation of metallic mercury or mercurous chloride depending upon the relative amounts of reactants

$$Hg^{++} + Sn^{++} \rightarrow Hg \downarrow + Sn^{++++} \text{ (excess } SnCl_2\text{)}$$
$$2\ Hg^{++} + SnCl_2 \rightarrow Hg_2Cl_2 \downarrow + Sn^{++++} \text{ (excess } Hg^{++}\text{)}$$

These reactions are used as a basis for qualitative tests for the presence of mercuric ions or stannous ions

Mercuric iodide, HgI_2, exists in two allotropic forms

$$\underset{\text{red}}{HgI_2} \overset{126°}{\rightleftharpoons} \underset{\text{yellow}}{HgI_2}$$

The yellow variety may be cooled to room temperature without change in color; however, slight friction produced by rubbing or scratching causes it to change over rapidly to the red form.

The treatment of mercury with nitric acid and alcohol yields *mercuric fulminate,* $Hg(ONC)_2$, a highly unstable and explosive compound. It is used in percussion caps as a detonator to initiate the explosion of TNT or gunpowder.

Mercuric thiocyanate, $Hg(CNS)_2$, may be prepared from a soluble mercury salt and a thiocyanate. It burns with a copious ash which is often referred to as "Pharaoh's serpents."

No hydroxides of mercury are known. The addition of sodium or potassium hydroxide to a solution containing mercurous or mercuric ions precipitates *mercurous oxide* and *mercuric oxide* respectively. Mercuric oxide exists in both a red and a yellow form; the red compound is usually obtained by heating mercuric nitrate. Mercuric oxide is of historical significance since Priestley's work with it led to the discovery of the element oxygen.

On addition of ammonium hydroxide to a solution of mercuric chloride, a white precipitate of mercuric aminochloride, $HgNH_2Cl$, forms:

$$HgCl_2 + 2\ NH_3 \rightarrow HgNH_2Cl \downarrow + NH_4Cl$$

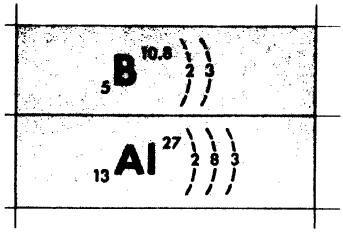
An amino group, NH_2, has been substituted for one of the chlorine atoms in mercuric chloride. The action of ammonium hydroxide on mercurous chloride is somewhat similar; in addition to the above products, metallic mercury in a very finely divided condition is obtained:

$$Hg_2Cl_2 + 2\ NH_3 \rightarrow Hg \downarrow + HgNH_2Cl \downarrow + NH_4Cl$$

In the latter reaction the finely divided mercury produces a black precipitate, and the reaction is often used as a confirmatory test for the presence of mercurous ions.

EXERCISES

1 List the formulas and mineral names for the more important ores of Zn, Cd, Hg.
2 Point out similarities and differences between these elements.
3 How could you distinguish chemically between Zn, Cd, Hg?
4 Describe the manufacture of "galvanized" iron. What are its advantages and its disadvantages?
5 Define the following: calomel, amalgam, lithopone, sherardizing, spelter.
6 What properties of mercury make it useful in the manufacture of thermometers?
7 By means of a single reagent, how could you distinguish between: Zn and Hg? Zn^{++} and Cd^{++}? $Zn(OH)_2$ and $Cd(OH)_2$? Cd^{++} and Hg^{++}? $ZnCl_2$ and Hg_2Cl_2? $HgCl_2$ and Hg_2Cl_2?
8 Mercury is sold in iron cylinders called flasks, which hold about $2\frac{3}{4}$ liters of liquid mercury. What is the approximate weight of this mercury in kilograms? in pounds?
9 Suggest a method for preparing: $ZnCl_2$ from Zn; $CdCl_2$ from $CdSO_4$; $HgSO_4$ from Hg; Hg_2Cl_2 from $HgCl_2$; $HgCl_2$ from Hg.
10 List several of the commercially important alloys of zinc, of cadmium, and of mercury.



thirty-five

GROUP III ELEMENTS: ALUMINUM AND BORON

ELEMENT	SYMBOL	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Boron	B	2.45	2300	2550	+3
Aluminum	Al	2.70	660	1800	+3

The five elements boron, aluminum, gallium, indium, and thalium appear in Group III*A* of the periodic table. Group III*B* includes scandium and yttrium plus the two rare-earth series—the lanthanide and actinide series (Chapter 4).

Aluminum and boron are present in the earth's crust in very appreciable quantities. The remaining elements are very rare, and extraction of them from earth rocks is very costly. All of the elements in this group are similar to aluminum in many respects; for example, all exhibit an oxidation state of +3. Boron, the first element of the group, is distinctly nonmetallic in properties. Aluminum is amphoteric, while the remainder exhibit metallic characteristics.

ALUMINUM

Although the element itself was isolated only a little more than a hundred years ago, compounds of aluminum have been known and used for centuries. The Romans used the word *alum* to describe any astringent substance, and it seems likely that the compound of aluminum which we know as alum today was included in this group.

Because of the activity of aluminum and the stability of its compounds, efforts to liberate the element were unsuccessful until 1827 when Wöhler succeeded in producing it by the reduction of aluminum chloride with metallic potassium:

$$AlCl_3 + 3\ K \rightarrow Al + 3\ KCl$$

However, the cost of the method prohibited its production in any quantity, and for many years the metal was only a curiosity. It was recognized that the element would be extremely useful if it could be produced economically, and many attempts were made to develop cheaper processes of manufacture. The substitution of metallic sodium for the potassium reduced the cost from \$160 to \$10 per pound. The development of electrolytic methods for the preparation of sodium reduced the cost further to \$4 a pound. Efforts to produce aluminum electrolytically from water solutions in a manner similar to that for many other metals failed; a coating of aluminum oxide was produced almost immediately which stopped the passage of the current. Likewise, the use of carbon as a reducing agent was not successful, as aluminum carbide was produced instead of the free metal. The problem was finally solved in 1886 by an American, Charles Martin Hall, while working as a student at Oberlin College. He found that electrolysis of aluminum oxide could be effected if the oxide was dissolved in melted *cryolite,* Na_3AlF_6, a double fluoride salt found in Greenland. When Hall's process was industrialized, the price of aluminum quickly dropped to about thirty cents a pound.

Occurrence Aluminum is the most abundant of the metals and stands third in abundance among the chemical elements, the percentage in the earth's crust being 7.4. It does not occur in the free state because of its activity, but its compounds are spread widely over the earth's surface. It is a constituent of most siliceous soils and rocks such as *clay,* $2\ H_2O \cdot Al_2O_3 \cdot 2\ SiO_2$; *feldspar,* $KAlSi_3O_8$ or $NaAlSi_3O_8$, and *mica,* $KH_2Al_3(SiO_4)_3$ or $NaH_2Al_3(SiO_4)_3$. The ore of aluminum is *bauxite,* $Al_2O_3 \cdot 2\ H_2O$, large deposits of which are found in France, British and Dutch Guiana, and in the states of Arkansas and Alabama. Bauxite is the only ore of aluminum at present because of the difficulties of extracting the metal from other naturally occurring compounds. As mentioned above, the double fluoride salt cryolite, Na_3AlF_6, is important as a solvent in the electrolytic production of metallic aluminum.

Metallurgy The process for the preparation of aluminum today is essentially the same as that developed by Hall in 1886. Purified dehydrated bauxite is dissolved in molten Na_3AlF_6, which acts as a solvent for the Al_2O_3. In modern practice, AlF_3 and CaF_2 are added to lower

the melting point and increase fluidity. The mixture, when melted, is a good conductor of the electric current, and electrolysis results in the decomposition of the Al_2O_3 to form metallic aluminum and oxygen. The electrolysis is carried out in carbon-lined vats which act as cathodes. The anodes are carbon rods (Figure 35–1) which dip into the electrolyte. At the beginning of the process, the carbon anodes are brought near the bottom of the carbon-lined vat to produce an arc to melt the cryolite. Electrolysis of the Al_2O_3 then begins with aluminum ions moving toward the sides and bottom of the vat, and the oxygen ions moving toward the carbon anodes. At the cathode, aluminum ions are discharged and metallic liquid aluminum settles to the bottom of the vat where it may be drawn off. Oxygen, which is produced at the anodes, rapidly oxidizes the latter. About 0.6 pound of carbon is used for every pound of aluminum produced; hence the carbon electrodes must be frequently replaced. The resistance to the passage of the current produces enough heat to keep the cryolite bath in a molten condition. The aluminum metal thus produced is above 99 per cent pure, which is adequate for most purposes.

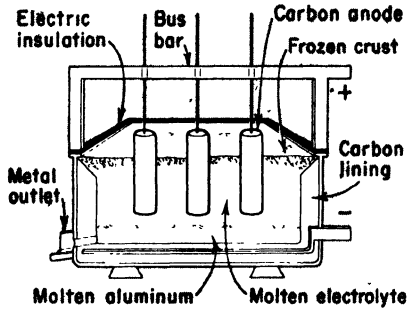


Figure 35–1 Preparation of aluminum by electrolysis (Hall process).

Principal costs of this method are the electric energy required and the treatment of the bauxite ore to prepare pure Al_2O_3. The bauxite ore is ground and treated with sodium hydroxide under pressure to convert the aluminum oxide to an aluminate:

$$Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O$$

Iron oxide, which is nearly always present as an impurity, is not amphoteric and hence is insoluble in the alkaline solution and may be filtered off. The solution of sodium aluminate is diluted with water and heated to hydrolyze the salt and precipitate aluminum hydroxide:

$$NaAlO_2 + 2\ H_2O \rightarrow Al(OH)_3 \downarrow + NaOH$$

The hydroxide is filtered off and ignited to the oxide, which may then be dissolved in the cryolite bath. The caustic soda is recovered.

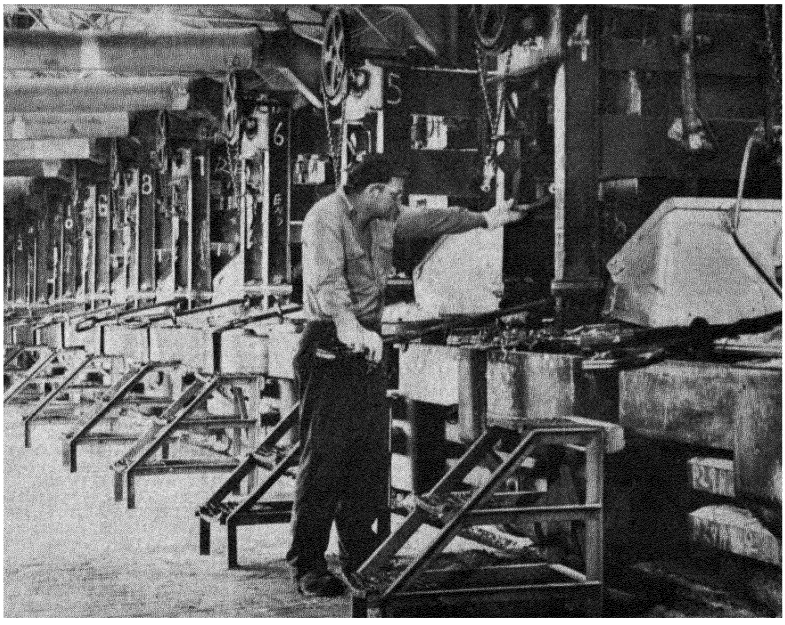


Figure 35–2 Workmen tending electrolytic pots in an aluminum production plant.

Properties of aluminum Aluminum, with a specific gravity of 2.7, is the lightest of the common metals with the exception of magnesium. At ordinary temperatures aluminum is soft, malleable, and ductile but when heated above 150° becomes quite brittle. The melting point is 660° and the boiling point about 1800°. Its tensile strength is high and it is a good conductor of heat and electricity. Although the metal is high in the activity series, it is quite resistant to corrosion because of the formation of a protective layer of oxide on the surface. At high temperatures, however, the metal burns vigorously; the aluminum sheeting of airplanes can burn completely after being ignited at high temperature. The action of aluminum with water is similar to that with oxygen; momentary reaction takes place to form the oxide which coats the surface and prevents further action, thus making it suitable for cooking utensils. Hydrochloric and sulfuric acids readily dissolve aluminum to form hydrogen, but nitric acid attacks the metal only slightly. Aluminum dissolves in sodium or potassium hydroxides with the formation of an aluminate salt and hydrogen, a behavior characteristic of amphoteric metals.

Uses Aluminum combines the properties of lightness, durability, and

strength—properties which make it suitable for a wide variety of uses. Its use in the manufacture of cooking utensils is familiar to everyone. The metal finds extensive use as a structural material in the manufacture of automobiles, airplanes, boats, streetcars, and railway coaches. In wire and cables it is used for the transmission of electric power. For wires of equal cross section, copper is a better conductor than aluminum, but on a pound for pound basis aluminum is the better conductor. Aluminum foil is used as a wrapping for soaps, food products, and tobacco. Aluminum powder is a constituent of "silver" paint and is used also in the reduction of certain metal oxides (see thermite process). Much aluminum metal is used in the manufacture of alloys, since these alloys possess greater tensile strength and are more easily machined than the pure metal. Among the more important alloys of aluminum are *duralumin* (Al with small amounts of Cu, Mg, and Mn) and *magnalium* (Al with a small amount of Mg), both of which are used in the construction of crankcases for automobiles and other automotive parts.

The thermite process If aluminum powder is mixed with certain powdered metallic oxides and the mixture ignited, aluminum takes away the oxygen from the metallic oxide and leaves the metal in the free state. At the same time a great quantity of heat and light energy is released. Advantage is taken of this affinity of aluminum for oxygen in the mixture called *thermite*, developed by Goldschmidt. Thermite is a mixture of iron oxide and aluminum, both in granular form. When the mixture is ignited by means of magnesium ribbon, a very vigorous reaction takes place:

$$Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe + 184{,}400 \text{ calories}$$

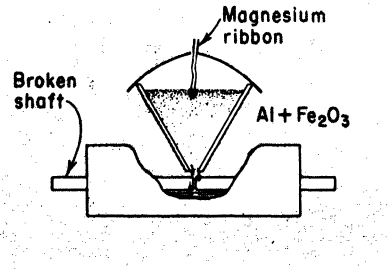


Figure 35–3 Thermite welding.

The heat energy produced in the reaction raises the temperature of the mixture to approximately 3000°, which is sufficient to melt both the aluminum oxide and the iron. The thermite mixture is convenient as a ready source of liquid iron for welding broken rails or steel shafts by placing it in a magnesia crucible as shown in Figure 35–3, directly above the object to be welded. The molten iron produced in the reaction is allowed to flow over the broken part and weld the pieces together.

Certain metal oxides which are difficult to reduce by other methods

may be reduced by heating with aluminum powder in a manner analogous to the reduction of Fe_2O_3. Manganese and chromium may be prepared from their oxides in this way.

Aluminum oxide Aluminum oxide is found in nature in several forms. Bauxite is the principal source of the metal. *Corundum* and *emery,* naturally occurring crystalline forms of the oxide, find extensive use as abrasives in grinding and polishing. An artificial product called *alundum,* produced by fusing bauxite in an electric furnace, is very inactive and resistant to corrosion of acids; it is used as a refractory and as a filtering medium for corrosive liquids.

Certain transparent crystalline forms of the oxide are prized gems. *Sapphire* is aluminum oxide containing small amounts of iron oxide and titanium oxide, while the *ruby* contains a small amount of chromium oxide. Synthetic rubies and sapphires are now produced by mixing aluminum oxide with the proper ingredients to give the desired color and passing the mixture through an oxyhydrogen flame; then the fused material is cut and polished. These synthetic gems possess the exact composition of the natural product. Apparently the only way to differentiate between the natural and synthetic varieties is by a microscopic examination which reveals a characteristic dispersion of tiny gas bubbles in the natural product. The synthetic gem industry has grown extensively in recent years and at the present time about six million carats of these gems are produced annually. Principal application of the artificial products is for jewels in watches and certain electrical measuring devices.

Aluminum hydroxide Aluminum hydroxide, $Al(OH)_3$, is formed as a white flocculent precipitate when ammonium hydroxide is added to the solution of an aluminum salt. The hydroxide is amphoteric, since it dissolves in both strong bases and acids:

$$Al(OH)_3 + 3\ H^+ \rightarrow Al^{+++} + 3\ H_2O$$
$$Al(OH)_3 + 3\ OH^- \rightarrow Al(OH)_6^{---} \text{ or } AlO_3^{---} \cdot 3\ H_2O$$

In the first reaction, aluminum acts as a metal and the hydroxide is neutralized by the acid to produce Al^{+++}. In the second reaction, the aluminum acts as a nonmetal and dissolves in the base to form aluminate ions, AlO_3^{---}. Meta-aluminate ions, AlO_2^-, may be formed by using a lesser amount of base, according to the reaction

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \text{ or } AlO_2^- \cdot 2\ H_2O$$

If aluminum hydroxide is precipitated in a solution containing an organic dye, the hydroxide adsorbs the color and removes it from solution. This adsorptive property of aluminum hydroxide is used advan-

tageously in the dye industry. Certain fabrics and materials will not adsorb a dye directly and the addition of a *mordant* is necessary—something which will fix the dye to the cloth. Aluminum hydroxide acts in this capacity if precipitated within the fibers of the cloth.

Aluminum hydroxide also finds use, because of its adsorptive capacity for suspended matter, in the purification of water.

Aluminum salts In general, aluminum salts are highly hydrolyzed in water solutions; in fact many of the salts do not exist at all in aqueous solution. *Aluminum sulfide,* which can be prepared by direct combination of the metal with sulfur, is completely decomposed when added to water. *Aluminum carbonate* likewise hydrolyzes and is not stable in aqueous solution. *Hydrated aluminum chloride,* $AlCl_3 \cdot 6\ H_2O$, is crystallized from solutions of aluminum in hydrochloric acid. The anhydrous salt cannot be prepared from this hydrate by heating, since hydrolysis takes place, with the formation of a basic salt and the evolution of hydrogen chloride. Aluminum chloride finds extensive use as a reagent in certain organic chemical syntheses and as a catalyst in the cracking of petroleum.

Aluminum sulfate, the cheapest of the soluble salts of aluminum, is prepared by the action of sulfuric acid on clay or bauxite. The salt crystallizes as the hydrate, $Al_2(SO_4)_3 \cdot 16\ H_2O$, from its solutions. It is used in the dyeing industry as a mordant, in sizing of paper, in the purification of water, and in the manufacture of other aluminum compounds.

Alums If equimolecular quantities of potassium sulfate and aluminum sulfate are dissolved in water and the solution allowed to evaporate, crystals of $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$, which is called ordinary alum or *potash alum,* are deposited. The term *alum,* however, does not necessarily refer to a specific substance but is applied to all double sulfate salts which have the general formula

$$M_2'SO_4 \cdot M_2'''(SO_4)_3 \cdot 24\ H_2O$$

where M′ may be Na^+, K^+, NH_4^+, and M‴ may be Fe^{+++}, Cr^{+++}, Al^{+++}. Examples are $(NH_4)_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\ H_2O$, *ammonium chrome alum;* $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24\ H_2O$, *potassium ferric alum.* Frequently the formula of alums is contracted to the form $M'M'''\ (SO_4)_2 \cdot 12\ H_2O$, *e.g.,* $KAl(SO_4)_2 \cdot 12\ H_2O$, etc. Alums usually produce octahedral crystals and are said to be isomorphous because they crystallize in the same crystal system. In aqueous solution the double salt behaves as two single salts, a monovalent sulfate and a trivalent sulfate, giving ions of all the constituents. Alums are used in water purification because they hydrolyze with the formation of aluminum hydroxide,

which adsorbs and carries down suspended matter in a precipitated form. Potash alum is a constituent of certain baking powders; the addition of water to the baking powder brings about hydrolysis of the aluminum sulfate to form hydrogen ions, which then act on the bicarbonate in the mixture to release carbon dioxide.

Ceramics Clay is a product of the weathering of complex silicates, particularly feldspar, $KAlSi_3O_8$ or $NaAlSi_3O_8$, which is the most abundant class of all minerals of the earth's crust. Although rock silicates are in general quite insoluble, ground waters, being dilute solutions of carbonic acid, have in geological time chemically altered them. Feldspar is progressively altered to the mineral *mica* and thence to *kaolin* according to such chemical changes as

$$3\ KAlSi_3O_8 + H_2CO_3 \rightarrow \underset{\text{mica}}{KH_2Al_3(SiO_4)_3} + 6\ SiO_2 + K_2CO_3$$

$$2\ KH_2Al_3(SiO_4)_3 + H_2CO_3 + 3\ H_2O \rightarrow 3\ \underset{\text{kaolin}}{H_4Al_2Si_2O_9} + K_2CO_3$$

The potassium carbonate is dissolved by water and the clay may be carried in colloidal suspension in streams and finally deposited in beds. Ordinary clays are quite impure—usually containing considerable quantities of iron. Kaolin, also called white clay or china clay, is a clay of high purity. When clay is mixed with water, a very plastic mass is formed which may be molded into any desired shape. This property of clay is the basis for the *ceramic* industries which produce bricks, tile, pottery, stoneware, and porcelain. After the molding and drying of the clay, the product is baked. Most of the residual molecular water is lost, leaving a very hard, resistant, highly porous product. If the porosity is undesirable, the product may be glazed by producing a very thin film of fused matter on the surface. A cheap glaze can be produced by throwing salt on the object while it is still hot; a thin liquid coating of sodium aluminum silicate forms, which becomes compact and impervious when cooled. Bricks and tiles are made from the cheaper and impure forms of clay, while china and porcelain are produced from kaolin.

BORON

Boron appears with aluminum in Group III of the periodic table. Although it is similar to aluminum in many of its chemical properties, in some respects the element is more like silicon in Group IV. Boron exhibits a characteristic oxidation state of $+3$, but because it is much more nonmetallic in character than aluminum its acid-forming properties are more pronounced.

Boron is a relatively rare element (about 0.001 per cent of the earth's crust). It does not occur in the free state but its compounds are found in many areas. *Boric acid,* H_3BO_3, occurs naturally in certain spring waters. *Borax,* $Na_2B_4O_7 \cdot 10\ H_2O$, is found in certain dry lake areas of California. The most abundant of boron compounds is *colemanite,* $Ca_2B_6O_{11} \cdot 5\ H_2O$, deposits of which are found in California and Nevada.

Borax is probably the most important compound of boron; large amounts are used in water softeners and washing powders; smaller amounts are used in making certain kinds of glass, and in forming glazes or enamels for both metal and pottery. Borax in a molten condition will dissolve many metallic oxides with the formation of a glass of a characteristic color. This is the basis for borax bead tests for such metals as cobalt, nickel, manganese, chromium, and iron, as well as the use of borax for cleaning metallic surfaces which are coated with oxide deposits. Borax is readily produced from colemanite by treatment with sodium carbonate solution, filtering off the insoluble calcium carbonate and crystallizing the borax from the solution.

Boric acid, because of its weakly acidic character and its mild antiseptic action is used as an eyewash. It is sparingly soluble in cold water and is precipitated on the addition of an acid to a solution of borax.

A borate may readily be tested for by the addition of sulfuric acid and ethyl alcohol. A volatile compound, *ethyl borate,* $(C_2H_5)_3BO_3$, is produced, which, when ignited, burns with a characteristic green-colored flame.

Boron fuels Boron is like the element carbon in its capacity to form such compounds with hydrogen as B_2H_6, diborane; B_4H_{10}, tetraborane; B_6H_{10}, hexaborane; and $B_{10}H_{14}$, decaborane. Diborane is a gas and decaborane is a white solid; the intermediate boranes are liquids at standard conditions.

These compounds are potential fuels for rockets and missiles, since they burn with evolution of a greater quantity of heat than gasoline. Boron hydride fuels must be kept free of water, with which they react to form boric acid; for example, diborane acts rapidly with water:

$$B_2H_6 + 6\ H_2O \rightarrow 2\ H_3BO_3 + 6\ H_2$$

At the present time, production costs of these hydrides are high.

OTHER ELEMENTS OF GROUP IIIA

Gallium, indium, thallium At the time that Mendeleev devised his periodic table in 1870, a blank space appeared just below aluminum.

This led to his predictions of the properties of an element called "eka-aluminum"—predictions which turned out to be remarkably accurate. Four years later the element now known as gallium was discovered with the aid of the spectroscope. Subsequently, the elements indium and thallium were also discovered with the aid of the spectroscope.

Small amounts of gallium and indium are associated with ores of zinc. Commercial zinc metal may contain as much as two or three ounces of these metals per ton. Aluminum ores, as might be expected, contain small amounts of these metals. Thallium is somewhat more abundant than the other two; small quantities of it may be obtained from flue dusts which result from the roasting of iron, zinc, copper, or lead sulfides. Small amounts may also be recovered in the refining of cadmium.

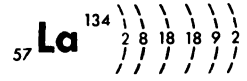
Thallium is a metal of about the density and appearance of lead; its melting temperature of 303° C. is near that of lead, 327° C. Thallium gives a green spectral line. It forms trivalent salts which are very poisonous; $Tl_2(SO_4)_3$, for example, may be used as an ant or rat poison.

Thallium has the unexpected property of forming monovalent compounds; TlOH is a strong, water-soluble base resembling the alkali hydroxides.

ELEMENTS OF GROUP IIIB

Group III*B* includes the elements scandium and yttrium and the two rare-earth series of elements. All of the elements in the *B* series, of course, are of the transitional type—that is, the atoms have incompleted inner shells of electrons. Scandium has the configuration 2, 8, 9, 2 (third shell incomplete) and yttrium has a similar configuration, 2, 8, 18, 9, 2 (again the next to outer shell is incomplete). Between lanthanum and hafnium is a space for elements, called the *rare earths,* of atomic numbers 57 to 71.

Lanthanum, of atomic number 57, is the first member of the rare-earth group. It has the following electronic structure:



Through lanthanum there has been no tendency for elements to present themselves with more than eighteen electrons in the fourth orbit, the capacity of which is thirty-two electrons. Suddenly then, a group of elements of atomic numbers 58–71 is encountered in which the added

electrons enter orbit four and progressively fill it from eighteen to thirty-two electrons. Meanwhile, the outer orbits remain essentially unchanged; thus, these rare-earth elements have almost exactly the same chemical properties. The entire list of these elements is shown below the periodic chart (page 59). The principal source of the rare earths is *monazite sand,* which contains a complex mixture of phosphates of these elements. It is an alluvial deposit found principally along the seacoasts of Brazil and India. Some black-sand river deposits of Rocky Mountain streams contain small quantities of monazite.

Cerium is the only rare earth having much practical use. An alloy of cerium and iron, when scraped by a rough, hard object, produces hot sparks and may be used in laboratory burners or cigarette lighters. Cerium oxide is occasionally used as a catalyst. Since cerium exhibits a valence of four as well as three, cerium compounds are used in oxidation-reduction reactions in analytical chemistry.

It is now believed that actinium is the first member of a second rare-earth series which at the present time would include elements of atomic numbers 89–102. The elements of this series are radioactive and are considered in Chapter 31.

EXERCISES

1 Although aluminum is more abundant in the earth's crust than iron, why is it more expensive?
2 Describe briefly the metallurgy of aluminum.
3 Define the following terms: alum; thermite; clay; mordant; bauxite; ceramics.
4 Write equations to show the amphoteric nature of $Al(OH)_3$.
5 Differentiate clearly between a double salt and a complex salt.
6 Why is aluminum hydroxide rather than aluminum sulfide precipitated when hydrogen sulfide is added to an alkaline solution of an aluminum salt?
7 In the purification of bauxite, what is the basis for the separation of iron and aluminum?
8 A one gram sample of impure bauxite when analyzed gave 0.510 g. of aluminum oxide. What was the per cent of aluminum in the bauxite? Ans. 27.
9 What quantities of ammonium sulfate and ferric sulfate would be needed to produce 100 g. of ammonium ferric alum?
10 Draw electronic configurations for the compounds BH_3 and NH_3. By what mechanism might these two compounds combine to form a third compound?
11 Give reasons for the inability to prepare pure aluminum either by reduction of its oxide with coke, or by electrolysis of aqueous $AlCl_3$ solution.
12 Fumes from electrolytic aluminum-producing pots are channeled through rotoclones to remove solid particles and thence through scrubber spray towers to remove gases. Complete the following table, which shows the success of the process in removing fluorine compounds.

ROTOCLONE			SCRUBBER			
F Intake ppm.*	F Discharge ppm.	% Removal	F Intake ppm.	F Discharge ppm.	% Removal	Over-all Efficiency
113	91.4		91.4	7.87		
78.6	63.2		63.2	3.65		

*ppm. = parts per million.

13 An aluminum plant produces 144,000,000 lb. of aluminum per year. The purchasing agent has at hand the following facts: For each pound of aluminum produced, 0.65 lb. of carbonaceous anode is used and 1.93 lb. of Al_2O_3. Weight of electrolytic material lost as production progresses reported as so many per cent of the aluminum made: cryolite, 1.5 per cent; AlF_3, 3 per cent; CaF_2, 0.15 per cent. What weights of these five most important materials must the purchasing agent plan to procure each year?

14 Write balanced equations for (*a*) the preparation of ethyl borate from boric acid and ethyl alcohol in the presence of concentrated sulfuric acid as a dehydrating agent, and (*b*) the combustion of ethyl borate.

15 Write formulas for: an alum containing gallium instead of aluminum; thallium nitrate; indium sulfide.

16 Write formulas for the sulfates of scandium, yttrium, and the rare-earth metals.

17 An alloy of magnesium and aluminum weighing 0.2 gram was burned in oxygen and converted to MgO and Al_2O_3. The mixture of oxides weighed 0.3593 g. What was the percentage of Mg in the alloy? Ans. 40.

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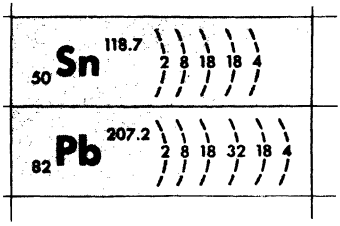
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thirty-six

GROUP IV METALS: TIN AND LEAD

ELEMENT	SYMBOL	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Germanium	Ge	5.5	1250	....	+4
Tin	Sn	7.3	232	2260	+2, +4
Lead	Pb	11.4	328	1620	+2, +4

Tin and lead are members of Group IV*A* along with carbon, silicon, and germanium. Carbon and silicon have been previously discussed, and germanium is relatively rare and unimportant.

TIN

There is some evidence to indicate that tin and lead were regarded as identical metals by early writers. Although lead and copper vessels are common in Roman and Greek relics, comparatively little tin has been found.

Since the metal does not occur in the free state, the ancients must have obtained it from its ores, probably by heating the oxide mineral in a wood fire.

Occurrence The only ore of tin of importance is the oxide, SnO_2, which is called *cassiterite.* At one time England led in the production of tin, but at the present time most of the ore comes from British Malaya, Bolivia, and the Dutch East Indies.

Metallurgy The fact that the metallurgy of tin is relatively simple undoubtedly accounts for its use in early times; the method of smelting by simply heating in a wood fire was probably discovered by accident. The oxide mineral is readily reduced with hot carbon, and the low melting metal flows from the waste rock into a collecting crucible.

$$SnO_2 + 2\,C \rightarrow Sn + 2\,CO$$

The liquid tin is cast into blocks. It is refined by heating the blocks to a temperature which melts the tin and leaves most impurities as solid matter. The tin may also be refined by electrolysis, by making impure tin the anode and pure tin sheet the cathode in a cell in which sulfuric and fluosilicic acids are used as the electrolyte.

Properties Tin is a silver-white metal of moderate hardness, and its melting point of 232° is quite low. It exists in at least two allotropic forms:

$$\underset{\text{gray}}{Sn} \overset{18°}{\rightleftharpoons} \underset{\text{white}}{Sn}$$

White tin is distinctly crystalline, and if the metal is bent back and forth, it produces a creaking noise, called "tin cry," due to the crystals slipping over one another. The gray variety is formed when the white form is subjected to low temperatures over a long period of time. When the change is once started, it progresses rapidly with a change in appearance from white metallic to a grayish powder. Tin buttons on coats of Russian soldiers have been known to crumble to a gray powder in winter. The action is termed "tin disease" or "tin pest."

The metal appears just above hydrogen in the activity series. It does not corrode or tarnish in the air, and dilute acids act on the metal only slowly. Hydrochloric and sulfuric acids act slowly on the metal to produce stannous salts:

$$Sn + 2\,H^+ \rightarrow Sn^{++} + H_2$$

Concentrated nitric acid acts vigorously on the metal to form metastannic acid:

$$Sn + 4\,HNO_3 \rightarrow H_2SnO_3 \downarrow + 4\,NO_2 + H_2O$$

Uses One of the principal uses of tin is in the production of tin plate. In the process, sheet iron which has been cleaned of oxide coating by "pickling" in acid is dipped into molten tin, and a thin layer of tin is coated onto the iron surface. The tin acts as a protective coating for the iron, which is the more active metal. If the surface of tin plate is scratched so that the iron is exposed, corrosion takes place rapidly,

probably because of an electric couple set up between the two metals. Most of the tin plate is used in the manufacture of cans for storage of foods, utensils of various kinds are also made from tin plate. Tin pipes are used for conveying distilled water, and tin foil is a common wrapping material. Considerable tin is used in the production of alloys: *bronze* (Cu, Sn); *pewter* (Cu, Pb, Sb, Sn), *solder* (Pb, Sn), and *type metal* (Pb, Sn, Sb). The distribution of tin used in the United States for various commercial products is approximately as shown in Figure 36–1.

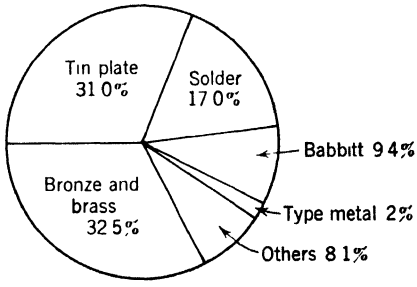


Figure 36–1 Uses of tin

Tin is a comparatively expensive metal, its price fluctuates around $2.00 a pound. A "tin can" is really an iron can with a very thin coating of protective tin on the surface. Similarly, a "tinsmith" works with iron sheeting, which may have a coating of tin, zinc, or other metals. Much zinc, aluminum, or lead foil now is substituted for the more expensive tin foil.

Compounds of tin Tin forms two series of compounds, *stannous* and *stannic*. The higher valence form, stannic, behaves more as a nonmetal than the stannous form, hence stannic salts are much less common than stannous. Both stannous and stannic hydroxides are amphoteric, since they are soluble in acid and base, the addition of sodium hydroxide to the hydroxides of tin produces stannites and stannates, respectively:

$$Sn(OH)_2 + 2\ OH^- \rightarrow Sn(OH)_4^{--} \text{ or } SnO_2^{--} \cdot 2\ H_2O$$
$$Sn(OH)_4 + 2\ OH^- \rightarrow Sn(OH)_6^{--} \text{ or } SnO_3^{--} \cdot 3\ H_2O$$

Stannous chloride, $SnCl_2$, is produced from hydrochloric acid and the metal

$$Sn + 2\ HCl \rightarrow SnCl_2 + H_2$$

The salt tends to hydrolyze and although it is particularly subject to oxidation, this may be prevented by the addition of metallic tin to the salt solution. Stannous chloride is an important laboratory reducing agent used in qualitative and quantitative analysis procedures. The salt also finds commercial application as a mordant in dyeing and in "weighting" silk. Brown *stannous sulfide*, SnS, is precipitated from solutions containing stannous ions, Sn^{++}, by the action of H_2S. Since the sul-

fide is soluble in ammonium or sodium polysulfides, it can be separated from many other metallic sulfides in qualitative analysis:

$$SnS + (NH_4)_2S_2 \rightarrow \underset{\text{ammonium thiostannate}}{2\ NH_4^+ + SnS_3^{--}}$$

$$SnS + Na_2S_2 \rightarrow \underset{\text{sodium thiostannate}}{2\ Na^+ + SnS_3^{--}}$$

Stannic chloride, $SnCl_4$, is formed from the action of excess chlorine on metallic tin:

$$Sn + 2\ Cl_2 \rightarrow SnCl_4$$

It is a colorless, fuming liquid at ordinary temperatures. The use of the salt as a mordant is based upon the fact that it hydrolyzes readily and the amphoteric hydroxide is precipitated within the fibers of the cloth. With excess sodium hydroxide, the salt forms *sodium stannate,* which is used to fireproof fabrics:

$$SnCl_4 + 6\ NaOH \rightarrow Na_2SnO_3 + 4\ NaCl + 3\ H_2O$$

Stannic sulfide, SnS_2, is precipitated as a yellow solid from solutions of stannic salts or stannates by the action of hydrogen sulfide. It is soluble in both ammonium and sodium polysulfide solutions to form the thiostannate ion, SnS_3^{--}.

LEAD

Lead statues and objects have been found in Egyptian tombs, and the element is mentioned several times in the Old Testament. Uses of the metal in early times included backing for glass mirrors, coffins, weights, net sinkers, and arrow tips. In the excavated ruins of Pompeii, which was covered by volcanic ash in 79 A.D., lead water pipe is seen in place as used so many years ago.

Occurrence Various estimates place the percentage of lead in the earth's crust at about 0.0005 per cent, which is much smaller than the percentage of such elements as zirconium, cerium, and vanadium, which we usually think of as being rare elements. There has been marked concentration of the limited natural occurrence of lead by percolating earth water and it occurs chiefly as PbS, *galena. Cerussite,* $PbCO_3$, and *anglesite,* $PbSO_4$, are less common ores but are found in sufficient quantities to warrant mining operations.

Lead ores are widely distributed over the earth's surface, the metal is produced on all of the five continents. In North America, principal deposits are in the United States in Missouri, Kansas, Oklahoma, Ari-

zona, and Idaho. In Europe, Spain is one of the principal sources. Australia is the largest producer in the British Commonwealth.

Metallurgy Crushed lead ores are usually concentrated by gravity and flotation processes. The concentrate is then subjected to a partial roasting process in which part of the lead sulfide is changed to lead oxide and part to lead sulfate:

$$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2$$
$$PbS + 2\ O_2 \rightarrow PbSO_4$$

The product of the roasting operation is mixed with limestone to act as a flux in the removal of siliceous impurities and with coke to act as a reducing agent on the oxides present. The mixture is smelted in a small blast furnace. Although the reactions are somewhat complicated, the principal ones may be represented by the equations:

$$2\ PbO + C \rightarrow 2\ Pb + CO_2$$
$$PbS + 2\ PbO \rightarrow 3\ Pb + SO_2$$
$$PbSO_4 + PbS \rightarrow 2\ Pb + 2\ SO_2$$

The product of the smelting is crude lead or lead bullion which contains small amounts of gold, silver, copper, and other metals. The metal may be partially refined by heating and stirring in the presence of air which oxidizes copper, arsenic, and antimony. The resulting oxides float on the surface of the metal and may be removed by skimming. To further purify the lead and to remove valuable metals, two methods are employed: (1) Betts process and (2) Parkes process (see page 451).

In Betts process, crude lead is made an anode in an electrolytic cell in which a sheet of pure lead is used as the cathode; the electrolyte is *fluosilicic acid,* H_2SiF_6. The process is similar to the refining of copper; lead dissolves from the anode and is plated out on the pure cathode. Gold, silver, and copper form anode mud, while other metallic ions remain in solution.

Properties Lead is one of the most dense of the common metals with a specific gravity of 11.3. It is soft and malleable but has little tensile strength. A freshly cut surface has a bright metallic appearance but on standing becomes coated with a thin coherent layer of oxide and a basic carbonate. Because of a protective covering on its surface, the metal is relatively inactive and resistant to corrosion.

In the activity series it appears above hydrogen, but the action of acids on it is very slow. With hydrochloric and sulfuric acids, a coating of lead chloride or lead sulfate quickly covers the surface, thus prevent-

ing further action. It is readily soluble in hot nitric acid, with the formation of the nitrate salt and oxides of nitrogen:

$$3\ Pb + 8\ HNO_3 \rightarrow 3\ Pb(NO_3)_2 + 2\ NO + 4\ H_2O$$

or $$3\ Pb + 8\ H^+ + 2\ NO_3^- \rightarrow 3\ Pb^{++} + 2\ NO + 4\ H_2O$$

The metal very slowly reacts with water which contains air, forming a loose deposit of lead hydroxide:

$$2\ Pb + 2\ H_2O + O_2 \rightarrow 2\ Pb(OH)_2$$

Because of this action, lead pipes should not be used for carrying drinking water; lead compounds are poisonous.

Uses Because of its relative inactivity and the ease with which it may be worked, lead is used extensively in the manufacture of a wide variety of articles. One of its principal uses is in the manufacture of plates for storage batteries. Sheet lead is used extensively in lining sinks and vats, and for conduits for corrosive chemicals. Other uses include lead shot, cable coverings, lead foil, alloys, lead pipes, and production of white lead for paints. The use of lead in the United States is shown in Figure 36–2. Principal alloys are pewter, solder, type metal, and bearing metal.

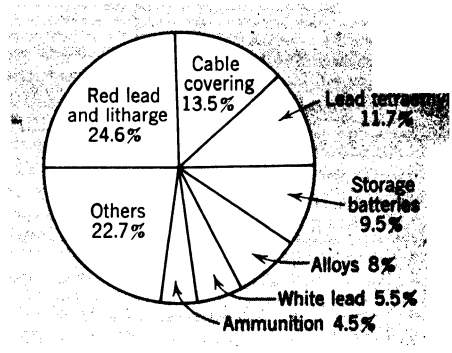


Figure 36–2 Uses of lead.

Compounds of lead Several oxides of lead are known, the more important ones being the *monoxide,* PbO; *red lead,* Pb_3O_4; and *lead dioxide,* PbO_2. Lead monoxide is a by-product of the refining of lead in which the crude metal is heated in contact with the air to oxidize other metals which may be present. During this process a considerable amount of lead is oxidized. The oxide is yellow in color and is known commercially as *litharge.* It finds use in the rubber industry and in the manufacture of optical glass, and it is mixed with glycerin for use as a plumber's cement. Pb_3O_4 may be obtained from lead or litharge by heating at temperatures below 500°. Nitric acid acts on this oxide with the formation of lead dioxide:

$$Pb_3O_4 + 4\ HNO_3 \rightarrow PbO_2 + 2\ Pb(NO_3)_2 + 2\ H_2O$$

PbO_2 is used as a pigment in paints, in storage battery plates, and in the manufacture of flint glass. Lead dioxide may also be prepared by the oxidation of litharge with a hypochlorite.

Lead resembles tin in that it forms series of divalent and tetravalent compounds. If sodium hydroxide is added to a soluble lead salt solution, white *plumbous hydroxide,* $Pb(OH)_2$, is precipitated.

$$Pb^{++} + 2\ OH^- \rightarrow Pb(OH)_2 \downarrow$$

The hydroxide is amphoteric, since an excess of alkali dissolves the precipitate, forming plumbite ion, PbO_2^{--}.

$$Pb(OH)_2 + 2\ OH^- \rightarrow Pb(OH)_4 \quad \text{or } PbO_2^{--} \cdot 2\ H_2O$$

Although $Pb(OH)_4$ is not known, salts of the compound exist, for example, Pb_3O_4 or Pb_2PbO_4 may be considered a salt of H_4PbO_4, and *calcium plumbate,* Ca_2PbO_4, is well known. Lead with a valence of four does not produce metallic ions but is present in the plumbate radical, PbO_4^{----}.

Lead forms many salts, only a few of which will be considered here. *Lead nitrate* and *lead acetate* are both soluble salts and may be formed from litharge and nitric or acetic acid The latter salt has a sweet taste and is sometimes called "sugar of lead," and like all soluble lead salts it is highly poisonous. Lead choride is precipitated when chloride ion is added to a solution containing lead ions

$$Pb^{++} + 2\ Cl^- \rightarrow PbCl_2 \downarrow$$

Because the compound is soluble in hot water, it can be separated from mercurous and silver chlorides, which are insoluble in both cold and hot water. Other halide salts of lead, *lead bromide* and *lead iodide,* are also insoluble. *Lead sulfide,* a black salt, is precipitated when H_2S is passed into alkaline or slightly acid solutions containing lead ions:

$$Pb^{++} + H_2S \rightarrow PbS \downarrow + 2\ H^+$$

It is readily soluble in dilute nitric acid:

$$3\ PbS + 8\ HNO_3 \rightarrow 3\ Pb(NO_3)_2 + 2\ NO + 4\ H_2O + 3\ S$$

or $$3\ PbS + 8\ H^+ + 2\ NO_3^- \rightarrow 3\ Pb^{++} + 2\ NO + 4\ H_2O + 3\ S$$

Lead chromate, $PbCrO_4$, is precipitated as a yellow salt by the addition of a soluble chromate to a solution of lead ions:

$$Pb^{++} + CrO_4^{--} \rightarrow PbCrO_4 \downarrow$$

The reaction is frequently used as a test for the presence of lead ions. Commercially the chromate salt finds use as a pigment in paints. *Lead*

tetraethyl, used in the manufacture of antiknock motor fuels, is prepared by the reaction of ethyl chloride and a sodium-lead alloy according to the equation:

$$4\,C_2H_5Cl + Na_4Pb \rightarrow Pb(C_2H_5)_4 + 4\,NaCl$$

Paints Ordinary paints contain three essential ingredients (1) a "vehicle," which is essentially a quick-drying oil; (2) a "body," or opaque substance of high covering power, and (3) a "pigment," if a color other than white is desired. Linseed oil is used as the vehicle or carrier of the body of the paint, which is usually white lead. The oil oxidizes in the air to form a hard, tough film which adheres to the surface of wood or other material and protects it. Linseed oil is usually boiled with lead and manganese oxides which act as catalysts and hasten the time of drying. *White lead,* $(PbCO_3)_2 \cdot Pb(OH)_2$, is a substance much used as a paint body because of its high covering power. The main objection to its use is the darkening action by hydrogen sulfide which produces black lead sulfide. Titanium oxide is now largely replacing white lead as a body material in paints.

Interior paints contain lithopone, a $BaSO_4$-ZnS mixture, as a body since lithopone is not darkened by hydrogen sulfide. If a colored paint is desired, a pigment is added to the lithopone. Common pigments are red lead, lead chromate, Prussian blue, iron oxide, chromium oxide, and carbon. In addition, a filler is frequently added to prevent the body from being spread too thin.

In recent years, so-called "water soluble" or "rubber latex" paints for interior use have become very popular. In these preparations, pigment and body are incorporated into an emulsion containing rubber-like polymerization products of styrene and butadiene. These emulsions may be thinned with water.

High-gloss paints or enamels may contain resins (resins from polymerization of glycerine and phthalic anhydride) in a wide variety of oil combinations. For example, enamel used for automobile finishes contains soybean oil, alkyd resins, and resins produced from polymerization of urea or melamine with formaldehyde.

GROUP IVB ELEMENTS: TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

ELEMENT	SYMBOL	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Titanium	Ti	4.5	1800	3000	+3, +4
Zirconium	Zr	6.4	1700	2900	+4
Hafnium	Hf	12.1	1700	3200	+4
Thorium	Th	11.2	1845	3000	+4

The first three are transitional elements of Group IV*B*. Although thorium is a member of the actinide series in Group III*B*, it will be discussed here, since its properties so closely resemble those of titanium, zirconium, and hafnium. The chemical properties of these elements resemble those of silicon but become increasingly more metallic from titanium to thorium, which definitely acts as a metal. The predominant oxidation state is +4 and, much as silica, SiO_2, occurs naturally, the oxides of these elements occur in small amounts. The formulas and mineral names of the oxides are TiO_2, *rutile;* ZrO_2, *zirconia;* HfO_2, *hafnia;* ThO_2, *thoria.* Titanium is more abundant than usually realized, constituting about 0.4 per cent of the earth's crust. Along with rutile, the mineral *ilmenite*, $FeTiO_3$, is fairly common. Zirconium and titanium ores are mined from diverse rock concentrations of their minerals. One large plant is effecting gravity and electromagnetic concentration of titanium-containing mineral from Florida heavy-beach sands. There is very little hafnium, and it is so intimately associated with zirconium that it is rarely separated; the chemistry and solubilities of their compounds are very similar. ThO_2, *thoria,* is concentrated from some black coastal sands of South America by gravity methods, since its density is quite high.

Titanium and zirconium metals are prepared by heating their chlorides with magnesium metal. Titanium and zirconium when pure are particularly resistant to corrosion and have high melting points. Zirconium metal has a comparatively high shielding effect from radiation. Ferrotitanium alloy is used in the steel industry, since titanium removes nitrogen from iron. A ferrozirconium alloy, by virtue of the affinity of zirconium for oxygen and sulfur, is used in attaining a purer fine-grained steel.

Pure TiO_2 is a particularly white substance which is taking the place of "white lead" in many paints. Smoke may be produced by discharging $TiCl_4$ liquid into moist air:

$$TiCl_4 + 2\ H_2O \rightarrow TiO_2 + 4\ HCl$$

Finely divided TiO_2 in a fog of HCl constitutes the smoke. Zirconia has a high melting point and low electrical conductivity and is used as a refractory or for electrical insulators. Thoria mixed with a little ceria and heated to a high temperature exhibits the bright white light of Welsbach gas mantles.

EXERCISES

1 Point out similarities and differences between carbon, silicon, tin, and lead.
2 Describe the production of tin from cassiterite.

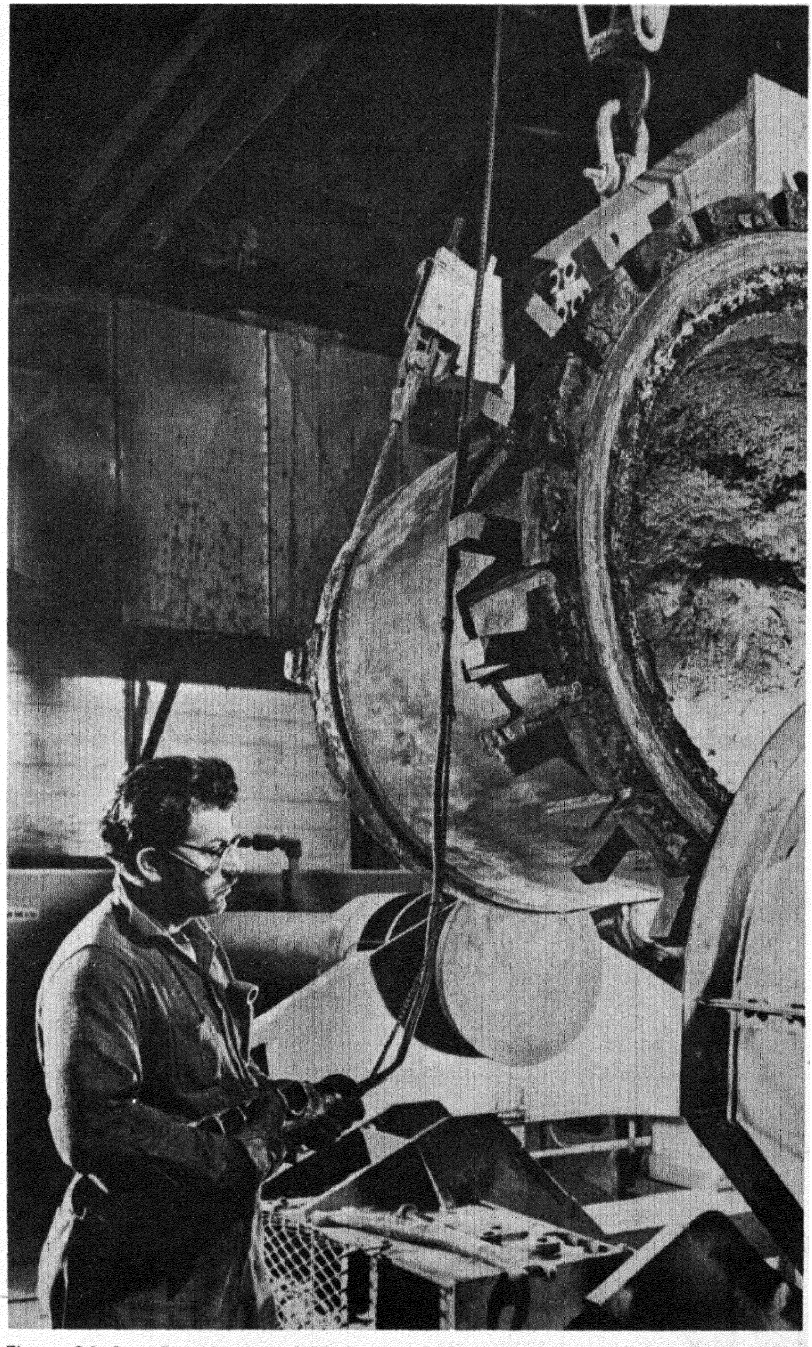


Figure 36–3 Reaction vessel filled with titanium.

3 Discuss the relative advantages and disadvantages of "tin plate" and "galvanized iron."

4 Outline briefly the methods generally employed in recovering metallic lead from galena ores.

5 Suggest a composition of a yellow paint.

6 Write equations to show that both tin and lead may exhibit nonmetallic characteristics.

7 Give formulas and names of three compounds containing the elements lead, arsenic, and oxygen.

8 Show by equations how tin and lead differ in their reactions with concentrated nitric acid. On the basis of these reactions, how could you easily differentiate between samples of tin and lead?

9 What tests would you apply in the laboratory to differentiate between PbO_2 and SnO_2? $PbCl_2$ and $SnCl_2$? $Pb(OH)_2$ and $Sn(OH)_2$? Pb^{++} and Sn^{++}?

10 Stannous chloride reduces ferric chloride according to the equation:

$$2\ FeCl_3 + SnCl_2 \rightarrow 2\ FeCl_2 + SnCl_4$$

A 1 g. sample of iron ore is treated with hydrochloric acid to convert all the iron into $FeCl_3$. If 0.747 g. of $SnCl_2$ is required to reduce the iron obtained as $FeCl_3$, what is the percent of iron in the sample? Ans. 44.

11 Approximately how many pounds of As_2O_3 are used in making 1 ton of $Pb_3(AsO_4)_2$?

12 By use of a diagram, account for the difference in melting points of different Pb-Sn solders. What is a eutectic?

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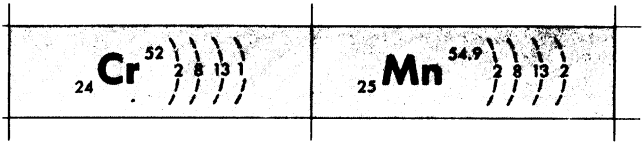
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thirty-seven

CHROMIUM, MANGANESE, AND RELATED METALS

ELEMENT	SYMBOL	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Chromium	Cr	7.1	1615	2200	+2, +3, +6
Manganese	Mn	7.2	1260	1900	+2, +3, +4, +6, +7

Although they are in different groups in the periodic table (Cr in Group VI*B* and Mn in Group VII*B*), chromium and manganese nevertheless behave similarly in many respects. Both of these elements exhibit several oxidation states, acting as metallic elements in lower oxidation states and as nonmetallic elements in higher oxidation states. Both chromium and manganese are widely used in alloys, particularly in alloy steels.

CHROMIUM

Occurrence and preparation The principal ore of chromium is $FeO \cdot Cr_2O_3$ or $Fe(CrO_2)_2$, called *chromite* or *chrome iron ore.*

The pure metal is most readily obtained by the reduction of chromic oxide with metallic aluminum (by the Goldschmidt process, which is described on page 472):

$$Cr_2O_3 + 2\ Al \rightarrow 2\ Cr + Al_2O_3$$

Ferrochrome, an alloy of iron and chromium used in the production of

steel alloys, is readily prepared from chromite and carbon in an electric furnace according to the reaction:

$$FeO \cdot Cr_2O_3 + 4\,C \rightarrow Fe + 2\,Cr + 4\,CO$$

Properties and uses Chromium is a very hard, silvery white metal, very resistant to corrosion. It dissolves slowly in hydrochloric acid with the liberation of hydrogen.

Alloyed with iron, chromium produces steels possessing properties of high tensile strength, toughness, hardness, and resistance to corrosion *Stainless steel* contains 12 to 14 per cent chromium. Chromium steels are valuable in making cutting tools because of the hardness of the alloy; they are also used in armor plate, safes, and vaults. It has been found that engraved plates coated with a thin layer of chromium last twice as long as casehardened steel plates.

Chromium is popular as a plating for automobile parts such as radiators or grills and bumpers; for tableware, and for fixtures used for a variety of purposes. Such plated articles are resistant to corrosion and possess a bright, lasting luster.

Other alloys of chromium include nichrome (Ni, Cr, Fe), which is used as electrical resistance wire, and *stellite* (Cr, W, Co), which is used for cutting tools.

The name of the element chromium is derived from the Greek word *chroma,* meaning color, since the compounds of the element are highly colored. Chromium exhibits three oxidation states, +2, +3, +6, and forms three series of compounds.

Chromous and chromic compounds Of these the chromic or trivalent compounds are the most stable and important. Chromous salts may be prepared by reduction of chromic salts with a reducing agent such as Zn in the presence of an acid. Chromous ion is readily oxidized in the air to chromic ion; hence chromous compounds are very good reducing agents.

If NaOH is added to a solution containing Cr^{+++} ions, green gelatinous $Cr(OH)_3$ is precipitated. The hydroxide is amphoteric and will dissolve in an acid to form a chromic salt:

$$Cr(OH)_3 + 3\,H^+ \rightarrow Cr^{+++} + 3\,H_2O$$

or will dissolve in an excess of alkali to form a chromite:

$$Cr(OH)_3 + 3\,OH^- \rightarrow Cr(OH)_6^{---} \text{ or } CrO_3^{---} \cdot 3\,H_2O$$

Chromic oxide, Cr_2O_3, may be produced by heating the hydroxide or by heating the metal in air at an elevated temperature. This compound,

green in color, is used as a paint pigment and for coloring certain ceramic products.

Chromic sulfate, $Cr_2(SO_4)_3$, used in the tanning of leather may be produced from chromic hydroxide and sulfuric acid.

Beautiful reddish violet crystals of *chrome alum,* $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\ H_2O$, may be obtained by crystallizing a solution containing equimolecular quantities of potassium and chromium sulfates.

Chromates and dichromates Oxidation of chromites in an alkaline solution with sodium peroxide or other oxidizing agents results in the formation of chromates; for example,

$$2\ Na_3CrO_3 + 3\ Na_2O_2 + 4\ H_2O \rightarrow 2\ Na_2CrO_4 + 8\ NaOH$$

or

$$2\ CrO_3^{---} + 3\ Na_2O_2 + 4\ H_2O \rightarrow 2\ CrO_4^{--} + 8\ OH^- + 6\ Na^+$$

The oxidation number of chromium changes from +3 to +6, and the color changes from green to a bright yellow. The chromium atom now appears in the chromate acid radical, thereby exhibiting its nonmetallic or acidic character in the higher state of oxidation.

Chromates are usually prepared from chromite ore by fusion with an alkali carbonate and an oxidizing agent, as in this reaction:

$$2\ Fe(CrO_2)_2 + 4\ K_2CO_3 + 7\ KNO_3 \rightarrow Fe_2O_3 \downarrow + 4\ K_2CrO_4 + 4\ CO_2 + 7\ KNO_2$$

Extraction of the fused mass with water yields a solution of K_2CrO_4, which is separated from the insoluble iron oxide by filtration.

Chromates are salts of *chromic acid,* H_2CrO_4. The anhydride of the acid, CrO_3, is readily obtained as a red crystalline compound by treatment of a chromate with concentrated sulfuric acid:

$$K_2CrO_4 + H_2SO_4 \rightarrow K_2SO_4 + H_2O + CrO_3$$

In the presence of a dilute acid, chromates are converted to dichromates containing the orange red dichromate ion, $Cr_2O_7^{--}$:

$$2\ K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

The addition of an alkali to a dichromate results in the re-formation of a chromate because of the equilibrium existing in solution between chromate and dichromate ions:

$$2\ CrO_4^{--} + 2\ H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$$

It is evident that the addition of H^+ ions (acid) will favor the reaction to the right, while addition of OH^- ions (base) will shift the equilibrium to the left.

Both chromates and dichromates are effective oxidizing agents. Reduction products include chromic ions. In the tanning of leather, a

dichromate is reduced to a chromic salt which undergoes hydrolysis and precipitates $Cr(OH)_3$ within the leather, thereby preventing its decay. A mixture of a dichromate with concentrated sulfuric acid is used in cleaning laboratory glassware. $PbCrO_4$ and $BaCrO_4$ are used as yellow paint pigments, and basic lead chromate, $PbO \cdot PbCrO_4$, called *chrome red,* is also used as a paint pigment.

MANGANESE

Manganese is found in nature principally as the ore MnO_2, called *pyrolusite.* It is a soft, black mineral which usually contains impurities of iron oxide, lime, and silica. Although small deposits of the ore have been found in the United States, this country produces only a small percentage of that consumed annually. Russia produces about half of the world's supply; smaller amounts are produced in Africa, India, and Brazil. Approximately 700,000 tons of the metal are consumed annually in this country, nearly all of which is imported. If manganese dioxide is heated with carbon, reduction takes place but the product contains carbon. The pure metal may be obtained by reduction of the dioxide with powdered aluminum (Goldschmidt process).

Properties and uses The pure metal resembles iron in many properties. It has a somewhat reddish color, and is relatively soft. Like iron, the addition of even a small percentage of carbon gives a very hard and brittle product. If the metal is heated to redness, reaction with steam takes place readily with the formation of hydrogen. In the activity series, the element appears between aluminum and zinc; hence, manganese dissolves readily in acids.

About 90 per cent of the manganese consumed in this country is used in the manufacture of steel. In small percentages its presence aids in the removal of sulfur and oxygen; in larger amounts (10 to 12 per cent) the manganese alloys with the iron to produce a product which is very hard and tough and which is more readily forged and machined than steels which are free of manganese. Manganese steel is particularly well adapted to the construction of steel rails and parts of machinery which are subject to extreme wear. For the purpose of producing manganese steels, two alloys of iron and manganese are employed—*spiegeleisen,* containing 10 to 20 per cent manganese, and *ferromanganese,* which contains 70 to 80 per cent manganese. Both are produced by the reduction of ores containing both manganese and iron oxides with carbon. *Manganese bronze* (Cu, Mn, Zn, Sn), an alloy particularly resistant to the action of sea water, is used in the production of ships'

propellers. Another alloy, *manganin* (Cu, Ni, Mn), is used as electrical resistance wire.

Compounds Manganese exhibits oxidation numbers of +2, +3, +4, +6, +7, and forms five series of compounds. A few typical compounds will be discussed.

Manganous compounds The addition of an alkali to a solution containing manganous ions, Mn^{++}, precipitates white $Mn(OH)_2$. The hydroxide rapidly oxidizes in the air to brown $MnO(OH)_2$ or $MnO_2 \cdot H_2O$. The more important manganous compounds are the sulfate and the chloride which is readily prepared from MnO_2 and HCl (see page 202). Pink MnS is precipitated from neutral or alkaline solutions containing Mn^{++} ions. In general, manganous compounds (except $Mn(OH)_2$ are fairly stable in the air.

Manganic compounds The hydroxide and several trivalent manganic salts are known but they are unstable and are easily reduced to manganous compounds.

Tetravalent compounds Of these, manganese dioxide is by far the most important. This compound, which occurs in nature, is insoluble in the nonreducing acids; in alkalies it does not dissolve readily but when fused with certain metallic oxides forms *manganites* such as $CaMnO_3$, salts of the hypothetical acid, H_2MnO_3.

Manganates When a manganous compound or MnO_2 is fused with an alkali hydroxide or carbonate in the presence of an oxidizing agent such as chlorate or nitrate, a greenish colored *manganate* salt is formed:

$$3\ MnO_2 + 2\ K_2CO_3 + 2\ KNO_3 \rightarrow 3\ K_2MnO_4 + 2\ CO_2 + 2\ NO$$

This reaction is frequently employed as a qualitative test for the presence of manganese; the appearance of the green color indicates the presence of the element. The manganates are stable only in alkaline solution; when water or acid is added, oxidation and reduction take place with the formation of MnO_2 and a permanganate. This behavior serves as a means of preparing permanganates:

$$3\ K_2MnO_4 + 2\ H_2O \rightarrow 2\ KMnO_4 + MnO_2 + 4\ KOH$$

Permanganates *Permanganic* acid, $HMnO_4$, may be prepared from a manganous salt or manganese dioxide by reaction with HNO_3 and PbO_2:

$$2\ Mn^{++} + 6\ H^+ + 5\ PbO_2 \rightarrow 5\ Pb^{++} + 2\ HMnO_4 + 2\ H_2O$$

The permanganates are purple in color, and the above reaction is frequently employed as a qualitative test for manganese.

The most important of the permanganates is $KMnO_4$, prepared as explained in the previous section. It is used widely as an oxidizing agent. In acid solution it is reduced by Fe^{++}, $C_2O_4^{--}$, SO_2, and C_2H_5OH to Mn^{++}. Since the MnO_4^- ion is purple in color and the Mn^{++} ion practically colorless, the endpoint of the reaction is readily evident by the disappearance of color. In neutral or alkaline solution, the permanganates are reduced to MnO_2. $KMnO_4$ is used also as a disinfectant and as a medicinal.

Uses of chromates and permanganates in analytical chemistry In addition to using acid-base titrations to evaluate concentration of solutions, the analytical chemist frequently uses oxidation-reduction changes to determine the amount of an ion in an unknown solution. Suppose a chemist desired to determine the percentage of iron in a gram sample of ore. The iron mineral could be dissolved from the sample to yield a solution with an unknown amount of Fe^{++}. By titration with a standard (known concentration) solution of $K_2Cr_2O_7$ or $KMnO_4$, the amount of Fe^{++} can be determined. The equations involved would be as follows:

(molecular)

$$K_2Cr_2O_7 + 6\,FeSO_4 + 7\,H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 7\,H_2O$$

(ionic)

$$Cr_2O_7^{--} + 6\,Fe^{++} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 6\,Fe^{+++} + 7\,H_2O$$

(molecular)

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 \rightarrow K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O$$

(ionic)

$$2\,MnO_4^- + 10\,Fe^{++} + 16\,H^+ \rightarrow 2\,Mn^{++} + 10\,Fe^{+++} + 8\,H_2O$$

Color change from purple permanganate to colorless manganous ion can itself indicate the end point of titration. Some other inorganic or dye chemical is usually employed to indicate end points in dichromate titrations. See exercises 5, 6, and 7 on page 498.

A further example is in titrations to evaluate arsenite concentration in, say, a solution of an insecticide.

$$3\,K_3AsO_3 + K_2Cr_2O_7 + 4\,H_2SO_4 \rightarrow K_2SO_4 + 3\,K_3AsO_4 + Cr_2(SO_4)_3 + 4\,H_2O$$

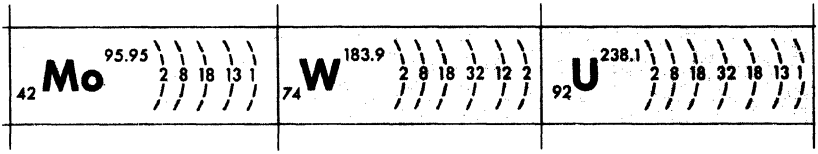
$$3\,AsO_3^{---} + Cr_2O_7^{--} + 8\,H^+ \rightarrow 3\,AsO_4^{---} + 2\,Cr^{+++} + 4\,H_2O$$

$$5\,K_3AsO_3 + 2\,KMnO_4 + 3\,H_2SO_4 \rightarrow K_2SO_4 + 5\,K_3AsO_4 + 2\,MnSO_4 + 3\,H_2O$$

$$5\,AsO_3^{---} + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,AsO_4^{---} + 2\,Mn^{++} + 3\,H_2O$$

Technetium and *rhenium* are elements appearing with manganese in Group VII*B*. Both are very rare and have no commercial uses at present. Rhenium compounds analogous to manganese compounds have been prepared. Technetium is so rare that little information about the element or its compounds is available in chemical literature at the present time.

RELATED METALS



ELEMENT	SYMBOL	SP. GR.	MELTING POINT	BOILING POINT	OXIDATION STATES
Molybdenum	Mo	10.2	2620	3700	+2, +3, +4, +6
Tungsten	W	19.3	3370	5900	+2, +4, +5, +6
Uranium	U	18.5	1850	3500	+3, +4, +6

Molybdenum, tungsten, and uranium In properties these elements closely resemble chromium. Like chromium they exhibit variable oxidation states and form several series of compounds. Examples of a few similar compounds are $CaCrO_4$, calcium chromate; $CaMoO_4$, calcium molybdate; $CaWO_4$, calcium tungstate; $CaUO_4$, calcium uranate; $Na_2Cr_2O_7$, sodium dichromate; $Na_2U_2O_7$, sodium diuranate; $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\,H_2O$, potassium chrome alum; $K_2SO_4 \cdot U_2(SO_4)_3 \cdot 24\,H_2O$, potassium uranium alum.

Like chromium, the principal use of molybdenum, tungsten, and uranium is in the elemental state. Molybdenum and tungsten form important alloys with steel.

The principal source of molybdenum is *molybdenite,* MoS_2. The largest mine for this mineral is in Colorado. It is a soft, shiny mineral which looks very much like graphite. The sulfide may be roasted to yield the oxide, which can then be reduced with carbon to produce metallic molybdenum. $PbMoO_4$, *wulfenite,* is mined in New Mexico and Norway.

Most of the molybdenum extracted from the above minerals is alloyed with iron to form *ferromolybdenum,* which is used in the production of special alloy steels. A steel containing molybdenum is quite heat resistant and may be used in making high-speed tools.

Tungsten is also an important element for alloy steels, particularly for armor plate and steels which are to be subjected to high temperatures, for tungsten steel may be heated to high temperatures without losing its "temper." Tungsten also finds use as filaments in incandescent lamps and radio tubes, as contact points in spark plugs, and so on. The principal minerals of tungsten are *scheelite,* $CaWO_4$, and *wolframite,* $FeWO_4 \cdot MnWO_4$. (The German name for tungsten is Wolfram; the symbol for tungsten is derived from this name.)

Tungsten is a very hard metal and it possesses the highest melting point of all the elements except carbon. It is very resistant to corrosion and to the action of chemicals.

Uranium has gained special attention as a source of material used in the production of atomic bombs (see page 414); the radioactive properties of uranium are discussed in Chapter 31. The principal sources of uranium are *pitchblende*, U_3O_8, and *carnotite*, $K_2O \cdot 2\,UO_3 \cdot V_2O_5 \cdot 3\,H_2O$. These minerals are found in the Belgian Congo and near Great Bear Lake in Canada. Small quantities of carnotite are mined in Colorado and Utah. All deposits of uranium minerals are now under the control of an international committee.

EXERCISES

1 Show similarities of chromium and manganese by listing formulas of analogous compounds of the two elements.

2 Complete and balance the equations:

(*a*) $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + K_2SO_4 +$

(*b*) $FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + K_2SO_4 +$

(*c*) $MnO_2 + HCl \rightarrow$

(*d*) $Cr_2O_3 + Al \rightarrow$

(*e*) $CrO_4^{--} + H^+ \rightarrow$

(*f*) $K_2Cr_2O_7 + HBr \rightarrow CrBr_3 +$

3 Outline a method by which you could prepare each of the following:

(*a*) $Mn(NO_3)_2$ from MnO_2

(*b*) K_2MnO_4 from MnO_2

(*c*) $CrCl_3$ from $K_2Cr_2O_7$

(*d*) $HMnO_4$ from $Mn(NO_3)_2$

(*e*) $K_2Cr_2O_7$ from K_2CrO_4

(*f*) $MnCl_2$ from $KMnO_4$

4 What desirable properties are possessed by chromium and manganese alloy steels?

5 A standard solution of $KMnO_4$ is often used in determining the amount of iron in a sample. Any iron in a sample is first converted to the ferrous state, after which the resulting solution may be titrated in acid solution with the standard $KMnO_4$ solution. The reaction is

$$5\,Fe^{++} + KMnO_4 + 8\,H^+ \rightarrow K^+ + Mn^{++} + 5\,Fe^{+++} + 4\,H_2O$$

The equivalent weight of an oxidizing agent (in this case $KMnO_4$) or reducing agent (in this case Fe^{++}) is determined by the number of electrons transferred per mole of substance. Since manganese changes from +7 to +2 in oxidation number, 5 electrons are gained per mole of $KMnO_4$ and its equivalent weight is 158 (mol. wt.) divided by 5, or 31.6. A normal solution of $KMnO_4$ would contain 31.6 g. of that salt per liter of solution. Only one electron is lost per mole of Fe^{++}; therefore, the equivalent weight of Fe^{++} is its atomic or ionic weight—that is, 55.8.

Suppose 50 ml. of a solution containing Fe^{++} is found to react with 100 ml. of 0.1 N $KMnO_4$ solution. (*a*) What is the normality of the Fe^{++} solution? (*b*) What weight of Fe^{++} would be contained in the 50 ml. of solution? (*c*) If this amount of Fe^{++} were obtained from a 1 g. sample of iron ore, what would be the percentage of iron in the sample? Ans. (*a*) 0.2, (*c*) 55.8.

6 (Work exercise 5 before attempting this one.) A standard solution of $K_2Cr_2O_7$ is also frequently used in determining Fe^{++} in a sample by titration in acid solution. The equation for the reaction is

$$6\ Fe^{++} + K_2Cr_2O_7 + 14\ H^+ \rightarrow 2\ K^+ + 2\ Cr^{+++} + 6\ Fe^{+++} + 7\ H_2O$$

The molecular weight of $K_2Cr_2O_7$ is 294.2. (*a*) What is the equivalent weight of $K_2Cr_2O_7$? (*b*) A 1 g. sample of iron ore is treated to obtain iron as Fe^{++}. 25 ml. of 0.1 *N* $K_2Cr_2O_7$ solution is used to titrate Fe^{++}. What is the percentage of iron in the sample? Ans. (*b*) 13.95.

7 Sodium oxalate ($Na_2C_2O_4$, mol. wt. 134) may be used to standardize a solution of $KMnO_4$. The reaction is

$$5\ Na_2C_2O_4 + 2\ KMnO_4 + 16\ H^+ \rightarrow 10\ Na^+ + 2\ K^+ + 2\ Mn^{++} + 10\ CO_2 + 8\ H_2O$$

If 50 ml. of $KMnO_4$ solution is used to titrate 0.335 g. of pure $Na_2C_2O_4$, what is the normality of the permanganate solution? Ans. 0.1.

8 How would you differentiate chemically between Mn and Cr? Mn^{++} and Cr^{+++}? MnO_4^- and $Cr_2O_7^{--}$? MnO_2 and Cr_2O_3?

9 Name the compounds and give the oxidation number of Cr or Mn in $Cr_2(SO_4)_3$; H_2CrO_4; $CrCl_2$; MnS; $KMnO_4$; Na_2MnO_4.

10 An ore contains 1.2 per cent tungsten as water-insoluble $CaWO_4$ in a water-insoluble siliceous rock. It is gravity concentrated to an 8 per cent tungsten-containing concentrate—no chemical change involved. The ground concentrate is now heat treated in a furnace with Na_2CO_3. Write an equation showing the reaction of calcium tungstate with soda. The resulting sodium tungstate may be water leached from the insoluble silicate and calcium carbonate. Write an equation to show what happens when calcium chloride is added to the sodium tungstate. What percentage of tungsten is in the precipitate? Write equations showing what would happen to any $PbMoO_4$ that might be present in the ore during the above processing.

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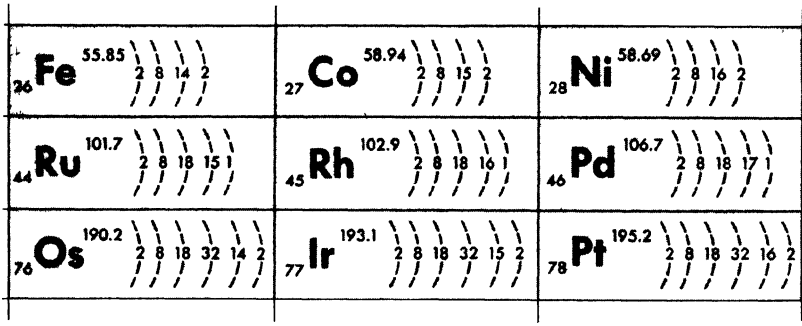
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thirty-eight

METALS OF GROUP VIII-B

METAL	SYMBOL	SP GR	MELTING POINT	BOILING POINT	OXIDATION STATES
Iron	Fe	7.86	1535	3000	+2, +3
Cobalt	Co	8.9	1480	2900	+2, +3
Nickel	Ni	8.9	1450	2900	+2, +3
Ruthenium	Ru	12.2	2450	> 2700	+2, +3, +4, +6, +7, +8
Rhodium	Rh	12.5	1950	> 2500	+2, +4
Palladium	Pd	12.0	1555	2200	+2, +4
Osmium	Os	22.5	2700	> 5300	+2, +3, +4, +8
Iridium	Ir	22.4	2350	> 4800	+3, +4
Platinum	Pt	21.5	1750	4300	+2, +3, +4, +6

Group VIII*B* contains the three triads of elements listed above. These triads appear at the middle of long periods of elements in the periodic table and are members of transition series of elements. The elements of any given triad have many similar properties, but there are marked differences between the properties of the triads, particularly between the first triad and the other two. Iron, cobalt, and nickel are much more active than members of the other two triads and are also much more abundant in the earth's crust. Metals of the second and

third triads have many properties in common and are usually grouped together and called the "platinum metals."

IRON AND STEEL

Without question iron is the most important and useful of the metals. The period in which we now live is often designated as the age of iron and steel, and it has been said that we probably could get along without all the other metals better than we could do without iron. Evidence indicates that iron was known in prehistoric times, although it seems likely that copper and bronze were known and used prior to its discovery. Ores of the metal are easily reduced with carbon, and its discovery probably came about by accidentally heating the ore in a wood fire.

The importance of iron as a commercial product depends upon the fact that the properties of the metal may be made to vary by the addition of small amounts of alloying elements, and, equally important, the properties vary with the heat treatment of the metal. Less than one per cent of carbon added to iron changes the relatively soft metal into a hard, strong product. Pure iron has little industrial importance; it is much too soft and weak for most purposes. However, the addition of small amounts of foreign substances so completely alters the original properties of the iron that it becomes adaptable to a wide variety of uses. Principal products of iron are cast iron, wrought iron, and steel.

Occurrence Iron stands fourth in abundance among the chemical elements present in the earth's crust (see page 15). The element is rarely found in the free state except in meteorites, which are largely iron with a small percentage of nickel. Compounds of iron are widely distributed and are constituents of many rocks and soils.

Ferrous iron compounds are greenish, whereas ferric compounds are yellow to brown or red. An esthetic chemist gazing at the magnificent coloring of the Grand Canyon of the Colorado might speculate that this would be a drab-colored world without iron compounds. Even the natural and sometimes artificial pink of cheeks and lips is due to iron compounds, and rocks or soils with a reddish color usually contain relatively large amounts of iron. Compounds of the other abundant elements are largely colorless. Iron is present in the hemoglobin of the blood. Concentrations of naturally occurring iron oxides are the ores which are used for the production of iron and its products. Among these ores are *hematite,* Fe_2O_3, and *magnetite,* Fe_3O_4, a mineral having magnetic properties and commonly called *lodestone.*

Most of the ore mined in the United States comes from the Mesabi

Range in the Lake Superior region of Minnesota. Ore from this region is obtained by the open-pit mining method; huge steam shovels scoop it up from the surface. Other iron-producing areas of the United States are Alabama and Michigan.

Iron pyrites, FeS_2, often called "fool's gold" because of its yellow, flaky appearance, is another abundant, naturally occurring compound of iron but is not much used for commercial extraction because of the greater ease of obtaining iron from other minerals. In England the principal ore of iron is *siderite,* $FeCO_3$.

Metallurgy Iron may be obtained from its oxide ores by reduction with carbon. This operation is carried out in a huge cylindrical furnace called a *blast furnace,* a cross section of which is shown diagrammatically in Figure 38–1. These furnaces vary in height from 75 to 100 feet and are 20 to 25 feet in diameter near the base. They are constructed from heavy steel plates and lined with firebrick. Ore, limestone, and coke are introduced at the top of the furnace through a series of hoppers, which are manipulated so that gases produced by the reactions are not lost. The operation of a blast furnace is continuous, and at intervals the iron is tapped and run off. The usual impurity present in iron ore is silica, so limestone is added as a flux to form a slag which may be drawn off. In the event that the impurity in the ore is of a basic nature, such as carbonates of calcium or magnesium, then silica is added as a flux to form the slag. The coke serves as a fuel to melt the iron and as a reducing agent to convert the oxide ore to metal. Near the bottom of the furnace a hot blast of air is introduced through nozzles called *tuyères* to burn the coke. An average charge for

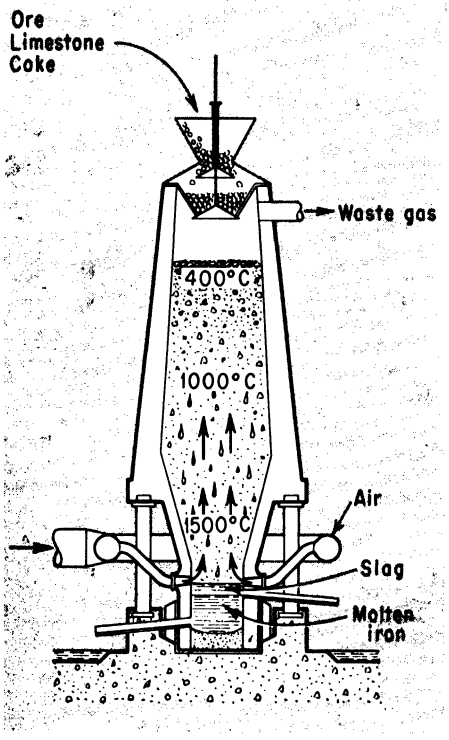


Figure 38–1 Blast furnace for the manufacture of pig iron.

a furnace at 15 minute intervals is 9 tons of ore, 3 tons of limestone, and 5 tons of coke. In addition, about 12 tons of air are necessary to burn the coke in this charge. Air combines with the carbon and forms carbon dioxide

$$C + O \rightarrow CO_2$$

which then passes upward through the hot carbon above and is reduced to carbon monoxide

$$CO_2 + C \rightarrow 2\ CO$$

The carbon monoxide ascends toward the upper part of the furnace and reduces the ore in successive stages, first to magnetic oxide of iron, then ferrous oxide, and finally iron, according to the equations:

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$$
$$FeO + CO \rightarrow Fe + CO_2$$

Slag formation occurs near the central portion of the furnace according to the reactions:

$$CaCO_3 \rightarrow CaO + CO_2$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$

Molten iron and slag collect in the *crucible* at the bottom of the furnace where they may be drawn off from time to time. The temperatures in the various parts of the furnace are shown in the diagram. The iron which is tapped from the furnace is an impure variety, called *pig iron*, which contains a considerable amount of dissolved carbon as well as sulfur and phosphorus as impurities. A large blast furnace produces approximately 600 tons of pig iron every 24 hours. In addition to the slag, a third product of the blast furnace is a mixture of gases which is sometimes called *blast furnace gas* or *producer gas*. Besides carbon dioxide and nitrogen (from the air), the furnace gas contains considerable carbon monoxide and some hydrogen, both of which are combustible. The mixture, therefore, has fuel value and much is employed in preheating air in giant stoves for use in the blast furnace. The preheated air enters the blast furnace at a high temperature, and combustion of the coke ensues rapidly, thus producing a higher temperature than if cold air were used. Blast furnace gas is removed near the top of the furnace. The products of the furnace with the approximate composition of each are shown in Table 38-1, page 504. Slag is used for road ballast and in the manufacture of certain types of cement.

Because there are impurities present in pig iron, the product cannot be welded or forged and possesses little tensile strength. Pig iron melted

TABLE 38–1 Products of the Blast Furnace and Their Composition

PIG IRON		GASES		SLAG
Fe	93–95%	CO	25%	Chiefly $CaSiO_3$
C	3–5%	CO_2	13%	Some $FeSiO_3$
Si	1%	N_2	57%	$Ca_3(PO_4)_2$
S	less than 1%	H_2	3%	$MgSiO_3$
P	0.1–0.3%			

with scrap iron produces *cast iron,* which is useful for objects that are not subject to sudden jarring or shock such as radiators, parts for stoves, and certain types of heavy machinery. Cast iron is comparatively easily melted and expands when cooled and thus fills every part of the mold into which it is poured. There are two varieties of cast iron; they are differentiated by the rate at which the molten metal is cooled. *Gray cast iron* is produced by cooling the metal slowly, in which case the carbon present in the iron separates as graphite. If the metal is suddenly quenched by plunging into water or oil, *white cast iron* is formed in which the carbon remains combined with the iron as the chemical compound *cementite,* a carbide of iron of the composition Fe_3C.

The location of blast furnaces for the production of pig iron depends to a great extent upon the accessibility of the three principal raw materials used in the furnace, namely, ore, coal (from which coke is obtained), and limestone. Principal iron and steel producing localities in the United States are Pittsburgh, Birmingham, Ala., and the Chicago district. Pittsburgh is admirably located for steel production because of its proximity to the limestone and coal deposits in Pennsylvania. The ore is transported by ship from the Lake Superior ore region to Buffalo where it is shipped overland the relatively short distance to Pittsburgh. Similarly, steel mills in the Chicago district are conveniently located near coal deposits, and water transportation through the Great Lakes brings the ore directly to the furnaces on Lake Michigan.

Steel The manufacture of steel consists essentially in the purification of pig iron, which, as has been pointed out, contains a rather high percentage of carbon in addition to smaller amounts of silicon, phosphorus,

TABLE 38–2 Common Types of Steel

TYPE	CARBON CONTENT	USES
Low carbon steel	less than 0.3%	rivets, wire, and nails
Medium carbon steel	0.3 to 0.8%	railroad rails and axles
High carbon, or tool steel	0.8 to 2%	tools, springs, and files

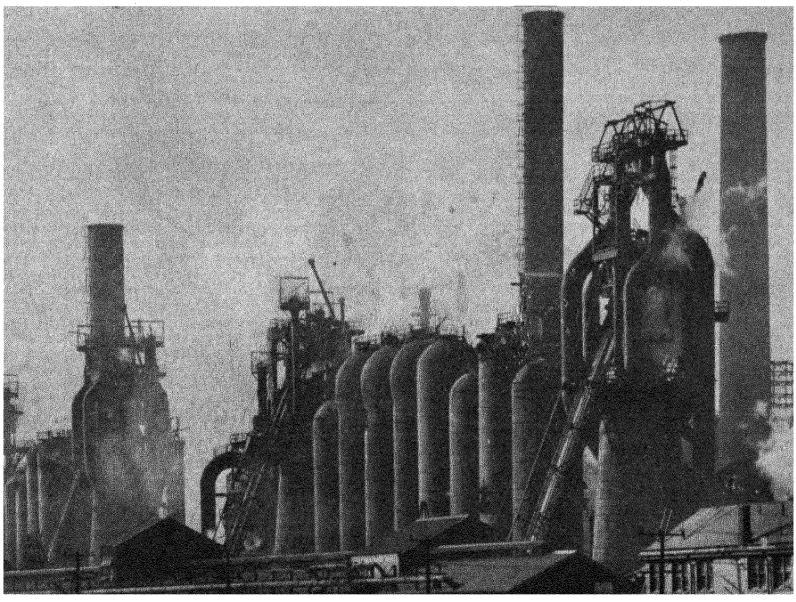


Figure 38–2 Blast furnaces and air preheating columns.

and sulfur. Since the latter three impurities are objectionable, it is desirable to remove as much of them as is possible. However, a certain amount of carbon is desirable as the properties of iron are considerably modified by even small percentages. Steel is a product which is nearly pure iron containing relatively small and varying amounts of carbon. The more common types of steel and their uses are shown in Table 38–2. In recent years small amounts of many other metals have been added to steel to impart certain characteristic properties. The addition of manganese produces a very tough steel; molybdenum and chromium yield a steel which is resistant to corrosion; tungsten forms an alloy which retains its temper when heated.

The removal of the impurities from pig iron is effected by oxidation, and the process depends upon the fact that the *impurities in the iron are more easily oxidized than the iron itself.* There are two principal processes for the conversion of pig iron to steel: (1) the Bessemer process and (2) the open hearth process. Each will be discussed briefly.

Bessemer process This process was invented by an American, Kelly, in 1852, and modified and improved a few years later by Bessemer, an Englishman. The Bessemer converter is a pear-shaped furnace of about

15 tons capacity and mounted on trunnions which allow it to be tilted to any desired angle. A cross sectional diagram of the furnace is shown in Figure 38–3. The furnaces are lined with either magnesia or silica brick, depending upon the impurities present in the pig iron. Pig iron containing relatively large percentages of phosphorus and sulfur must be treated in a magnesium oxide brick-lined furnace, since the lining acts as a flux to combine with these two elements to form slag. Most of the converters in the United States are silica-lined since they use pig iron produced from ores of low phosphorus and sulfur content. The bottom of the furnace is perforated with a number of small holes through which air may be blown into the converter.

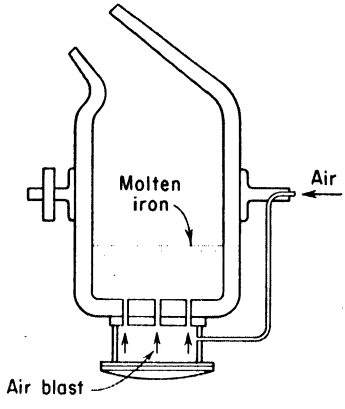


Figure 38–3 Bessemer converter for the manufacture of steel.

The converter is charged with about 15 tons of molten pig iron while in a nearly horizontal position. The air blast is then turned on and the converter is tilted to a vertical position. The blast of air passing through the molten iron oxidizes the impurities present; the carbon is nearly completely removed as carbon monoxide and carbon dioxide, and the oxides of sulfur and phosphorus form a slag with the basic lining of the converter. Since a good deal of heat is produced from the oxidation of carbon, a dazzling shower of sparks is emitted from the mouth of the converter. A single "blow" requires only fifteen to twenty minutes after which the steel produced is poured into ingot molds. Enough carbon is added to the mold to bring the carbon content of the steel up to the desired percentage. The advantage of the process lies in the rapidity with which steel may be produced; its disadvantage is a lack of uniformity of the finished product the reactions take place so rapidly that careful control is not possible.

Basic open hearth process Most of the steel in the United States is produced by this process. The basic open hearth furnace consists of a shallow crucible lined with calcite and magnesia. Below the crucible is a checkerwork of brick so arranged that the heat from the spent gases is used to preheat the entering gases (Figure 38–4). Fuel for the furnace is either producer gas from the blast furnace or oil in the form of

a spray. The fuel gas and air are passed over the hot brick checkerwork and allowed to come together just above the crucible of the furnace. Combustion takes place rapidly because the gases have been preheated to a high temperature. The spent gases pass through the checkerwork on the other side of the furnace where their heat is imparted to the brickwork. Every few minutes the direction of the gases is reversed so that the incoming gases are always preheated to a high temperature, the spent gases meantime passing over the checkerwork which has been cooled by the incoming gases.

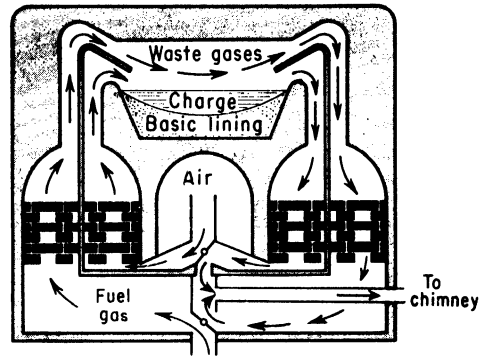


Figure 38–4 Open hearth furnace.

The capacity of an open hearth furnace varies between 50 and 150 tons. The furnace is charged with molten pig iron, limestone to act as a flux, and rusty scrap or iron oxide which acts as an oxidizing agent to oxidize the carbon and other impurities. Sulfur and phosphorus are particularly objectionable in steel as they give a brittle product; therefore, these elements must be reduced to a small percentage. The slag floats on top of the molten iron and prevents its rapid oxidation by the incoming air used to burn the fuel gas. Carbon is slowly oxidized and converted to carbon dioxide. Since from four to twelve hours are required for the oxidation, very careful control of the product is possible. When the carbon content has been reduced to the required percentage and the sulfur and phosphorus have been removed, the iron is tapped and run into ingot molds. When the ingots are finally removed, they are taken to the rolling mill and processed. If an alloy steel is wanted, the same process is followed; however, just before tapping, a certain amount of the alloying element is added to the furnace.

Wrought iron The purest form of commercial iron is *wrought iron,* which is produced in a *puddling* furnace (Figure 38–5), arranged in such a way that the heat is reflected onto the surface of the metal from the low roof. The bottom of the furnace is covered with a layer of ore which acts as an oxidizing agent. The furnace is charged with pig iron and some limestone is added as a flux. Carbon and sulfur are oxidized and lost by volatilization, while the other elements are oxidized and combine with the lime to form a slag. As the impurities are removed,

the melting point of the iron gradually rises and the mass becomes plastic or semifluid. In order to increase the rate of oxidation, the mass is stirred or "puddled" with long iron rods called "rabbles." As the mass becomes less fluid, it is removed on the rabbles in balls weighing about one hundred pounds each. These plastic balls of iron are subjected to squeezing or rolling to remove most of the slag. Not all of the slag is removed, however, as examination shows the product to consist of long fibers of iron separated by thin sheets of slag. Wrought iron is very tough and strong and is used in the manufacture of such articles as horseshoes, chains, and other products, where these properties are desired. Wrought iron, about 99.8 per cent iron, is more expensive than steel because of the labor of producing it; in recent years it has been largely replaced by low carbon steels which have similar properties and are produced much less expensively.

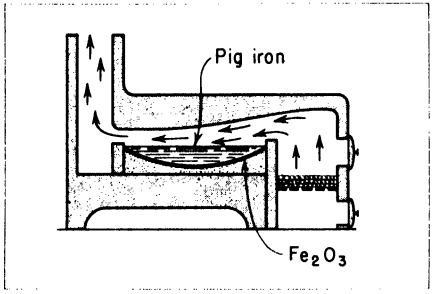


Figure 38–5 Puddling furnace for preparation of wrought iron.

Crucible steel Very high grades of steel such as those used for watch springs, razor blades, files, and so on, are usually prepared by heating small batches of wrought iron or better grades of open hearth steel in small crucibles. An electric furnace allows a very careful control of temperature. Carbon and alloying elements may be added in required amounts. Such high grade steels are called "crucible steels."

Allotropic forms of iron The properties of steel may be modified greatly by conditioning the crystalline form of the iron. At ordinary temperatures a body-centered cubic lattice form of iron exists which is comparatively soft and magnetic and in which carbon is insoluble—it is termed *alpha* iron. When alpha iron is heated above 900°, an allotropic modification known as *gamma* iron forms as a face-centered cubic lattice. Gamma iron is very hard and nonmagnetic and possesses the important property of forming a solid solution with carbon. At 1400° there is formed a further allotrope, called *delta* iron, whose properties are not well known. The equilibrium relations between the three allotropes may be shown in the following manner:

$$\text{Alpha} \overset{900^\circ}{\rightleftharpoons} \text{Gamma} \overset{1400^\circ}{\rightleftharpoons} \text{Delta}$$

Tempering of steel If a steel at a temperature above 900° is quickly cooled by "quenching" in water or oil, the gamma iron, which is hard and dissolves carbon, does not have time to alter to alpha iron, which is soft and does not dissolve carbon. At room temperatures the unstable gamma iron would require centuries to transform completely to the alpha form. Gamma iron is much too hard to be mechanically worked or fashioned; however, a steel containing some gamma iron for strength may be heated for a time to some temperature between 200° and 600° to enable some *tempering* of its hardness—to enable a desired amount of gamma to convert to alpha iron according to the particular strength and hardness qualities wanted in the product. During this reheating, called "annealing," cooling stresses are also removed.

In the higher-carbon steels, a very hard compound of iron and carbon called *cementite,* Fe_3C, appears to be formed. Crystals of cementite, which may be viewed through a microscope, have marked effects on the properties of the steel. Heat treatment will cause some of the cementite to decompose to iron and graphite flakes, resulting in a softer product. The size of crystals formed is also important in determining properties—a steel of minute crystals or grains has more strength than a coarse-grained product. Grain size is somewhat regulated by heat treatment and also by mechanical pounding or pulling of the metal. In general, a mechanically worked product has smaller grain size and greater tensile strength.

Casehardening A low-carbon steel makes a good structural beam; it has toughness and strength and yet enough "bend" so that it does not readily break. However, a low-carbon steel, since it is relatively soft, is easily surface marred; therefore, it is often heated in a carbon or carbon-compound (often cyanide) bath, in which some carbon dissolves into the outer $\frac{1}{16}$ inch or so of the iron to yield a high-carbon, hard, wear-resisting surface. This process is called *casehardening.*

Properties of pure iron Pure iron is a soft, silver-white metal with a melting point of 1535°. Since the metal is fairly high in the activity series, it is classed as one of the more active metals. It does not react with cold water but decomposes steam to form hydrogen. It readily displaces hydrogen from hydrochloric and sulfuric acids. When iron is placed in concentrated nitric acid, the metal assumes a *passive* condition which, according to one explanation, is due to the formation of an adherent oxide film, in which iron exhibits a higher oxidation state.[1] If the surface is scratched, the metal acts in a normal manner. The metal is magnetic, which makes it useful in the construction of motors, generators, and other electrical devices.

[1] Chromium and nickel likewise become passive in highly oxidizing media.

Corrosion Iron exposed to the action of moist air rusts rapidly with the formation of a loose, crumbly deposit of the oxide. The oxide does not adhere to the surface of the metal as does aluminum oxide and certain other metal oxides, but instead peels off, thus exposing a fresh surface of iron to the action of the air. As a result, a piece of iron will rust away completely in a relatively short time unless steps are taken to prevent the corrosion. The chemical steps in rusting are rather obscure, but it has been established that the rust is a hydrated oxide of iron and is formed by the action of both oxygen and moisture, and is markedly enhanced by the presence of minute amounts of carbon dioxide.

Corrosion of iron is inhibited by coating it with numerous substances. It may be covered with paint, an aluminum powder gilt, with tin, or with organic tarry substances. Galvanizing or sherardizing iron with zinc has been discussed (page 461). Alloying iron with metals such as nickel or chromium yields a less corrosive steel.

Compounds of iron Iron forms two series of compounds, *ferrous,* in which the valence of iron is two, and *ferric* compounds, in which the valence is three. Solutions of these compounds produce ferrous, Fe^{++}, and ferric, Fe^{+++}, ions respectively. Ferric compounds are the more stable, since in general, ferrous compounds may be oxidized to the higher state of valence quite easily, often by the oxygen of the air.

The addition of a soluble hydroxide to a solution containing ferrous ions results in the formation of a pale green precipitate of *ferrous hydroxide.* The compound is easily oxidized by oxygen of the air and soon after precipitation, unless oxygen is excluded, oxidation to *ferric hydroxide* occurs. Ferric hydroxide is precipitated as a brownish-red solid by the addition of a soluble base to a solution containing ferric ions. Neither ferrous nor ferric hydroxides are amphoteric and are thus insoluble in an excess of base.

Iron compounds with alkali cyanides form two series of complex salts —*ferrocyanides* which provide $Fe(CN)_6^{----}$ ions in solution and *ferricyanides* which provide $Fe(CN)_6^{---}$ ions. *Potassium ferrocyanide,* $K_4Fe(CN)_6$, is produced by heating together organic matter, potassium carbonate, and scrap iron. The salt is obtained as yellow crystals by evaporation of the solution obtained in leaching the above mixture. *Potassium ferricyanide* may be obtained as dark red crystals by oxidizing potassium ferrocyanide with chlorine. These two compounds are important in testing for the presence of ferrous and ferric ions. Ferric ions react with ferrocyanides to form a characteristic blue precipitate of *ferric ferrocyanide,* called *Prussian blue:*

$$\overset{III}{4\,Fe^{+++}} + 3\,\overset{II}{Fe(CN)_6^{----}} \rightarrow \overset{III\ \ II}{Fe_4[Fe(CN)_6]_3}$$

Ferrous ions react with ferricyanide ions to form *ferrous ferricyanide*, a blue insoluble compound which is called *Turnbull's blue:*

$$3\ \overset{II}{Fe}^{++} + 2\ \overset{III}{Fe(CN)_6}^{---} \rightarrow \overset{II}{Fe_3}[\overset{III}{Fe(CN)_6}]_2$$

The two colors are identical blues in the above cases, and it seems likely that the two compounds have the same composition due to intramolecular rearrangement. Nevertheless, the presence of ferrous and ferric ions may be detected in a sample even in the presence of each other. The formation of the blue precipitate by the addition of a ferrocyanide to a solution must mean the presence of ferric ions, and the formation of the blue precipitate by the addition of a ferricyanide must mean that ferrous ions are present. Of course, the formation of the blue precipitate by the addition of both ferrocyanide and ferricyanide would mean that both ferrous and ferric ions were present in the sample.

If iron is dissolved in dilute sulfuric acid and the solution evaporated to dryness, light green crystals of the heptahydrate of ferrous sulfate, $FeSO_4 \cdot 7\ H_2O$, sometimes called *green vitriol* or *copperas*, are obtained. This salt is one of the more widely used salts of iron, and much is obtained by the evaporation of "pickling" solutions, which are by-products of the cleaning of iron by dipping it into sulfuric acid before galvanization. The compound is important as a disinfectant and weed killer and is also used in the purification of water and as a reducing agent in the laboratory. If equimolecular quantities of ferrous sulfate and ammonium sulfate are dissolved in water and the solution allowed to evaporate, bluish-green crystals of *Mohr's salt*, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$, are obtained. This compound is ordinarily employed in quantitative procedures as a reducing agent because it is more stable than green vitriol.

Blueprints Blueprint paper is made by dipping paper into a solution of ferric ammonium citrate and potassium ferricyanide. When such paper is covered with tracing cloth or tracing paper on which the lines of a drawing are recorded in black ink, and exposed to sunlight, the ferric salt will be reduced to a ferrous salt where the light comes in contact with the paper. When the blueprint paper is wetted, the ferrous salt reacts with the ferricyanide to form Turnbull's blue. The latter compound will form everywhere on the paper except directly under the black lines of the drawing. When the paper is washed, the ferricyanide and ferric salt remaining are removed, and the drawing appears as white lines on a blue background.

COBALT AND NICKEL

The largest source of nickel and cobalt ores is a deposit in the Sudbury district of Ontario, Canada The minerals are largely sulfides and arsenides of cobalt and nickel associated with some copper, silver, and iron sulfides Because of the mixed nature of the ore deposit, the metallurgy of obtaining cobalt and nickel metals is quite complex. Rock masses containing 2 to 3 per cent of nickel silicate have been found in Oregon and Washington, and an iron-nickel alloy is now produced from this material.

Both cobalt and nickel depend for their major uses on their ability to resist corrosion The metals may be plated electrolytically over iron to give a cobalt or nickel plate or may be alloyed with other metals to give corrosion resisting products Nickel alloys are used in coinage, in electrical resistance wire (nichrome), and in a noncorrosive *monel metal*, which is 72 per cent nickel, 26.5 per cent copper, and 1.5 per cent iron. A very hard, noncorrosive alloy called *stellite* contains cobalt, chromium, and tungsten.

Like iron, cobalt and nickel form two series of compounds with characteristic oxidation states of $+2$ and $+3$. The divalent compounds are the more stable and more important Cobalt salts in hydrated form or in solution are usually pink or blue, nickel salts are usually green A dilute solution of $CoCl_2 \cdot 6\ H_2O$, light pink in color, may be used as an invisible ink. After drying, heat will bring out a visible blue color due to the dehydration of the salt Cobalt oxide may be incorporated into glass or glazes to give a beautiful blue color. Both cobalt and nickel may be detected by a borax bead test in which cobalt gives a dark blue color and nickel gives a brown color

THE PLATINUM METALS

Platinum and the platinum-like elements—ruthenium, rhodium, palladium, osmium, and iridium —are somewhat like gold and silver in that they do not displace hydrogen from mineral acids, they occur in the free state as nuggets or specks in alluvial or quartz rock, have relatively high densities, and may be fashioned into polished objects which are resistant to tarnishing. As transition elements below iron, cobalt, and nickel in Group VIII*B*, they resemble these metals in electronic structure, general catalytic activity, and tendency to form complex compounds.

Predominant oxidation states for the elements are $+2$ and $+4$. *Platinous chloride,* $PtCl_2$, *platinic chloride,* $PtCl_4$, *palladous chloride,* $PdCl_2$, and *palladic*

chloride, $PdCl_4$, are well known compounds. The tendency of the elements to form complex compounds is evidenced in *potassium chloroplatinate*, K_2PtCl_6, and *potassium chloro-osmiate*, K_2OsCl_6. When platinum is dissolved in aqua regia, *chloroplatinic acid*, H_2PtCl_6, is formed.

Ruthenium and osmium have the unusual property of exhibiting an oxidation number of +8 in the compounds OsO_4 and RuO_4. These two compounds are produced when the finely divided metals are heated in oxygen. OsO_4 melts at 40° C. and boils at 130° C.; its vapor is poisonous, irritating to the eyes, and has the odor of bromine.

Although rhodium and iridium resemble platinum in many chemical properties, they also are like cobalt, which is above them in the periodic table. Like cobalt, they exhibit an oxidation state of +3 in numerous complex compounds—for example, $K_3Co(NO_2)_6$, $K_3Rh(NO_2)_6$, and $K_3Ir(NO_2)_6$.

Platinum is placer mined from alluvial gravel in the Ural Mountains and concentrated from the rock material with which it is associated by virtue of its high specific gravity (21.5). Only osmium and iridium have higher densities than platinum. Small amounts of platinum are associated with gold in Colombia, South Africa, and the western United States. Other platinum metals are found associated with, or alloyed with, platinum. Platinum and palladium are by-products in the purification of nickel from certain Canadian ores

Platinum is used in jewelry, in dentistry, and in the making of laboratory crucibles and articles which may have to withstand corrosion or high temperature It has a specific use in finely divided form as a catalyst, usually mixed with a carrier such as asbestos fibers. Because it has about the same coefficient of expansion as glass, it may be sealed through glass for the conduction of electricity. The other platinum-like metals are used as substitutes for platinum or may be alloyed with it. Rhodium and iridium increase the hardness of platinum or of gold and thus increase the wearing qualities of these metals. A platinum-rhodium alloy is commonly used as a thermocouple. Platinum varies in price (about $90 per ounce in recent years), whereas gold is stabilized by governmental regulation at $35 per ounce.

EXERCISES

1 With reference to the manufacture of pig iron in the blast furnace give
(*a*) Raw materials, relative amounts, and functions of each
(*b*) Products of the blast furnace.
(*c*) Equations for reactions taking place in the furnace.

2 What property of iron makes it such a valuable substance to man?

3 Contrast the differences in composition and properties of (*a*) pig iron, (*b*) Bessemer steel, (*c*) open-hearth steel, (*d*) wrought iron

4 Name eight elements that are sometimes alloyed with iron in an alloy steel.
5 Write equations for the preparation of a household bluing from ferric oxide, common acids, and potassium ferrocyanide.
6 Name four elements other than Fe that may be found in pig iron.
7 What are "transition" groups? List similarities of the elements: cobalt, nickel, and iron.
8 How could you differentiate between the three metals: iron, cobalt, and nickel?
9 List the formulas and mineral names of important minerals of iron.
10 Describe the changes taking place during the tempering of steel.
11 Describe exactly how you would test a sample for the presence of both ferrous and ferric salts.
12 A hematite ore analyzes 28 per cent iron. What weight of Fe_2O_3 is present per ton of ore? What weight of coke is needed per ton of iron ore? Assume that the coke is 60 per cent efficient in the chemical change

$$Fe_2O_3 + 3\,C \rightarrow 2\,Fe + 3\,CO$$

13 What is the chemical nature of the coating given to iron in each of the following processes: galvanizing; sherardizing; casehardening?
14 (*a*) A green glaze may be given pottery by heating nickel carbonate with sodium silicate. Write the equation. (*b*) Cobalt oxide reacts with borax to form blue cobalt metaborate and sodium metaborate. Write the equation.
15 Complete the equations:

$$Cl_2 + Pt \rightarrow \qquad H_2PtCl_6 + KNO_3 \rightarrow$$
$$PtCl_4 + HCl \rightarrow \qquad PdCl_2 + Zn \rightarrow$$

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INTRODUCTION TO ORGANIC CHEMISTRY I

Most of the compounds thus far considered in this book have been classified as acids, bases, salts, and oxides of metals or nonmetals—substances which are derived from minerals in the earth's crust. Frequently these are referred to as inorganic compounds and their chemistry as *inorganic chemistry,* one of the major divisions of the field of chemistry.

Organic chemistry is concerned with the study of the compounds of carbon. It may seem curious that an entire division of chemistry is concerned with one element; however, this one element forms a tremendous number of compounds—several hundred thousand are known. The existence of organic chemistry is further justified by the importance of carbon compounds or mixtures in our lives. For example, carbon is common in the molecular composition of such substances as gasoline, vitamins, hormones, plastics, explosives, fats, proteins, carbohydrates, perfumes, medicinals, alcohols, and wood products. All plant and animal tissues are largely composed of carbon compounds, water, and a small mineral content.

The multiplicity of carbon compounds is explained in the exceptional ability of carbon atoms to combine with one another to form long continuous chainlike structures containing many carbon atoms. In inorganic compounds the number of like atoms in a molecule rarely exceeds five, but organic molecules containing a dozen or more carbon atoms are common. Carbon, with four electrons in its valence orbit, forms compounds by sharing its electrons with atoms of other elements or *with itself.* Two given carbon atoms may share one, two, or three pairs of electrons between themselves to give rise to three fundamental classes of compounds. Different arrangements of the same atoms within a molecule produce different compounds, and thus the number of carbon

compounds is further increased. Although the number of organic compounds currently known seems very large, we can say with certainty that the field is still in its infancy; the number of possible organic substances is exceedingly great.

Many of the materials listed above as examples of organic compounds were once believed to be products of living organisms—and so were called organic. Following much laboratory experimentation, however, chemists were able to demonstrate that certain products, which had previously been considered the results of vital or living processes, could be produced in the laboratory. One of the classical examples of this type of work was Wöhler's synthesis of urea. In the year 1828, Wöhler, a German chemist, produced urea, a decomposition product of proteins, by heating ammonium cyanate, a compound of inorganic origin:

$$NH_4CNO \rightarrow CO(NH_2)_2$$

This was the beginning of a new era in the synthesis of carbon compounds which scientists had previously thought impossible to prepare in the laboratory. The vital-process idea was discarded. Today, rapid strides are being made in the preparation of sugars, vitamins, and related compounds. Every day, new compounds are produced in the laboratory of the synthetic organic chemist, and many of these compounds have an important bearing on our everyday life.

In the discussion of the conductivities of aqueous solutions of acids, bases, and salts, it was pointed out that, as a group, they were relatively good conductors of the electric current. In marked contrast to this is the fact that aqueous solutions of alcohol, sugar, glycerol, and the like are very poor conductors. These facts suggest that there is little or no ionization in the case of organic compounds. Thus, although ionic inorganic reactions proceed almost instantaneously, organic reactions frequently require, even under the most favorable conditions, considerable time before they approach completion.

Some sources of organic compounds Reference to Table 39–1 will show sources of some of the more familiar organic substances.

Of the substances listed, some—such as benzene, phenol, wood alcohol, and acetic acid—are pure compounds; others—such as fats, proteins, coal tar, and petroleum—are complex mixtures. Starch and cellulose molecules are highly complex, and their structures have not been fully determined.

Petroleum is an extremely valuable raw material of nature. From it are obtained such important commodities as gasoline, kerosene, fuel oils, lubricating oils, paraffin, and wax. The importance of the petroleum industry in our national economy is evident from the fact that the

TABLE 39–1 Sources of Organic Substances

SOURCE	ORGANIC COMPOUNDS OR MIXTURES
Animals	fats, proteins
Plants	starch, cellulose
Coal (destructive distillation)	coal tar, benzene, phenol, naphthalene
Wood (destructive distillation)	wood alcohol, acetone, acetic acid
Petroleum (fractional distillation)	cleaner's naphtha, gasoline, kerosene, mineral oil, vaseline
Fermentation processes	ethyl alcohol, acetone, butyl alcohol
Laboratory synthesis	almost unlimited numbers and types of compounds

United States markets several billion dollars worth of petroleum products annually.

A vast variety of products are obtained from coal tar, which is one product from the destructive distillation of coal. Benzene, toluene, phenol, naphthalene, and many other compounds obtained from coal tar are the starting materials in the preparation of a great number of dyes, perfumes, medicinals, plastics, and explosives.

The importance of the synthetic organic chemical industries cannot be overemphasized. The organic chemist has been able in many instances to duplicate natural products in his laboratory and, probably more important, has produced substances never found in nature. In many cases synthetic products are superior to natural products, and we can accurately say that man has improved over nature.

Perhaps no other field of chemistry has such a direct bearing on our everyday lives. More than 50 per cent of our trained graduate chemists are "organic" chemists engaged in the research and production of the hundreds of substances which were unknown two or three generations ago. With the exception of a few basic inorganic substances such as iron and steel, sulfuric acid, caustic soda, and soda ash, the tonnage of organic substances produced by chemical industry far exceeds that of inorganic products.

HYDROCARBONS

Compounds composed of the elements carbon and hydrogen only are termed *hydrocarbons.* They are among the simplest of organic compounds and will be considered first. Although hundreds of hydrocarbons are known, we shall limit our discussion to a few of the simpler ones. For convenience we may group the hydrocarbons into series, four

TABLE 39–2 Some Common Hydrocarbons

ALKANE C_nH_{2n+2}		ALKENE C_nH_{2n}		ALKYNE C_nH_{2n-2}		BENZENE C_nH_{2n-6}	
Methane	CH_4					Benzene	C_6H_6
Ethane	C_2H_6	Ethene	C_2H_4	Ethyne	C_2H_2	Toluene	C_7H_8
Propane	C_3H_8	Propene	C_3H_6	Propyne	C_3H_4	Xylene	C_8H_{10}
Butane	C_4H_{10}	Butene	C_4H_8	Butyne	C_4H_6		
Pentane	C_5H_{12}						
Hexane	C_6H_{14}						
Heptane	C_7H_{16}						
Octane	C_8H_{18}	Octene	C_8H_{16}	Octyne	C_8H_{14}		

of which will be considered: *alkane, alkene, alkyne,* and *benzene* series. The first few members of each series are shown in Table 39–2. In the general formula for each series, n is equal to the number of carbon atoms in the molecule.

Each of these four series is called a *homologous series,* since any member of each group differs from the preceding or following member by one carbon atom and two hydrogen atoms (CH_2). For example, butane, C_4H_{10}, in the alkane series differs from propane, C_3H_8, immediately preceding it by CH_2, and also differs from pentane, C_5H_{12}, the member following by the same amount (CH_2). In any given series the members possess similar chemical properties; the physical properties show a gradual change in progressing from the compounds of few carbon atoms to those containing a large number. Compounds of the first three series are often referred to as *chain* compounds, since the carbon atoms are arranged one after another as in a chain; members of the benzene series are referred to as *ring* compounds because the carbon atoms are joined together as a closed system or ring.

Structural formulas The inorganic chemist uses such molecular formulas as H_2SO_4, H_2O, and NaCl to show the composition of compounds; but molecular formulas are inadequate in representing many organic compounds, since different arrangements of atoms in the molecule give rise to different compounds. This property, which is termed *isomerism,* will be discussed in more detail later (page 522).

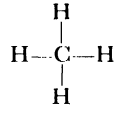
The molecular formula C_2H_6O may represent either ethyl alcohol or dimethyl ether. Thus, it is necessary in organic chemistry to show *how* the atoms are joined together in the molecule—in other words, to show the arrangement of the atoms in the molecule—in order to get an accurate idea of the substance. Friedrich Kekulé about a century ago instituted the use of *structural* or *graphic* formulas to clarify the molecular structure of organic compounds. Kekulé's contributions brought order out of chaos and enabled the organic chemist to make great strides in

the synthesis of organic substances on the basis of this so-called "picture chemistry."

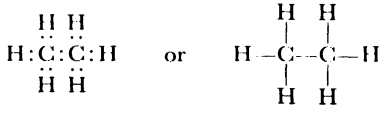
The basis for structural formulas is the valence number four of the carbon atom. The carbon atom with four electrons in its outer shell neither gives up nor takes up electrons but rather shares these electrons with other atoms of carbon or with atoms of other elements; thus the compounds of carbon are covalent and nonionic. A structural formula shows how these electrons are shared with other atoms; for example, methane, CH_4, may be represented:



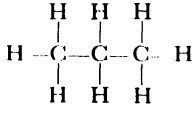
Four electrons from the carbon atom and four electrons from the hydrogen atoms are mutually shared; the formula shows four pairs of shared electrons. Each pair of electrons represents a covalence of one. In writing structural formulas, a pair of electrons is usually replaced with a dash to indicate a single bond of valence; thus methane would be shown as



Carbon atoms may share a pair or more of electrons between themselves; thus ethane, C_2H_6, would be shown



and propane, C_3H_8



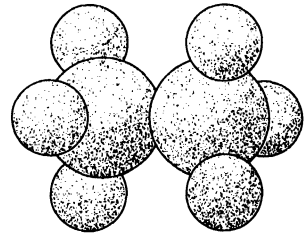


Figure 39–1 Structural model of ethane.

Where there can be no question of the arrangement of the atoms in a compound, a condensed structural formula may be used; for example, the above hydrocarbons might be represented as CH_4; $CH_3—CH_3$; $CH_3—CH_2—CH_3$.

The alkane series of hydrocarbons This series is sometimes referred to as the *methane* series, after the first member, or the *paraffin* series, the term paraffin meaning inactive. The general formula of the series is C_nH_{2n+2}, where n is an integral number: 1, 2, 3, 4, and so on. The first four members of the series are gases at ordinary temperatures; members containing from five to fifteen carbon atoms are liquid, and the higher members of the series are solids. Thus it is evident that a gradual increase in the boiling points of these compounds takes place as the number of carbon atoms in the molecule increases.

Methane is the principal constituent of natural gas. It is also formed during the decay of organic matter under water in marshes and swamps in the absence of air; thus is derived its common name of *marsh gas.* In coal mines where it is known as *fire damp,* it is the principal cause of explosions. It may be produced in the laboratory by fusing together sodium acetate and sodium hydroxide:

$$NaC_2H_3O_2 + NaOH \rightarrow Na_2CO_3 + CH_4 \uparrow$$

Chemical properties of the alkanes These hydrocarbons are characterized by their inactivity; they show little tendency to react with other substances. However, strong oxidizing agents may react with these compounds; for example, if methane and chlorine gases are mixed and allowed to stand in the sunlight, chlorine atoms are substituted successively for the hydrogen atoms in the molecule according to the following equations:

$$CH_4 + Cl_2 \rightarrow CH_3Cl \text{ (methyl chloride)} + HCl$$
$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 \text{ (methylene chloride)} + HCl$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 \text{ (chloroform)} + HCl$$
$$CHCl_3 + Cl_2 \rightarrow CCl_4 \text{ (carbon tetrachloride)} + HCl$$

Chloroform has been used as a general anesthetic in surgery; carbon tetrachloride is used for solvent and cleaning purposes. Other members of the alkane series react similarly with chlorine and other halogens.

All hydrocarbons are combustible and, if complete burning is allowed to take place, carbon dioxide and water are formed as oxidation products, as in these reactions:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$
$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O$$
$$2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$$

Incomplete combustion results in the formation of some carbon monoxide or free carbon:

$$2\ C_8H_{18} + 23\ O_2 \rightarrow 13\ CO_2 + 2\ CO + C + 18\ H_2O$$

Because of incomplete combustion, all internal combustion engines produce some carbon monoxide.

Petroleum This black oily liquid—so important that nations may wage war for it—is the principal source of the paraffin hydrocarbons. Petroleum is a mixture of gaseous, liquid, and solid hydrocarbons, most of which belong to the methane series. The United States annually produces more than a billion barrels.

The hydrocarbons contained in petroleum are separated by means of fractional distillation (page 194), a process which takes advantage of a difference in the boiling points of the compounds. When petroleum is heated, those constituents with the lowest boiling points distil over first, followed by the higher boiling components. By changing the receivers of the distillate at intervals, several fractions are obtained. By repeated fractional distillation of these fractions, the hydrocarbons may be separated in relatively pure form. Principal products of the refining of petroleum are shown in Table 39–3.

One of the most important products of the refining of petroleum is gasoline; because of the great demand for gasoline for use in automobiles and airplanes, efforts have been made to increase the yield of this important fuel. It is evident from Table 39–3 that gasoline is a mix-

TABLE 39–3 Principal Products of the Refining of Petroleum

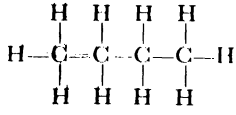
HYDROCARBONS	PRODUCTS	BOILING POINT RANGE	USES
CH_4 C_2H_6 C_3H_8 C_4H_{10}	natural gas	−160° to 0°	fuel gas for heat and power
C_5H_{12} C_6H_{14}	petroleum ether or ligroin	35° to 70°	solvent for fats and oils
C_7H_{16} C_8H_{18}	gasoline	70° to 150°	motor fuel, solvent
C_9H_{20} to $C_{14}H_{30}$	kerosene fuel oil	150° to 250°	fuel, illuminating oil
$C_{15}H_{32}$ to $C_{20}H_{42}$	middle fraction or cracking oil, lubricating oil	250° and up	lubrication; cracked to gasoline
Above $C_{20}H_{42}$	vaseline paraffin tar residue petroleum coke		medicinal candles road surfacing fuel

ture of the lower hydrocarbons, which have an average of seven or eight carbon atoms. By subjecting petroleum fractions to high heat and pressure, it is possible to break down fuel oils and higher-boiling fractions which contain higher hydrocarbons into gasoline and lower hydrocarbons. This process is referred to as *cracking* petroleum. The following equation is typical of the cracking operation:

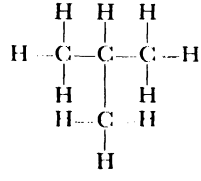
$$C_{14}H_{30} \rightarrow C_8H_{18} + C_5H_{12} + C$$

By means of the cracking process, it is possible to utilize less desirable petroleum-distillation fractions and to increase greatly the yield of gasoline.

Isomers If we study the graphic formulas for butane and higher hydrocarbons of the methane series, we may note that it is possible to arrange the atoms in the molecule in more than one way, thus giving rise to two or more different arrangements for the same formula. For example, we may write the graphic formula for butane, C_4H_{10}, as



in which the carbon atoms are arranged in a continuous chain. In no case in this formula are more than two carbon atoms attached to any single carbon atom. But it is possible to write a formula for butane as



in which three carbon atoms are attached to a single carbon atom. The result is a branched chain compound. Both of these butanes are known and have been prepared; the latter is termed *isobutane* to differentiate it from the continuous chain butane which is called *normal* butane. Such compounds with the same molecular formula, but with a different arrangement of the constituent atoms in the molecule, are called *isomers*, and the name applied to this phenomenon is *isomerism*. Careful study of the formulas for butane will show that these two arrangements are the only ones possible which will satisfy all valence requirements. As the number of carbon atoms increases, the number of isomers also in-

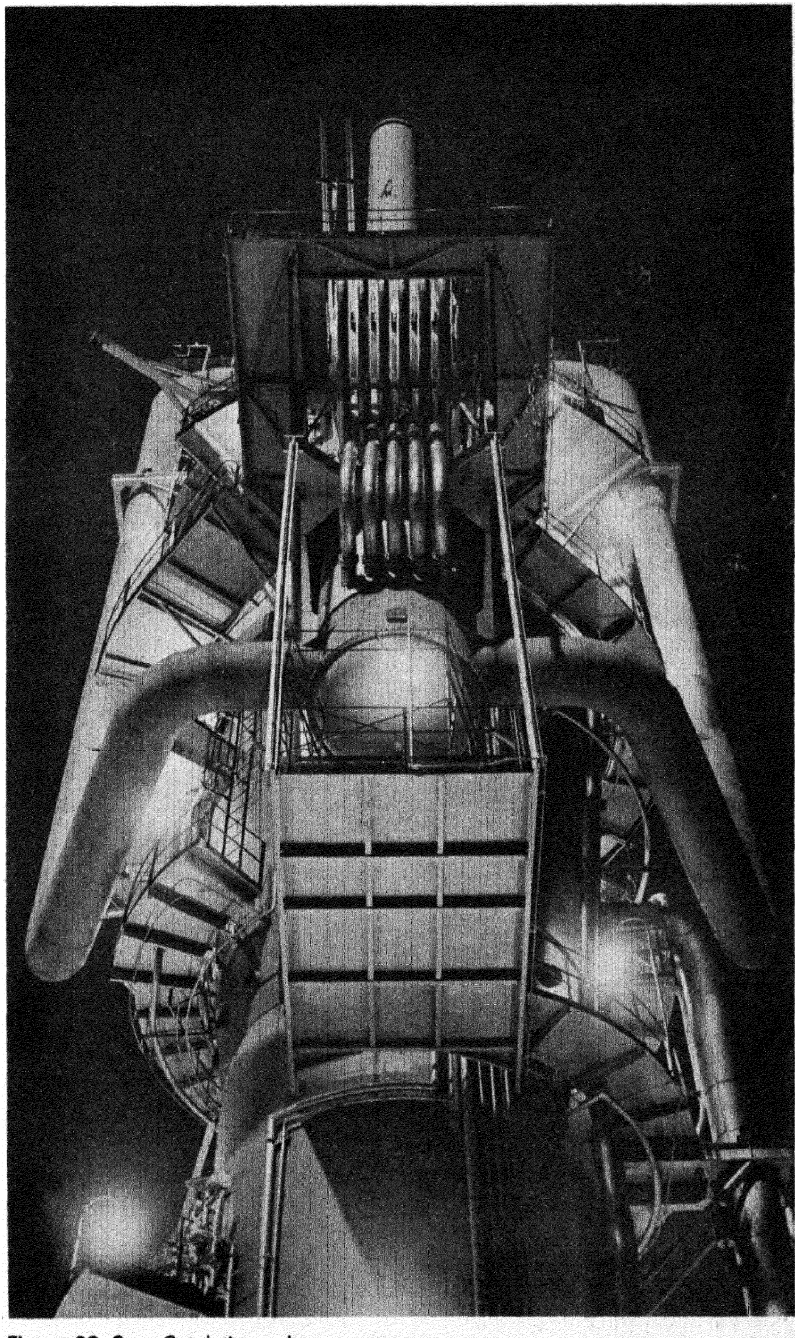
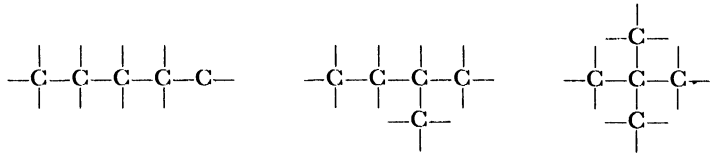


Figure 39–2 Catalytic cracker.

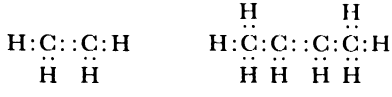
creases. A study of the formulas for pentane will reveal the following three possible isomers (hydrogen atoms are not shown):



The student will find it interesting to draw structural formulas for the possible isomers of hexane, C_6H_{14}, and heptane, C_7H_{16}.

The alkene series of hydrocarbons This series has the general formula C_nH_{2n} and is sometimes referred to as the *olefin* series or the *ethylene* series after ethylene, the first member. Names for the members of the alkene series are derived from names of compounds of the alkane series with the same number of carbon atoms, by changing the *ane* ending to *ene;* thus C_4H_8 is *butene* from butane, C_4H_{10}; and so on.

Members of the series are characterized by carbon-to-carbon linkages which involve the sharing of two electron pairs, thus:



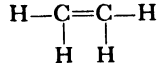
Ethene, C_2H_4, commonly called ethylene, is the simplest member of the series; it may be prepared by the dehydration of ethyl alcohol with concentrated sulfuric acid at a temperature of about 160°

$$C_2H_5OH \xrightarrow[\text{heat}]{H_2SO_4} C_2H_4 + H_2O$$

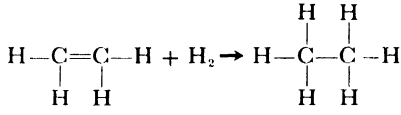
or may be obtained as a product of the cracking of petroleum.

Ethylene gas, either alone or mixed with ether, is now used as an anesthetic since it causes less nausea and discomfort than ether. It is also employed to hasten the ripening of citrus fruits because it causes the development of a uniform orange or yellow color. In addition, ethylene is used as a starting material in the preparation of many organic compounds.

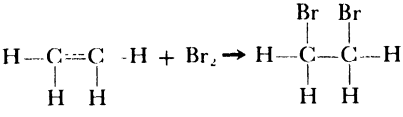
Unsaturation When we write the structural or graphic formula for ethene, we employ the usual method of putting down the carbon atoms in a chain and dividing the four hydrogen atoms equally between the two carbon atoms:



In order to satisfy valence requirements of carbon, we may put an additional bond between the carbon atoms making two bonds or a double bond. The double bond obviously stands for two pairs of shared electrons. That we are justified in so representing the formula for ethene becomes clear when we consider the chemical properties of the compound. Ethene has the property of adding two hydrogen atoms to form ethane, and we might represent the change as

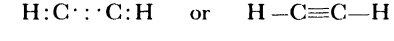


Other elements may also add to the compound; for example, ethene readily absorbs bromine to form ethylene dibromide, $C_2H_4Br_2$:

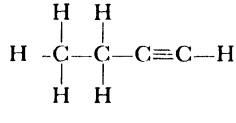


Because it has the capacity to add atoms, ethylene is said to be *unsaturated.* All members of the alkene series contain a double bond between a pair of carbon atoms and thus are unsaturated.

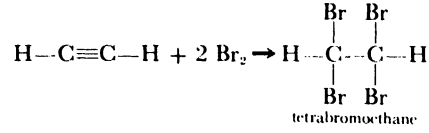
The alkyne series of hydrocarbons Members of this series have the general formula C_nH_{2n-2}. The names are derived from the hydrocarbons of the methane series by replacing the *ane* ending of the methane series with *yne;* thus C_3H_4 is propyne, from propane, C_3H_8; and so on. This series possesses a higher degree of unsaturation than the alkene series. Ethyne, more commonly called *acetylene,* is written with a triple bond:



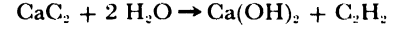
This triple bond denotes a sharing of three electron pairs between two carbon atoms. Another example is butyne, C_4H_6



These compounds as would be expected add more bromine or hydrogen than do corresponding members of the alkene series:

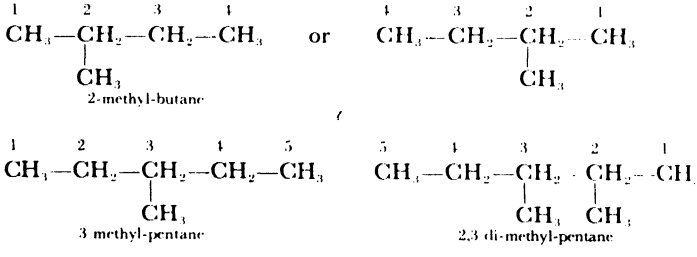


Acetylene is readily produced by the action of water on calcium carbide:

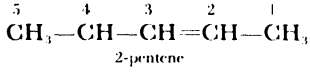


The gas has a high heat of combustion, a property which is taken advantage of in the acetylene-oxygen torch for welding purposes. Acetylene also finds use as a starting material in the preparation of *neoprene,* an artificial rubber.

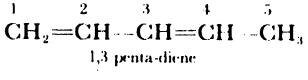
Naming of higher hydrocarbons As the number of carbon atoms increases, the complexity of possible structures becomes greater. In order to show the presence of branched chains and their position, a system of nomenclature has been devised to define adequately the structure of the molecule. In this system the longest chain is taken as the basic structure, and the carbon atoms are numbered from the end of this chain closest to a branch chain or other modification of simple alkane structure. The positions of substituents in the chain are indicated by the number of the carbon atom or atoms to which they are attached. Study the following examples:



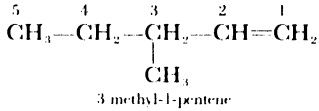
In the case of unsaturated hydrocarbons, the position of the double or triple bond is similarly indicated, the numbering starting at the end of the chain nearest the double bond.



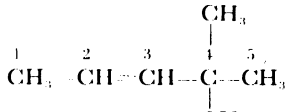
Two double bonds are indicated by the suffix *-diene:*



Other examples are:



3 methyl-1-pentene

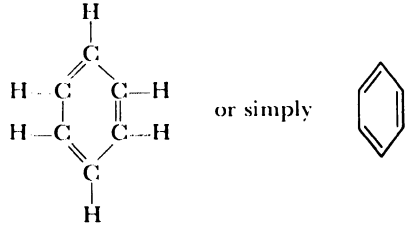


4,4 di-methyl-2-pentene

Polymerization Like molecules of many organic substances may be made to combine to form complex molecules with new properties. This phenomenon is known as *polymerization*, and the product may be termed a *polymer*. Thus, the formation of benzene, C_6H_6, from a condensation of three molecules of C_2H_2, might be termed polymerization, and benzene could be considered to be a polymer of acetylene. Synthetic rubbers appear to be polymers of simple hydrocarbons.

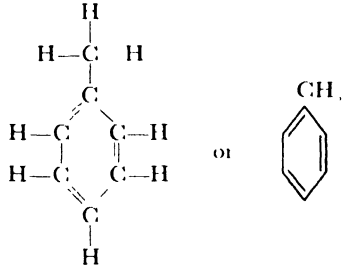
The benzene series of hydrocarbons The general formula for members of this series is C_nH_{2n-6}. Many of these compounds are obtained from coal tar, a by-product of the destructive distillation of coal. The smaller ratio of hydrogen atoms to carbon atoms in the molecules of these compounds than in any of the preceding series would lead us to the conclusion that they are unsaturated. Although certain reactions show that these compounds possess some degree of unsaturation, nevertheless they do not add the elements hydrogen and bromine with the facility of members of the alkene and alkyne series.

Kekulé suggested that members of this series possess a ring structure with six carbon atoms joined together; for example, benzene has a structure which is most frequently represented thus:

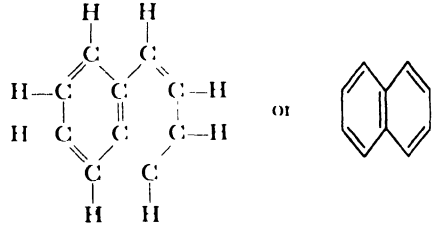


The carbon atoms are arranged in the form of a hexagon with double bonds between alternate carbon atoms and with a hydrogen atom attached to each carbon. The benzene ring structure is usually shown

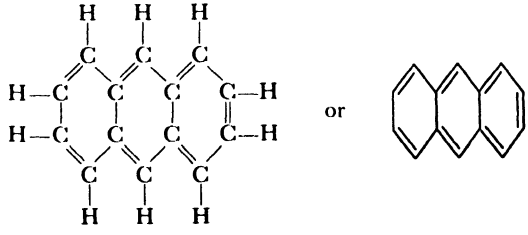
simply as the figure of a hexagon. The reactions of benzene indicate that it possesses a symmetrical structure—that is, the carbon atoms all bear the same relationship to each other. This hexagon arrangement of carbon atoms seems to be the basic structure of all members of the benzene series of hydrocarbons as well as their many derivatives. Toluene, the member following benzene, has a CH_3 group substituted for one of the hydrogen atoms and is shown structurally as



Aliphatic and aromatic hydrocarbons Hydrocarbons of continuous chain structures are referred to as *aliphatic* hydrocarbons while those possessing a ring structure with alternating double bonds between carbon atoms are termed *aromatic* hydrocarbons. In accordance with these definitions, the first three series of hydrocarbons discussed—alkanes, alkenes, alkynes—would be aliphatic compounds and the last series—benzene—would be classed as aromatic hydrocarbons. Examples of aromatic hydrocarbons of other series might include naphthalene



and anthracene



both of which are obtained as products of coal tar and serve as starting materials for the preparation of many dyes and medicinals.

EXERCISES

1 Define the following terms: hydrocarbon, homologous series, unsaturated hydrocarbon, polymerization, structural formula, isomers.
2 Draw structural formulas for methane, acetylene, propane, ethylene, benzene.
3 Write structural formulas for all possible isomers of heptane, C_7H_{16}. How many possibilities did you find?
4 Write an equation for the complete combustion of ethane. Compare the volume of reacting substances with the total volume of products, all measured under the same conditions of temperature and pressure.
5 One liter of gasoline (average composition, C_8H_{18}) weighs 798 g. Calculate the volume of air (20 per cent oxygen) at standard conditions necessary for its complete combustion. What would the total volume of products be at standard pressure and a temperature of 546° C.? Ans. 9800 l.; 8000 l.
6 How could you determine whether or not a given hydrocarbon was unsaturated?

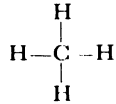
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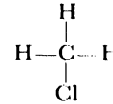
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forty INTRODUCTION TO ORGANIC CHEMISTRY II

DERIVATIVES OF THE HYDROCARBONS

The substitution of elements or radicals for one or more of the hydrogen atoms in a hydrocarbon results in the formation of many types of compounds which are referred to as *derivatives* of the hydrocarbons. For example, methyl chloride, CH_3Cl, one of the products formed by the treatment of methane with chlorine, may be considered to be derived from the hydrocarbon methane:


methane


methyl chloride

The CH_3 radical is termed *methyl* and derives its name from the parent hydrocarbon methane. Corresponding radicals of other hydrocarbons of the methane series are similarly derived. The general term, *alkyl* radicals, includes all radicals derived from the methane series. The specific name of the radical is obtained by replacing the ending *ane* by *yl*. The composition of the radical will be the same as the parent hydrocarbon except it will contain one less hydrogen atom; thus, C_2H_5 is the *ethyl* radical, C_3H_7 the *propyl* radical, and so on. Obviously, the valence of alkyl radicals must be 1.

Because of the relative inactivity of the hydrocarbons, their derivatives in most cases cannot be produced directly by substitution of another element or group but are produced from reactions of other types of organic compounds. These derivatives of the hydrocarbons may be classified into groups or types of compounds depending upon

TABLE 40–1 Organic Derivatives with General Formulas

TYPE OF COMPOUND	GENERAL FORMULA*
Alcohol	R—OH
Alkyl halides	R—X (where X = F, Cl, Br, I)
Amine	R—NH_2
Ether	R—O—R′
Aldehyde	R—C(=O)—H
Ketone	R—C(=O)—R′
Acid	R—C(=O)—OH
Ester	R—C(=O)—O—R′

* R stands for an alkyl radical, R′ is also an alkyl radical which may be the same or different from R

the atom or group of atoms substituted for the hydrogen atom. Such groups are called *functional* groups and determine in a large measure the properties of the compound Compounds with the same functional group or groups exhibit very similar chemical properties. In Table 40–1 are summarized several of the more important types of derivatives with the general formula for compounds of each type.

Similar to the hydrocarbons, a homologous series of each type of compound is possible. For example, the following amines constitute such a series: CH_3NH_2, $C_2H_5NH_2$, $C_3H_7NH_2$, $C_nH_{2n+1}NH_2$.

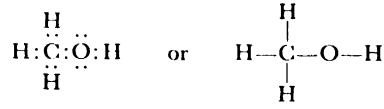
ALCOHOLS

Alcohols have the general formula R—OH and in some respects are similar to metallic hydroxides or bases. However, they show no tendency to form hydroxide ions in solution, and thus those properties which we usually associate with bases—such as bitter taste, soapy feeling, and effect on litmus—are not exhibited by the alcohols. Alcohols might also be considered to be derived from water in which one of the hydrogen atoms in the water molecule has been replaced with an alkyl radical. Indeed in most respects alcohols resemble water more in chemical properties than they resemble metallic hydroxides.

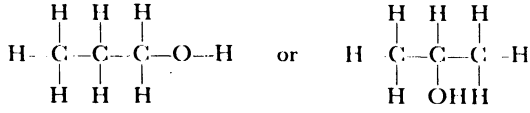
While it is theoretically possible to substitute more than one OH group for hydrogen atoms in methane, such a compound is not actually known and it seems likely that compounds in which more than one OH

group is attached to the *same* carbon atom are very unstable if indeed they exist at all.

Structurally the oxygen atom present in the hydroxide group of an alcohol is linked to the carbon atom in the alkyl radical by a single pair of shared electrons. The oxygen atom also shares a pair of electrons with the hydrogen atom of the hydroxide group; thus methyl alcohol would be shown:



Isomers become possible in alcohols of more than two carbon atoms; for example, propyl alcohol, C_3H_7OH, may be written structurally as



The first isomer is called a *primary* alcohol since the OH group is attached to a carbon atom which itself is linked directly to but one carbon atom: the second is called a *secondary* alcohol, since the OH group is attached to a carbon to which are directly linked two other carbon atoms. With the higher alcohols it is possible to have an OH group attached to a carbon atom, which is directly linked to three other carbon atoms, in which case the alcohol is termed a *tertiary* alcohol. The structural formulas above for the propyl alcohols are usually written in a semistructural manner—that is, $CH_3—CH_2—CH_2OH$ for *normal* propyl alcohol, and $CH_3—CHOH—CH_3$ or, better still, $(CH_3)_2CHOH$ for *isopropyl* alcohol.

In naming alcohols, the ending *-ol* is sometimes substituted for the ending *e* of the hydrocarbon from which the alcohol is derived; thus methyl alcohol is *methanol;* ethyl alcohol is *ethanol;* propyl alcohol is *propanol,* etc.

Methyl alcohol Methyl alcohol or *methanol,* also called wood alcohol, is one of the products of the destructive distillation of wood. Until a few years ago this method provided almost the sole source of methanol; however, a catalytic process has recently been developed in which the following reaction takes place:

$$CO + 2\,H_2 \rightarrow CH_3OH$$

The gases are passed over zinc oxide or other suitable catalysts at an elevated temperature and under pressure.

Methyl alcohol is a colorless liquid which boils at 67°. It is extremely toxic when taken internally. Large quantities of methanol are

employed commercially as a solvent for varnishes, shellacs, and lacquers, which are readily soluble in the alcohol. It is used also as a denaturant for ethyl alcohol, and as a starting material in the preparation of formaldehyde and other chemicals.

Ethyl alcohol Ethyl alcohol or *ethanol,* C_2H_5OH, sometimes referred to as "grain" alcohol, is a colorless liquid which in physical properties is quite similar to methanol. It is much less poisonous than methyl alcohol, although if taken in large amounts it may be decidedly harmful. The boiling point of ethanol is 78°, which is not very different from that for methanol, 67°. A mixture of the two, therefore, is not easily separated by distillation.

As an industrial chemical, ethyl alcohol finds extensive application. Like methanol, it is used as a solvent for varnishes and lacquers. Tinctures are alcoholic solutions; tincture of iodine is familiar to all. Flavoring extracts, tonics, lotions, and many medicines contain large percentages of alcohol. Ethanol is used as a starting material in the preparation of ethyl acetate, ethylene, ether, and other important chemical compounds. Because of its low freezing point, −117°, alcohol is employed as an antifreeze in automobile radiators. Many other uses of lesser importance for ethyl alcohol might be listed. In the United States alone nearly 200 million gallons are produced annually.

Ethyl alcohol is produced industrially by the fermentation of glucose and fructose. Glucose or fructose may be obtained by hydrolysis of cane or malt sugar or starch (page 545). The reaction occurring during the fermentation may be represented by the equation:

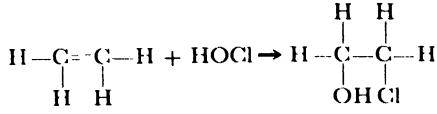
$$C_6H_{12}O_6 \rightarrow 2\,C_2H_5OH + 2\,CO_2$$

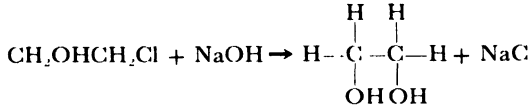
The fermentation is catalyzed by certain *enzymes,* which are organic compounds produced from yeast cells. Solutions containing 10 to 15 per cent alcohol are usually produced by these fermentation processes since higher concentrations of alcohol would kill the yeast cells. By fractional distillation of these solutions a concentration of approximately 95 per cent alcohol is readily prepared and in this concentration industrial alcohol is usually marketed.

The concentration of an alcoholic solution is usually expressed in terms of "proof" rather than percentage. A 95 per cent alcohol solution is 190 proof, 100 per cent alcohol is 200 proof, a 45 per cent whisky is 90 proof, etc. Alcohol used for beverages is taxed highly by the federal government; however, alcohol used for industrial purposes is tax free. Usually some nonpalatable substance (denaturant) is added to ensure that it will not be diverted to beverage manufacture.

Other alcohols *Ethylene glycol,* $C_2H_4(OH)_2$, because of its relatively high boiling point, 198°, and its noncorrosive action on metals finds use

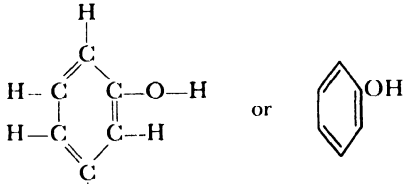
as an antifreeze in automobile radiators. It is produced commercially by means of the following reactions:





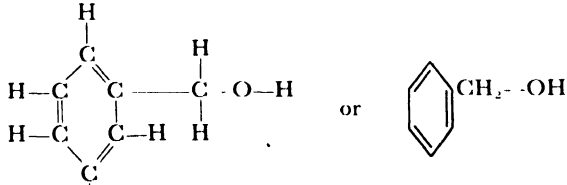
Glycerin, $C_3H_5(OH)_3$, is a colorless, viscous liquid with a sweet taste produced as a by-product of soap manufacture. Besides its use in many toilet preparations, it is the starting material in the manufacture of nitroglycerin, a powerful explosive.

Phenol, C_6H_5OH, commonly known as *carbolic acid,* is obtained from coal tar. It is highly corrosive and produces severe burns on the skin, yet it is useful as an antiseptic in killing certain bacteria. Although phenol contains the characteristic group of an alcohol, OH, it behaves chemically as a weak acid and may be neutralized with strong bases to form salts. Phenol is the starting material in the preparation of many important commercial products including resins, picric acid, many dyes, aspirin, and other drugs. Phenol is an example of a derivative of an aromatic or ring structure hydrocarbon.



phenol

Benzyl alcohol is a typical aromatic alcohol.



benzyl alcohol

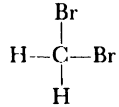
ALKYL HALIDES

Compounds with the general formula R—X where X is one of the halogens are called *alkyl halides.* They may be prepared by the action of the free halogen on the hydrocarbon (page 520) or by the treatment of an alcohol with a hydrohalogen acid as in this reaction:

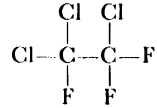
$$C_2H_5OH + HCl \rightarrow \underset{\text{ethyl chloride}}{C_2H_5Cl} + H_2O$$

Examples of other alkyl halides are: CH_3F, methyl fluoride; C_3H_7Br, propyl bromide; and C_4H_9I, butyl iodide.

Substitution of more than one hydrogen of a hydrocarbon by halogen atoms is also possible. Examples are:



di brom methane



tri chlor tri fluorethane

AMINES

Amines may be considered as derivatives of ammonia in which one or more of the hydrogen atoms of the ammonia molecule have been replaced with an organic radical. As a matter of fact, these compounds are very similar in chemical properties to ammonia. The simpler amines are gaseous at ordinary temperatures and have an odor very much like ammonia. Like ammonia, they show basic properties and react with acids to form salts; for example,

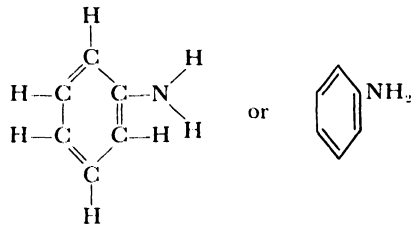
$$CH_3NH_2 + HCl \longrightarrow \underset{\text{methyl ammonium chloride}}{CH_3NH_3Cl}$$

One method by which amines may be prepared is the action of ammonia on an alkyl halide:

$$R—X + 2\,NH_3 \rightarrow R—N\begin{matrix}H\\ \diagup\\ \diagdown\\ H\end{matrix} + NH_4X$$

If two hydrogens in ammonia are replaced by two alkyl groups, a *secondary* amine results: $(CH_3)_2NH$ is *dimethyl amine,* $(C_6H_5)_2NH$ is *diphenyl amine,* and so on. The substitution of three alkyl groups for the three hydrogen atoms gives a *tertiary* amine; $(C_2H_5)_3N$ is *triethyl amine,* and so on.

Aniline,

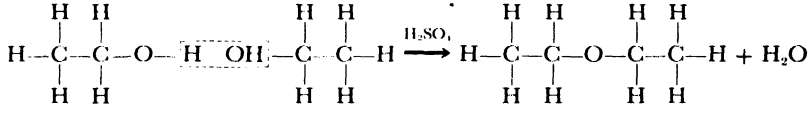


is one of the more important aromatic amines. It is a starting material in the preparation of many aniline dyes, medicinals, and drugs.

ETHERS

The general formula for ethers is R—O—R′ where R and R′ may be the same or different alkyl radicals. They may be considered to be derived from water by the replacement of the two hydrogen atoms in the water molecule with alkyl radicals.

In general ethers are prepared by the dehydration of alcohols with sulfuric acid. If ethyl alcohol is mixed with concentrated sulfuric acid, and the mixture is warmed to 140°, *diethyl ether* and water are formed according to the reaction



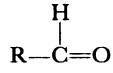
If the above mixture is heated to 160° or above, further dehydration takes place with the formation of ethylene.

Diethyl ether, commonly called *ether,* is used as an anesthetic in surgery. It is a highly inflammable and volatile liquid with a boiling point of 35°. Ether is also used as a solvent for waxes, gums, resins, and fats. In the analysis of certain food products for fat content, the fat is extracted with ether.

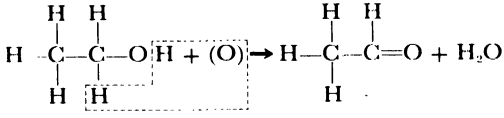
In naming the ethers, the names of the alkyl radicals present are given followed by the term "ether"; or, if the alkyl radicals are the same, the prefix di- may be employed; thus, $C_3H_7OC_2H_5$ is propyl ethyl ether; CH_3OCH_3 or $(CH_3)_2O$ is methyl methyl ether, or better, dimethyl ether. The latter compound is isomeric with ethyl alcohol.

ALDEHYDES

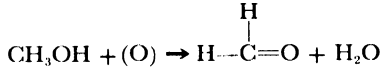
The gentle oxidation of a primary alcohol containing the $—CH_2OH$ group results in the formation of an *aldehyde* with the general formula



For example, the oxidation of ethyl alcohol produces *acetaldehyde:*

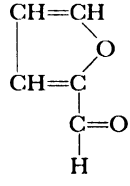


The slow oxidation of methyl alcohol yields *formaldehyde,* HCHO, which is the simplest of the aldehydes. In this case the R of the general formula is a hydrogen atom rather than an alkyl radical.



Formaldehyde is one of the more important of the aldehydes; a 40 per cent solution is commonly marketed under the trade name of *formalin.* It is used as a preservative for museum specimens and as a disinfectant and insecticide. One of its principal uses is in the preparation of synthetic resins. If phenol and formaldehyde are heated slowly together in the presence of a catalyst, a resinous product similar to hard rubber is formed, which may be molded into any desired shape. These plastics are used in the manufacture of such items as telephone transmitters and receivers, radio equipment, other electrical equipment, combs, pencils, pipestems, and ash trays.

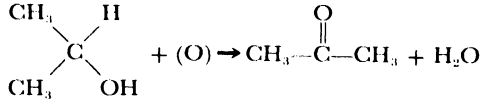
Furfuraldehyde,



a product obtained from waste oat hulls, is becoming increasingly important as a solvent and in the preparation of synthetic plastics and resins.

KETONES

If a secondary alcohol containing the —CHOH group is gently oxidized, a *ketone* of the general formula R—C(=O)—R′ is obtained. The C=O group is termed the *carbonyl* group and is characteristic of both aldehydes and ketones. The oxidation of isopropyl alcohol yields *dimethyl ketone,* more commonly called *acetone:*



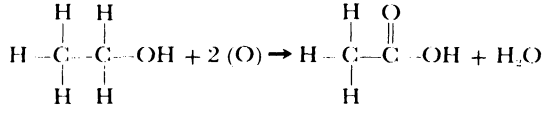
Acetone is obtained also in the destructive distillation of wood along with methyl alcohol and acetic acid, or it may be prepared by heating calcium acetate:

$$Ca(C_2H_3O_2)_2 \xrightarrow{\text{heat}} CaCO_3 \downarrow + CH_3COCH_3$$

At the present time much acetone is produced through the fermentation of corn with certain bacteria. Acetone is one of the more important solvents for varnishes and lacquers, and is used in the manufacture of cordite and smokeless powders, in the preparation of chloroform, and as a solvent for compressed acetylene.

ACIDS

Acids contain the $-\overset{\overset{O}{\|}}{C}-OH$ or *carboxyl* group as the functional group and may be obtained by the oxidation of alcohols and aldehydes. The oxidation of ethyl alcohol yields acetic acid:

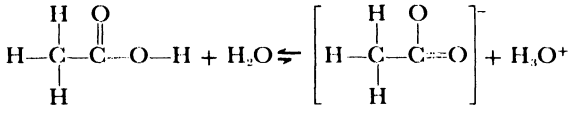


It should be pointed out that the product obtained in the oxidation of an alcohol depends upon the stage of oxidation. An aldehyde may be considered the first stage of oxidation of an alcohol; acids are obtained by further oxidation of the aldehyde. Complete oxidation of an alcohol results in the formation of carbon dioxide and water. It is very often difficult to control the oxidation so that only one type of compound is formed.

Acetic acid is a member of the *fatty acid series* having the general formula R—COOH where R may be a hydrogen atom or an alkyl radical. Common acids of this series are:

$HCOOH$	formic acid
CH_3COOH	acetic acid
C_2H_5COOH	propionic acid
C_3H_7COOH	butyric acid
C_4H_9COOH	valeric acid
$C_{17}H_{35}COOH$	stearic acid

The hydrogen atom in the —COOH group is responsible for acid properties. In water solutions, these acids are weakly ionized; for example, acetic acid ionizes:



The ionizations are strictly analogous to the ionization of an inorganic acid such as hydrochloric acid:

$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

The acid radical of the organic acid is the R—COO group and derives its name from the *ic* acid by replacing that ending with *ate;* thus, CH_3COO is the acetate radical, C_3H_7COO the butyrate radical, HCOO the formate radical, and so on. Like the mineral acids, organic acids are neutralized with bases:

$$R—COOH + NaOH \rightarrow H_2O + \underset{\text{sodium salt}}{R—COONa}$$

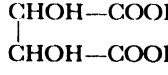
If alcohol produced in the fermentation of sugars and fruit juices is allowed to come in contact with bacteria from mother of vinegar, further oxidation of the alcohol takes place with the formation of vinegar which contains about 4 per cent acetic acid. Hard cider will in time yield a vinegar containing acetic acid. Acetic acid is used in the production of calcium acetate from which acetone may be obtained by heating; in the manufacture of "white lead" for paints; in the preparation of acetic anhydride used in making cellulose acetate, a type of rayon; and in the manufacture of many dyes, aspirin, and medicinals.

Pure acetic acid is a colorless liquid with a sharp, penetrating odor. At 18° it freezes to a white solid, very similar in appearance to ice; hence it is often called *glacial* acetic acid.

Other organic acids *Formic acid,* HCOOH, is the simplest acid of the fatty acid series. It is found in certain nettles and is responsible for their sting. Red ants and bees also contain the acid, which is injected when these insects bite or sting. Formic acid may be prepared by the oxidation of methyl alcohol; however, there is very little demand for the acid.

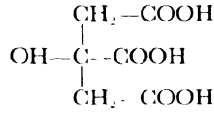
The acids so far described are classed as *monobasic* acids since they contain only one —COOH functional group per molecule. It is possible to have organic molecules containing, two, three, or more —COOH groups. A few of them are:

Tartaric acid,



is a *dibasic* acid since it contains two carboxyl groups. It is obtained from grape and other fruit juices.

Citric acid,

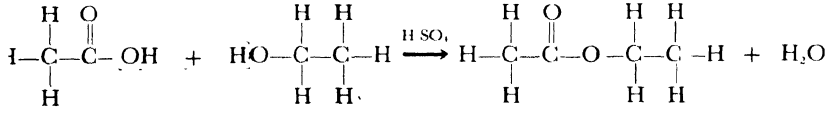


is a *tribasic* acid. It is found in lemons, oranges, and other citrus fruits. It is a solid at ordinary temperatures.

Lactic acid, $CH_3CHOHCOOH$, is found in sour milk as a result of the oxidation of lactose, or milk sugar.

ESTERS

Esters are formed from chemical change between alcohols and acids. For example, if ethyl alcohol is added to acetic acid in the presence of concentrated sulfuric acid as a dehydrating agent:



or, semistructurally as:

$$CH_3COOH + HOC_2H_5 \xrightarrow{H_2SO_4} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

The reaction is similar to the neutralization of an acid with a base in inorganic reactions. However, the inorganic acid-base reactions are much more rapid than those between alcohols and acids, probably because of the ionization which takes place with inorganic substances. The reaction of an alcohol with an acid is called *esterification*

The general formula for an ester is R—COO—R′ where R—COO$^-$ is the acid radical and R′ is the radical derived from the alcohol from which the ester was prepared. Esters, then, according to their formulas appear to be similar to inorganic salts; as a matter of fact, they are sometimes referred to as *ethereal salts* because of their volatile nature. One essential difference between esters and salts is the ionic nature of most salts in contrast to the nonionic character of esters.

In naming an ester, the alkyl radical of the alcohol is named first, followed by the name of the acid radical. The following formulas, written semistructurally with their names, will make this clear:

$C_2H_5COO—CH_3$	is	methyl propionate
$HCOO—C_2H_5$	is	ethyl formate
$C_3H_7COO—C_4H_7$	is	propyl butyrate

Many of the esters have a pleasant odor of fruit or flowers, and upon this property depends the use of certain esters as perfumes and artificial flavorings. *Amyl acetate,* $CH_3COOC_5H_{11}$, has the odor of bananas and is called "banana oil"; *methyl salicylate,* $C_6H_4OHCOOCH_3$, is "oil of wintergreen"; *ethyl butyrate,* $C_3H_7COOC_2H_5$, has the odor of pineapple.

Esters of inorganic acids may also be prepared; for example, glycerin reacts with nitric acid in the presence of sulfuric acid:

$$\underset{\text{glycerin}}{C_3H_5(OH)_3} + 3\,HNO_3 \xrightarrow{H_2SO_4} \underset{\text{glyceryl trinitrate}}{C_3H_5(NO_3)_3} + 3\,H_2O$$

Esters, like inorganic salts, may undergo hydrolysis, forming an acid and an alcohol. The process is the reverse of esterification:

$$\underset{\text{ester}}{R{-}COO{-}R'} + H_2O \rightarrow \underset{\text{acid}}{R{-}COOH} + \underset{\text{alcohol}}{R'{-}OH}$$

FOODS

Foods consist largely of organic compounds and must be considered as an important part of the field of organic chemistry. Foods may be classified into the following groups, of which numbers 1, 2, 3, and 6 are organic compounds:

1. Fats
2. Carbohydrates
3. Proteins
4. Water and oxygen
5. Minerals
6. Vitamins

Food serves to produce new body tissue for growth and to replace worn-out tissue, to maintain body temperature, and to produce energy for work and physical activity. While some of the groups of compounds listed above contribute to all three of these functions, we may say in general that proteins are largely responsible for new tissues and building of muscle; carbohydrates and fats through oxidation produce heat and maintain body temperature and furnish energy. Carbohydrates constitute the bulk of a normal diet.

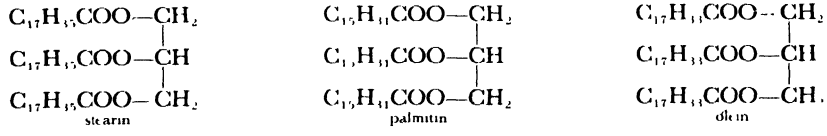
While water and oxygen are frequently not classified as foods, nevertheless both are necessary for the maintenance of life. Minerals are necessary for building the bones and solid structure of the body. Calcium and phosphorus are necessary for bone structure, which is largely calcium phosphate. Iron is a constituent of hemoglobin, the oxygen-carrying portion of the red blood cells. A small amount of iodine is necessary for proper functioning of the thyroid gland. From sodium chloride the body produces hydrochloric acid found in the gastric juice. Although mineral matter in general is needed in only relatively small quantities, these small amounts play a vital role in the life processes.

In addition to the above substances, certain organic compounds called *vitamins* are necessary in small amounts. A lack of any of these vitamins in our diet results in vitamin-deficiency diseases such as rickets, pellagra, nervous disorders, and others. Most vitamins are present in the fruits, vegetables, and meats which we eat daily, and if we consume a fairly balanced diet, it is likely that these vital compounds will be obtained in sufficient quantity for maintenance of health in most individuals.

FATS AND OILS

Fats are *glyceryl esters* of the higher molecular weight acids of the continuous chain type. They are obtained from both plants and animals. Usually those fats from animals, such as stearin and butterfat, are solid or semisolid, while those derived from plants—olive oil, cotton seed oil, and corn oil, for example—are liquids and are designated as oils. Oils as applied to organic compounds may be classified into three groups: (1) mineral oils, which are derived from petroleum or petroleum products, (2) essential oils, which are volatile liquids derived from plants, (3) glyceryl esters. We shall limit our discussion here to fats and oils which are glyceryl esters.

The principal fats are *stearin, palmitin,* and *olein*



These esters may be considered to be derived from glycerol and a fatty acid; for example:

$$\underset{\text{glycerol}}{C_3H_5(OH)_3} + 3\ \underset{\text{stearic acid}}{C_{17}H_{35}COOH} \rightarrow \underset{\text{stearin or glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} + 3\ H_2O$$

Stearin and palmitin are saturated esters and are solids at ordinary temperatures; olein is an unsaturated ester with one double bond in each $C_{17}H_{33}$ chain and is a liquid. The hardness of a fat depends upon the relative amounts of these three esters present. Beef tallow, a hard fat, is about 75 per cent stearin and 25 per cent olein. Lard is softer and is composed of about 60 per cent olein and 40 per cent palmitin; butterfat contains both olein and palmitin, and in addition, butyrin, the glyceryl ester of butyric acid.

There is some evidence to indicate that the greater softness of women's skin as compared to men's skin is due to a slightly higher glyceryl oleate content.

Liquid fats are frequently hydrogenated to convert them to saturated esters which are solid or semisolid; for example, the hydrogenation of olein may be represented by the equation:

$$\underset{\text{olein}}{(C_{17}H_{33}COO)_3C_3H_5} + 3\,H_2 \rightarrow \underset{\text{stearin}}{(C_{17}H_{35}COO)_3C_3H_5}$$

Similarly, fish oil, peanut oil, soy bean oil, castor oil, and other unsaturated liquid oils may be hydrogenated to edible solid fats.

Saponification Soaps are prepared by heating together a fat with sodium or potassium hydroxide solution. Sodium hydroxide produces a hard soap while potassium hydroxide gives a soft soap (liquid). Fats such as tallow, coconut oil, and palm oil are usually employed for soap manufacture. These and similar reactions of an ester with a base are termed *saponification* reactions. The general reaction may be illustrated by the following equation for the preparation of soap from stearin:

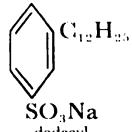
$$(C_{17}H_{35}COO)_3C_3H_5 + 3\,NaOH \rightarrow 3\,\underset{\text{sodium stearate}}{C_{17}H_{35}COONa} + C_3H_5(OH)_3$$

Sodium salts of the higher fatty acids such as sodium stearate, sodium palmitate, and sodium oleate are the principal constituents of ordinary soaps. Glycerin is a by-product of the preparation of soap; it is removed and purified by distillation.

DETERGENTS

Synthetic detergents, sometimes called syndets, are cleansing agents which have found wide use in both home and industry. These substances lower interfacial tension and promote ease of wetting. Sale of syndets in the United States is now three times that of soaps, on a pound basis. Syndets may be used to advantage in waters in which soaps would be precipitated as a curd by ions such as Ca^{++} and Mg^{++}.

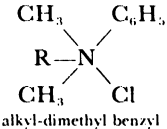
Formulas for three important detergent compounds are:



dodecyl benzene sulfonate

$C_{12}H_{25}SO_3Na$

dodecyl sodium sulfate



alkyl-dimethyl benzyl ammonium chloride

The term "builder" has been accepted as meaning a compound which has little or no cleansing action in itself but which will greatly enhance the cleansing action of a detergent, whether syndet or soap. Accordingly, note the composition of a typical heavy-duty syndet:

Lactose, or milk sugar, is obtained from the milk of mammals. Cow's milk contains about 5 per cent lactose, human milk 8 to 10 per cent. Hydrolysis of lactose produces one molecule each of glucose and galactose:

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{galactose}}{C_6H_{12}O_6}$$

Maltose may be produced by the action of the enzyme, *diastase*, on starch. Upon hydrolysis it yields two molecules of glucose.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow 2\ \underset{\text{glucose}}{C_6H_{12}O_6}$$

Starch Starch is usually represented by the formula $(C_6H_{10}O_5)_x$. The magnitude of x is probably about 20 to 25 so that the molecular weight is large.

Starch is present in nearly all plants; potatoes contain about 20 per cent; dried rice and corn contain about 75 and 50 per cent, respectively. These substances provide the source of starch for commercial production. Starch is very insoluble in cold water, but with hot water the granules of starch swell and produce a colloidal solution which if concentrated will set to a gel when cooled Boiling with hydrochloric acid results in hydrolysis to form glucose.

Cellulose Cellulose, $(C_6H_{10}O_5)_y$, is a polysaccharide of even higher molecular weight than starch. Although it has the same empirical formula as starch, its properties are very different. It is insoluble in water and organic solvents and is not easily hydrolyzed, although boiling for a long time with dilute sulfuric acid gradually results in the formation of glucose.

Cellulose is the principal constituent of all plant fiber Cotton, which is practically pure cellulose, and wood are the principal sources of cellulose. Wood fibers, in addition, contain lignin and resins which bind the material together. In the production of cellulose from wood, the lignin and resin are usually dissolved by means of calcium acid sulfite, or a sodium hydroxide and sodium sulfide solution, to leave pure cellulose. The manufacture of paper is essentially a process of washing and bleaching the cellulose and pressing it into a compact form in sheets.

Since carbohydrates contain the alcohol group, OH, we might expect them to react with acids to form esters. If cellulose is treated with nitric acid in the presence of concentrated sulfuric acid to act as a dehydrating agent, cellulose nitrates are formed. Intensive nitration results in the production of *guncotton,* a highly explosive compound which is used in the production of smokeless powders, cordite, and as an explosive in torpedoes. Incomplete nitration forms *pyroxylin,* which is used

in the production of artificial leathers, photographic film, lacquers, and collodion. It is soluble in mixtures of organic solvents. This permits its separation from guncotton, which is insoluble.

Fabric treated with an organic solvent solution of pyroxylin will on evaporation of the solvent have a tough flexible finish that resembles natural leather. *Collodion* is a solution of pyroxylin in a mixture of alcohol and ether. A common lacquer is a solution of pyroxylin in amyl acetate (banana oil). *Celluloid* is produced from cellulose nitrates by forming a plastic mass with camphor; the product may be molded into desired shapes. It is highly inflammable.

Rayon The principal difference between silk and rayon is in the chemical composition. Silk is a protein; rayon is cellulose or a cellulose derivative. Cotton or cellulose fibers are short, irregular, and dull; the fibers of silk are long, smooth, and bright. The production of rayon requires changing the structure of the cotton or wood cellulose fibers. There are several methods employed for doing this; however, all methods are the same in principle. In brief, the process consists of dispersing cellulose or cellulose derivative in a liquid in colloidal form which can then be forced through a small orifice or nozzle into a solution which will precipitate the cellulose or its derivative in tiny filaments. These tiny filaments are twisted together to form a larger thread which is then used for weaving purposes. One of the more common methods of producing rayon is by the *viscose* process in which the cellulose is treated with sodium hydroxide and carbon disulfide. A cellulose xanthate solution is formed which is forced through small openings into a bath of sulfuric acid and sodium bisulfate where the cellulose is precipitated in desired fibrous form.

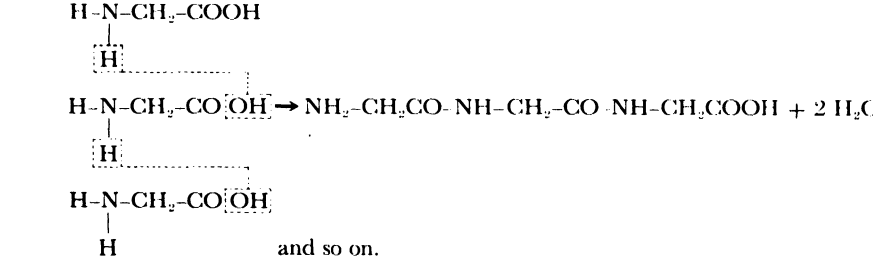
Cellophane The elastic, transparent, heat-resistant, water-and-oil-insoluble material which we call *cellophane* is likewise made from a cellulose xanthate solution by precipitation of the cellulose in film form by ammonium salts.

PROTEINS

Proteins are complex compounds composed of the elements carbon, oxygen, hydrogen, and nitrogen. In addition, the elements phosphorus and sulfur may be present. Proteins are found in plants and are particularly abundant in animals and animal products such as lean meat, cheese, milk, and eggs. Because of their complexity, knowledge of their chemical structure is incomplete, although it has been established that their molecular weights are very large.

Hydrolysis of proteins yields *amino acids* which contain the amine

group, NH_2, and the carboxyl group, COOH. About twenty different amino acids have been obtained from proteins, of which the simplest is amino acetic acid or *glycine*, CH_2NH_2COOH. Such compounds are amphoteric (may function as either acids or bases), since they contain the basic NH_2 group and the acidic COOH group. These facts have led to the belief that proteins are built up by a combination of amino acids. The basic part of one molecule may combine with the acidic part of another molecule, whose basic part in turn may combine with another acidic group of still another amino acid; thus, a chain containing many molecules of amino acid molecules may be built up. We may illustrate how this combination might take place between glycine molecules:



and so on.

When we consider that molecules of many different amino acids may combine in this fashion, we may appreciate the complexity of the actual protein molecules.

VITAMINS

The importance of these vital substances in the diet of man has already been mentioned. Because vitamins are present in foods in only minute amounts and because they are complex, extreme difficulties in their preparation and study in a pure state have been encountered. All are thought to be definite chemical compounds, although the formulas have not been established in all cases. Vitamin studies have progressed rapidly in the last decade, and no doubt in the future new vitamins will be found; in addition, we shall know more about the composition and synthesis of those already discovered.

The various vitamins have been designated by letter as well as by name; following are the more common ones, with brief statements regarding their sources and functions:

Vitamin A is the general good health vitamin, since it is necessary for growth. It also promotes vision in dim light—an early symptom of vitamin A deficiency is night blindness, diminished vision in dim light.

This vitamin has been obtained from *carotene,* a compound found in carrots, and its composition is thought to be represented by the formula $C_{20}H_{30}$. Vitamin A is found in abundance in dairy products, in green vegetables of all kinds, and in cod-liver and halibut-liver oils.

The *vitamin B complex* is a mixture of several distinct vitamins. Vitamin B_1 is *thiamine chloride,* $C_{12}H_{17}N_4OSCl$. It is present in yeast and in whole cereals as well as in most vegetables. It has an important function in oxidation processes in the body. Other important B vitamins are B_2 or *riboflavin,* $C_{17}H_{20}N_4O_6$; *nicotinic acid,* C_5H_4NCOOH, which helps prevent pellagra; and B_{12} or *cobalamin,* the anti-pernicious anemia factor.

Vitamin C is *ascorbic acid,* $C_6H_8O_6$. This vitamin helps prevent scurvy; it is present in citrus fruits, particularly oranges and lemons, and in cabbage and tomatoes.

Vitamin D is necessary for normal development of bones; lack of it may result in rickets. It is essential in the diet of children. Principal sources of the vitamin are milk and cod-liver oil. *Ergosterol,* a fat found in many foods, is converted to vitamin D by the action of ultraviolet rays; many foods are irradiated to increase their vitamin D content. Ergosterol is also present in the skin, and exposure to the sun's rays results in the formation of vitamin D. For this reason, vitamin D is sometimes called the sunshine vitamin.

Vitamin E is essential for reproductive processes in some animals; its necessity for man has not been established. Lettuce, meat, and certain vegetable oils are rich sources of this vitamin.

Vitamin K aids in prevention of hemorrhage by hastening the clotting time of blood. Green vegetables, tomatoes, and eggs are sources.

HORMONES

Hormones are as important to the proper functioning of vital processes as are vitamins. These secretions of the ductless glands of the body are absorbed directly into the blood stream and carried to various parts of the body. The fact that these secretions are produced in only minute amounts makes their study and analysis difficult. Lack of any one of the hormones results in profound effects on the biological processes of the human anatomy.

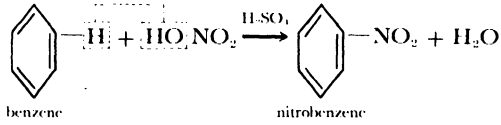
Epinephrine, one of the secretions of the adrenal glands, has been prepared in the laboratory and is available under the trade name of *adrenaline;* its formula is $C_9H_{13}NO_3$. It acts as a stimulant to the sympathetic nervous system and is thus used to increase blood pressure and restore the tone of blood vessels.

Thyroxine, $C_{16}H_{11}O_4NI_4$, has also been prepared in the laboratory. It is a secretion of the thyroid gland which has a stimulating effect on growth and metabolism.

Insulin is secreted by the pancreatic gland. Lack of insulin appears to be the cause of diabetes. Fortunately, the hormone is obtained from the pancreas of animals for medical administration to humans.

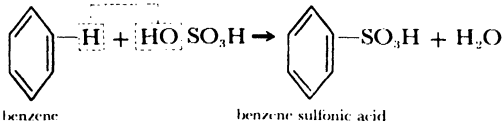
NITRATION AND SULFONATION PRODUCTS OF BENZENE

Nitro compounds When benzene is heated with a mixture of nitric and sulfuric acids, *nitration*—a process in which an NO_2 (nitro) group is substituted for a hydrogen atom attached to the ring—takes place to form nitrobenzene:

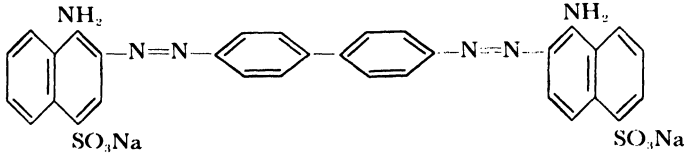


Further nitration results in the substitution of two or three nitro groups in the benzene nucleus. Reduction of nitro compounds results in the formation of amines; thus reduction of nitrobenzene gives aniline, $C_6H_5NH_2$, which is used in the production of dyes and medicinals.

Sulfonic acids The treatment of aromatic hydrocarbons with hot concentrated sulfuric acid results in *sulfonation* and the formation of sulfonic acids. The reaction of benzene with sulfuric acid results in the formation of benzene sulfonic acid:



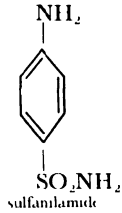
Many dyes are produced from sulfonic acids or their derivatives. A typical formula for a dye is that of Congo red:



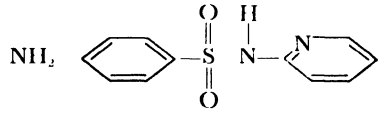
SULFA DRUGS AND PENICILLIN

The remarkable curative power of sulfanilamide came to be known in 1935. Since that time, thousands of compounds allied to sulfanila-

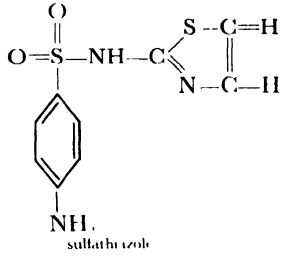
mide have been described as researchers have tried to develop more potent germ killers with less toxicity to the patients. Formulas for a few of the sulfa drugs are:



sulfanilamide



sulfapyridine



sulfathiazole

Sulfapyridine and sulfathiazole are examples of *heterocyclic* compounds —compounds which contain some element in addition to carbon in the ring structure.

Penicillin is a specific secretion which diffuses from a mold. It was found to inhibit bacterial growth near the mold on bacterial test plates, and it is specifically effective against gonorrhea and certain other organisms. There are many organisms against which both sulfa drugs and penicillin are effective; penicillin will act on some for which sulfa is ineffective, and sulfa is useful for treatment in some cases—such as dysentery—in which penicillin seems ineffective.

SYNTHETIC RESINS AND PLASTICS

Natural resins such as pine resins and various tree gums have found considerable use in varnishes. *Shellac* is made from bodies of certain insects that infest some trees in India. Modern-day demand has resulted in the construction of large synthetic resin and plastic plants. A synthetic resin is a basic material which may be made by certain chemical changes of a polymerization, condensation, or combination type. The resin may be a plastic or may be subject to plasticizing. Plastics that cannot be remelted once they have been molded and set are called *thermosetting* plastics, plastics that may be remelted or softened and reformed a number of times are called *thermoplastic* plastics.

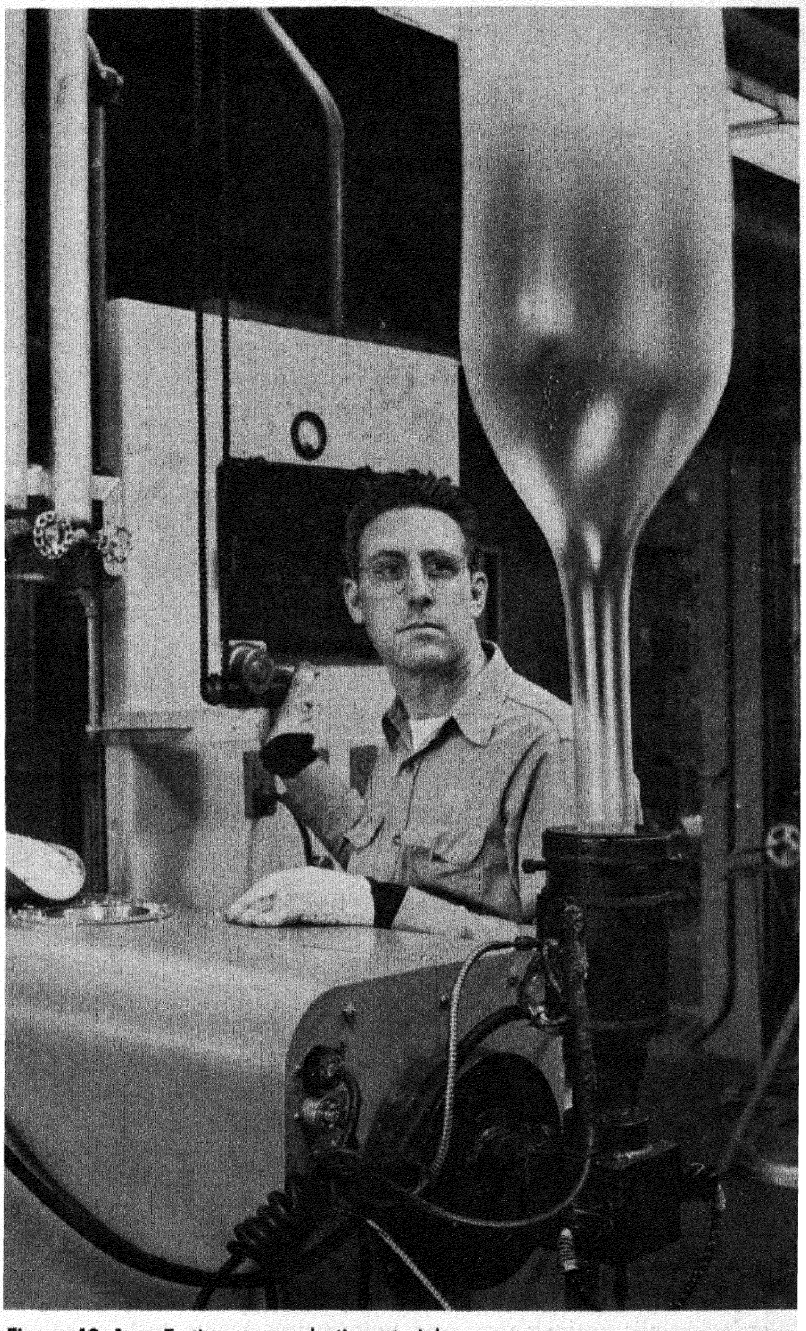
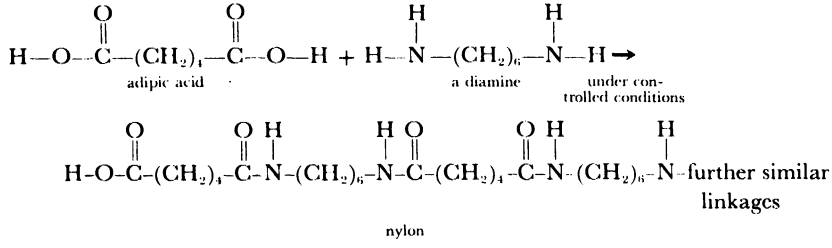


Figure 40–1 Testing a new plastic material.

Since many plants were built during World War II to produce styrene in making buna S synthetic rubber, styrene is currently a comparatively cheap chemical which can be polymerized to give a thermoplastic material which has many uses. The composition of styrene is $C_6H_5—CH=CH_2$.

Cellulose nitrate, cellulose acetate, or cellulose propionate may be plasticized by compounding with various agents such as triphenyl phosphate, $(C_6H_5)_3PO_4$.

It is beyond the scope of this book to describe the chemistry of the many plastic materials. Feminine interest in the plastic substance *nylon* suggests a note on the chemistry of its manufacture. If a diamine and a dibasic carbon chain acid are subjected to dehydration, long molecules constituting nylon result:



When nylon is melted, it can be forced through small openings in a disk, to produce threads. When these threads are subjected to cold pulling or stretching, they set to a strong fiber with marked elastic and durable qualities, usable for hosiery, brush bristles, tennis racket strings, parachutes, tow lines for gliders, etc.

The *alkyd* resins have assumed a controlling position in the surface coating industry. They are made by the esterification and condensation of dibasic acids such as phthalic acid (an oxidation product of the well-known moth repellent naphthalene) with polyhydroxy alcohols such as glycerin. A drying oil such as linseed may be added. See page 487.

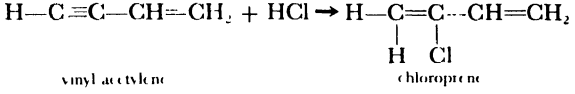
RUBBER AND ELASTOMERS

Natural rubber was first obtained from sap of a species of tree in Brazil. Such trees were selectively planted and grown in the East Indies, and with care a better yield of rubber tree sap (latex) was obtained. Latex when heated with acid yields crude rubber, which in turn may be compounded for desired properties by incorporation of filler materials, antioxidants, and vulcanizing agents such as sulfur.

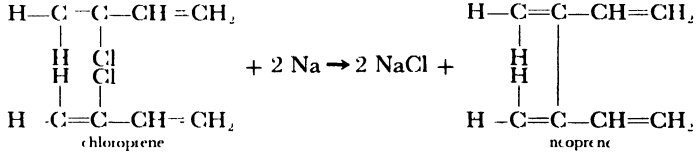
Natural rubber is essentially a high-molecular-weight hydrocarbon with numerous unsaturated bonds.

In World War II, the supply of natural rubber was cut off, and at the same time there was a great increase in demand for rubber. Chemists solved the problem by developing rubber substitutes which go under the general name of *elastomers*. In many ways, industrially produced elastomers are better than natural rubber; for example, most elastomers are more oil resistant and some are less permeable than rubber. The chemistry of production of a few synthetic rubbers will be briefly described.

Neoprene is produced from acetylene by polymerization to form vinyl acetylene. When this compound is treated with hydrochloric acid, chloroprene is formed.



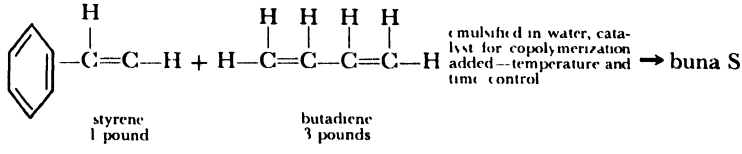
When chloroprene is treated with metallic sodium under carefully controlled conditions, carbon-to-carbon linkages are effected between many four-carbon chain units to give neoprene:



Many molecules like the last one shown polymerize to rubberlike products.

Thiokol is obtained by controlled heating of hydrocarbon dichlorides such as ethylene dichloride, $ClCH_2—CH_2Cl$, with sodium polysulfide, Na_2S_x. The ethylene dichloride can be made from chlorine and ethylene. Ethylene is made by dehydration of ethyl alcohol or by dehydrogenation of ethane.

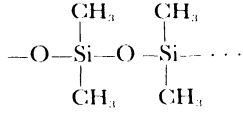
One of the elastomers manufactured in great bulk has been known as buna S, GR-S, or butadiene-styrene product. Butadiene, $H_2C=CH—CH=CH_2$, results from dehydrogenating butane.



When the desired amount of molecular union has taken place to give a product of desired properties, a stopping agent such as phenyl naphthalene is added, and the crude synthetic rubber latex is separated, purified by washing, and compounded for use.

SILICONES

We have already noted the chemical similarity of carbon and silicon. Recently, many compounds of chainlike structures containing both carbon and silicon have been prepared. They possess the general structure:



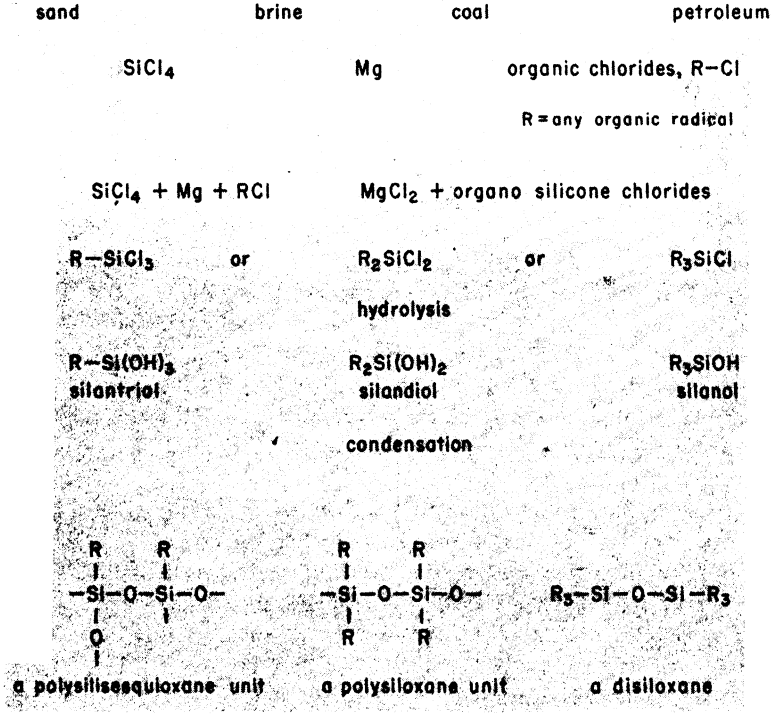


Figure 40–2 The chemistry of silicones.

These compounds, known as *silicones,* are remarkable in their stability and resistance to the action of chemicals. The lower-molecular-weight silicones are oils which are nearly as fluid at low temperatures as at high temperatures. They find application as lubricants in regions of very low temperatures. High-molecular-weight silicones have properties of elastomers and make suitable rubber substitutes. A puttylike silicone called "bouncing putty" exhibits nearly perfect elasticity when struck a sharp blow and may be bounced in the same manner as a rubber ball. Under certain conditions, silicones are plastic and can be shaped as desired. Silicones are used as moistureproofing and fireproofing agents and as insulating coatings for electrical equipment. A silicone finish for textiles makes them water repellent even after laundering or dry cleaning. Because silicone films can be made much thinner than other kinds of insulation, electrical motors can now be made much smaller. The chemistry of the silicones is summarized in Figure 40–2. Note that cross linking of chains may take place to produce three-dimensional structures of great complexity.

EXERCISES

1 Write structural formulas for ethyl amine, butyl acetate, propionic acid, glyceryl oleate, dibutyl ether, methyl propyl ketone, ethyl iodide, calcium acetate.

2 Write equations for the

(*a*) hydrolysis of methyl acetate.
(*b*) reaction of ethyl alcohol with butyric acid.
(*c*) saponification of glyceryl stearate.
(*d*) neutralization of formic acid with calcium hydroxide.
(*e*) hydrolysis of starch.
(*f*) inversion of sucrose.
(*g*) fermentation of glucose.
(*h*) combustion of ethyl alcohol in air.
(*i*) nitration of benzene.

3 By means of equations, indicate the steps you would take to prepare

(*a*) ethylene from ethyl acetate.
(*b*) aniline from benzene.
(*c*) ethyl amine from ethane.
(*d*) ethyl alcohol from starch.
(*e*) nitroglycerin from glyceryl palmitate.
(*f*) acetone from acetic acid.
(*g*) acetic acid from ethyl alcohol.

4 Name and classify the following compounds as to type: C_3H_7Br; $HCOOH$; $CH_3COC_4H_9$; C_2H_5CHO; CH_3NH_2; $(C_2H_5)_2O$; $(C_3H_7COO)_3C_3H_5$; $CH_3COOC_3H_7$; $C_3H_7COOCH_3$; $HCOOCH_3$; CH_3COOH; C_4H_9OH; $C_6H_{12}O_6$; $C_6H_5COCH_3$; $C_6H_5NH_2$; C_6H_5COOK.

5 Write structural formulas and names of the four butyl alcohols.

6 Indicate the meaning of these terms: functional group, alcohol proof, enzyme, carbohydrate, esterification, saponification, vitamin, elastomer, protein.

7 Illustrate each of the following with an example (formulas or equations): (*a*) homologous series, (*b*) unsaturation, (*c*) esterification, (*d*) isomers, (*e*) saponification, (*f*) nitration, (*g*) polymerization.

8 Name the following: (*a*) C_3H_7OH (*b*) C_3H_4 (*c*) $(CH_3)_2NH$ (*d*) HCHO (*e*) C_2H_5COOH (*f*) $CH_3COC_2H_5$ (*g*) $(C_2H_5)_2O$ (*h*) $CH_3CH_2CH_3$ (*i*) $CH_3COOC_3H_7$ (*j*) $CH_3CHOHCH_3$ (*k*) C_2H_2 (*l*) $(CH_3COO)_2Ca$ (*m*) $C_2H_5NH_3I$ (*n*) C_6H_5OH (*o*) HCOOK (*p*) $C_3H_5Br_3$.

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SCIENCE DISCERNS THE LAWS OF NATURE, INDUSTRY APPLIES THEM TO THE NEEDS OF MAN

forty-one

CHEMICAL INDUSTRY AND CHEMICAL ENGINEERING

Chemistry, as a basic science, has applications in many industrial pursuits of man; thus, we speak of such fields as biochemistry, geochemistry, metallurgical chemistry, medicinal chemistry, chemotherapy, agricultural chemistry, and food chemistry. To supply chemicals for all man's diverse enterprises, a "chemical industry" has developed which is concerned with raw materials, conversion of them to chemical products, their uses, and the techniques involved in their manufacture.

Chemical engineering is concerned with the understanding and application of all those practical processes involved in the handling and production of chemical materials. In the handling of raw materials and the conversion of them to chemical products, the chemical engineer makes use of diverse kinds of equipment and many "unit operations," both chemical and physical. Some of the more important ones are listed in Table 41-1.

The fundamental knowledge possessed by the experienced industrial chemist and chemical engineer leads to his service in many varied capacities in industry—with the result that man's health, food, clothing, shelter, and transportation, as well as a growing list of semi-necessities and luxuries, are improved and made more varied, more artistic, and more available through lowered production costs. Chemists and chemical engineers are to be found everywhere in modern industry; in some units every man, from the president down through the plant superintendent to the departmental foreman, is professionally trained

TABLE 41-1 Principal Chemical Engineering Processes

CHEMICAL UNIT OPERATIONS	PHYSICAL UNIT OPERATIONS
Combustion	Fluid flow
Oxidation	Heat transfer
Neutralization	Proportioning
Silicate formation	Materials handling
Causticization	Gathering
Electrolysis	Storing
Double decomposition	Transporting
Calcination	Conveying
Nitration	Fluid handling
Esterification	Disintegration of material
Reduction	Mixing
Ammonolysis	Heat transfer
Halogenation	Separation
Sulfonation	Leaching, extracting
Hydrogenation	Dissolving
Condensation	Filtering
Polymerization	Crystallizing
Fermentation	Condensing
Pyrolysis	Evaporation
Isomerization	Humidification and dehumidification
Hydrolysis	Absorption
Various organic syntheses	Adsorption
	Catalyzing
	Sampling
	Indicating and recording
	Automatic or manual controls
	Compressing or expanding
	Coagulating

in chemistry or chemical engineering. Naturally, a great number serve in the research departments of industry.

Research activities may be divided into two groups for the purpose of discussion: (1) Experimental research, which comprises fundamental studies; exploratory work on processes, products, and methods; pilot-plant development work; full-scale experimental work; and product utilization. (2) Research on paper—desk work—which comprises correlation of data; process design; economic studies; plant technical service; report and paper preparation; literature search; and supervision and direction of research. An individual chemist may specialize in one of these activities or perform a combination of them.

Since many chemists are employed in research, we may well ask, "What are the achievements of research?" Some research achievements have been well publicized—the effectiveness of the wonder drug penicillin which is specific and highly effective against certain pathogenic organisms; the large-scale production of magnesium and toluene; the establishment of a synthetic rubber industry in a few months; the synthesis of 100 octane gasoline from petroleum; the replacement of

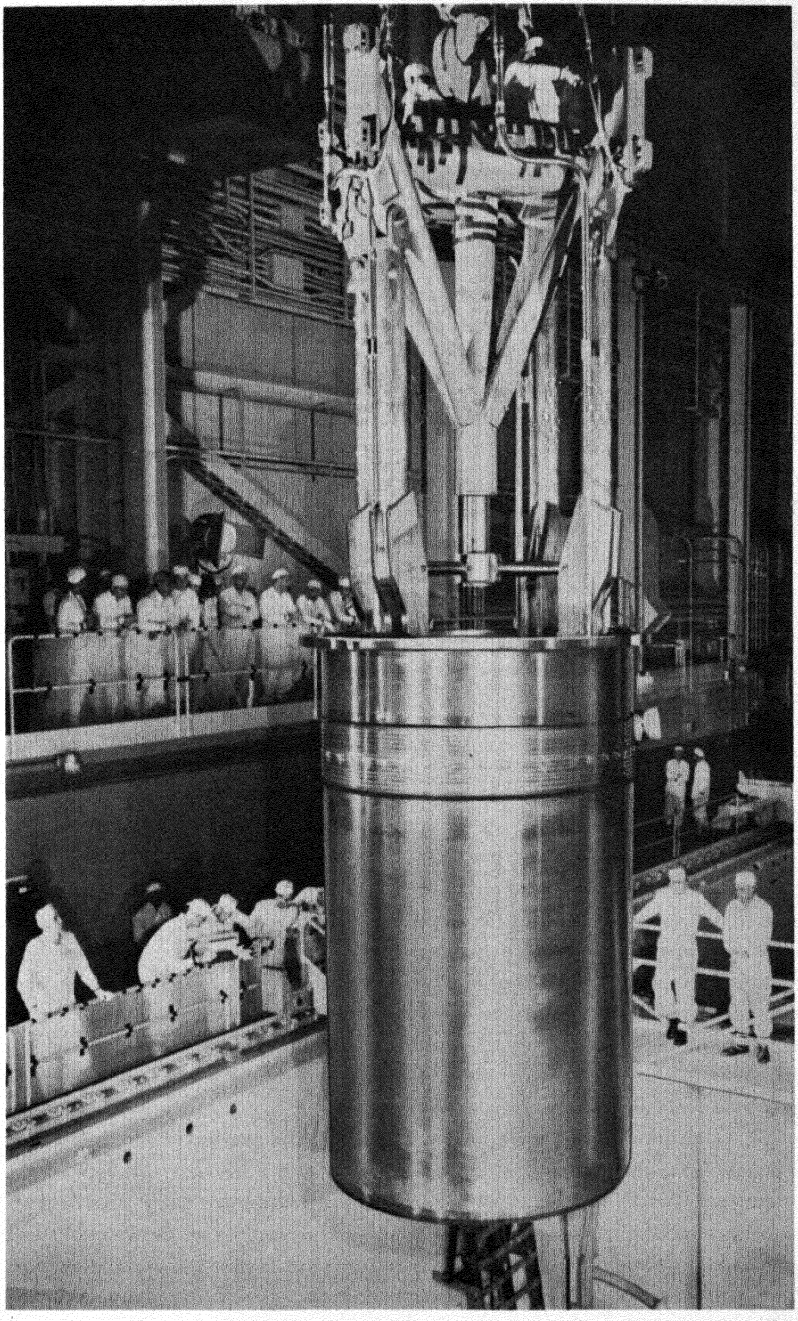


Figure 41–1 Installation of the nuclear core for an atomic power station. Cooperative efforts of scientists in many fields is behind this achievement.

silk and boar-brush bristle by nylon; and many more. Less well known are many thousands of improved articles in everyday use.

It is the steady year-to-year improvements that really pay for the research in industry. They go unnoticed but can be seen very clearly by looking back a decade or two. Perhaps one of the more clear-cut examples is that of the automobile tire. In 1915, the motorist was fortunate indeed if his tires lasted 5000 miles at less than twenty-five miles per hour, even with the greatest care, including repeated vulcanization. Today, tires made from rubber derived from the same trees and cotton of the same quality last 30,000 miles or more at forty-five miles per hour—and the cost per pound of tire is less.

Why is this? Some people say, "That's easy! Antioxidants made all the difference." Others say, "It's the improvement in accelerators." But it is none of such things individually. Research studies by many hundreds of chemists over a period of years have resulted in many thousands of big and little changes, the summation of which is a tire that lasts more than six times as long and costs less. It is doubtful that even a rubber chemist can itemize in a reasonable length of time all the research accomplishments that contributed to this result.

Chemists are not, of course, limited to research activities. For example, the vital control laboratories, where tests are performed to maintain standards of uniformity, purity, and quality of product, utilize many chemists to test procedures and to act in a supervisory capacity while technicians make the more routine tests. In the process industries, many successful patent attorneys have had training in chemistry, and chemists serve in a consulting capacity in many industries.

Applied chemistry has grown tremendously in the past several decades. In 1863, at the height of the Civil War, the annual production of steel in the United States was one-half pound per person. Eighty years later, in 1943, it was 1326 pounds per person. A greater tonnage of every mineral commodity has been mined (and most such raw material minerals are chemically converted to useful products) since 1900 than during all previous history. During the past twenty-five years, industrial research has expanded ten times.

As chemistry has grown in importance, the professional stature of chemists has increased. Today, the American Chemical Society, now numbering over 80,000 chemists and chemical engineers, is the largest professional organization in the world. The Society sponsors the publication of *Chemical Abstracts,* which indexes the world's chemical, scientific, and technical publications and patents.

Some idea of the chemical knowledge and engineering skill required to develop and operate plants in the field of chemical industry can be

gained by studying the flow-sheet diagrams (Figures 41–2, 3, and 4) for three industries. Writing a few chemical equations or carrying out these reactions in the school laboratories seems far removed from the large-scale plant production represented on the flow sheets. Yet a knowledge of the fundamentals discussed in this text is the essential first step in any kind of chemical operation.

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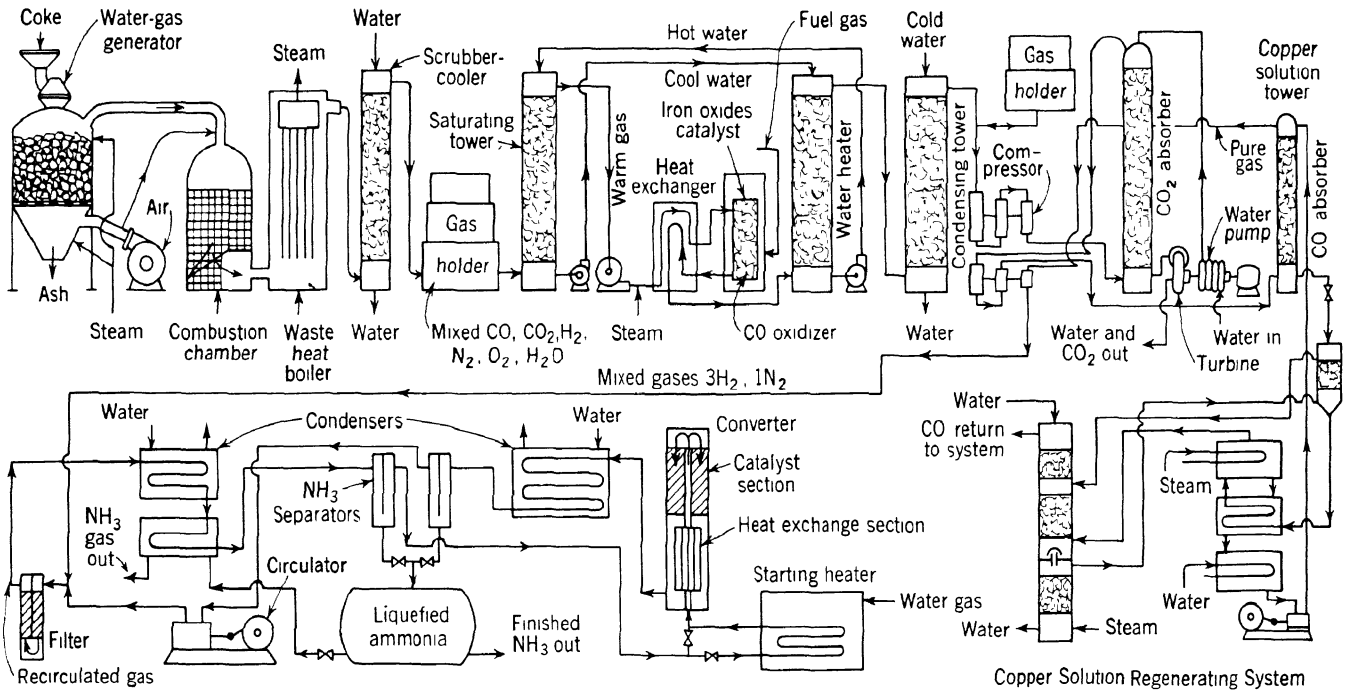


Figure 41–2 Ammonia synthesis by the Nitrogen Engineering Corporation process. One ton of liquefied ammonia requires 1.65–1.75 tons of coke, 31,000 gallons of water, 25 tons of coal for steam and power, and 20 man-hours of labor.

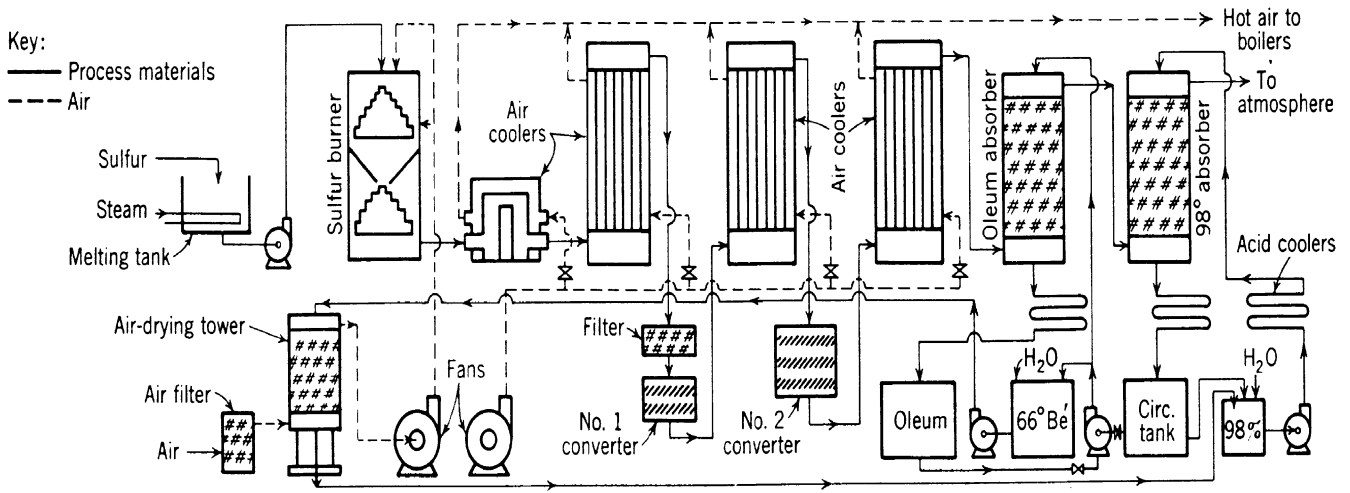


Figure 41–3 Manufacture of sulfuric acid by the contact process, with vanadium catalyst. Each ton of 100 per cent acid requires 684 pounds of sulfur, 5000 gallons of water, 25 kilowatt-hours of electricity, and 1.1 man-hours of direct labor. A plant with a capacity of 50 tons of acid per day represents an investment of $230,000.

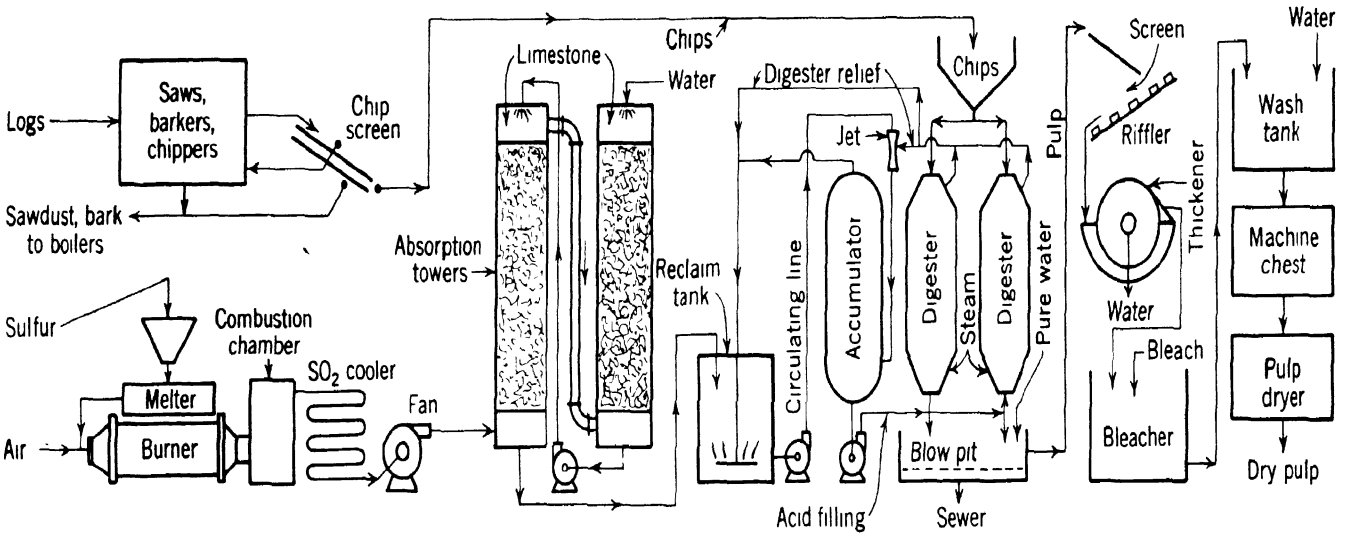


Figure 41–4 Sulfite pulp manufacture. The production of one ton of pulp requires 1.7–2.2 cords of wood, 220–300 pounds of sulfur, 260–370 pounds of limestone, 5000–7500 pounds of steam, 410 kilowatt-hours of electricity, and 4.9 man-hours of direct labor.

APPENDIX

UNITS OF MEASUREMENT

Linear

1 meter = 10 decimeters = 100 centimeters = 1000 millimeters
1 meter = 39.37 inches
1 kilometer = 1000 meters = 0.6214 mile
1 inch = 2.54 centimeters
1 micron = .001 millimeter = 1×10^{-3} mm.
1 millimicron = .000001 millimeter = 1×10^{-6} mm.
1 angstrom = 1×10^{-7} millimeter

Volume

1 liter = 1000 milliliters = 1000.027 cubic centimeters
1 liter = 1.056 quarts
1 cubic foot = 7.48 gallons = 28.32 liters

Weight

1 gram = weight of 1 milliliter of water at 4°
1 gram = 10 decigrams = 100 centigrams = 1000 milligrams
1 kilogram = 1000 grams = 2.205 pounds avoirdupois
1 pound = 453.6 grams = .4536 kilogram
1 ounce = 28.35 grams
1 metric ton = 1000 kilograms = 2205 pounds
1 long ton = 2240 pounds
1 short ton = 2000 pounds

Temperature

0° centigrade = freezing point of water = 32° Fahrenheit
100° centigrade = boiling point of water = 212° Fahrenheit
Centigrade temperature = $\frac{5}{9}$ (F − 32)
Fahrenheit temperature = $\frac{9}{5}$ C + 32
0° absolute temperature = −273° centigrade
Absolute temperature = centigrade temperature + 273

Electrical

1 ampere = strength of current required for the deposition of .001118 gram of silver per second
1 volt = potential necessary to cause a current of 1 ampere to flow through a resistance of 1 ohm
1 ohm = resistance of a column of mercury 106.3 cm. long of uniform cross-section and weighing 14.4521 grams
1 coulomb = 1 ampere second
1 faraday = 96,500 coulombs = quantity of electricity required to deposit electrically 1 gram equivalent of an element
1 joule = 1 volt coulomb
1 watt = 1 ampere volt (unit of power)
1 horsepower = 746 watts
1 kilowatt = 1000 watts

OXIDATION-REDUCTION POTENTIALS

Use of oxidation potentials The tendency for a given half-reaction (or couple) to proceed may be expressed in terms of an oxidation potential (in volts). In the table on page 437, a number of representative half-reactions are listed. In this table, the substance to the left and at the top is the strongest reducing agent; the substance to the right and at the bottom is the strongest oxidizing agent. Thus, as we go down the list, the reducing ability of the substance on the left side of the equation decreases; as we go from the bottom to the top of the list, the oxidizing ability of the substance on the right side of the equation decreases. For example: in the table, K is the strongest reducing agent and K^+ is the weakest oxidizing agent; F_2 is the strongest oxidizing agent and F^- is the weakest reducing agent.

In such a list of oxidation potentials, a substance on the left will reduce any substance on the right which appears below it—that is, which has a lower oxidation potential. Similarly, any substance on the right will oxidize any substance on the left which has a higher oxidation potential. These oxidizing potentials are a measure of the driving force of a reaction. With the aid of the table, various combinations of half-reactions may be made, and the tendency of the reaction to proceed as written may be determined.

An abbreviated table of oxidation-reduction potentials

Half-reactions are written as oxidation processes—if the equation is reversed, it then represents a reduction reaction. The $E°$ values are for the following conditions: aqueous solution, 1 molar; temperature, 25° C.; pressure, 1 atmosphere.

HALF-REACTION			$E°$
K	$\rightleftharpoons$	$K^+ + e$	2.92
Na	$\rightleftharpoons$	$Na + e$	2.71
Al	$\rightleftharpoons$	$Al^{+++} + 3e$	1.66
Mn	$\rightleftharpoons$	$Mn^{++} + 2e$	1.18
AsH_3	$\rightleftharpoons$	$As + 3H^+ + 3e$	.60
Cr^{++}	$\rightleftharpoons$	$Cr^{+++} + e$	.41
$Pb + SO_4^{--}$	$\rightleftharpoons$	$PbSO_4 + 2e$	.36
Ni	$\rightleftharpoons$	$Ni^{++} + 2e$	.25
Sn	$\rightleftharpoons$	$Sn^{++} + 2e$	.14
H_2	$\rightleftharpoons$	$2H^+ + 2e$	0.00
PH_3	$\rightleftharpoons$	$P + 3H^+ + 3e$	− .06
$2S_2O_3^{--}$	$\rightleftharpoons$	$S_4O_6^{--} + 2e$	− .08
H_2S	$\rightleftharpoons$	$S + 2H^+ + 2e$	− .14
$H_2O + H_2SO_3$	$\rightleftharpoons$	$SO_4^{--} + 4H^+ + 2e$	− .20
Cu	$\rightleftharpoons$	$Cu^{++} + 2e$	− .34
$S + H_2O$	$\rightleftharpoons$	$H_2SO_3 + 4H^+ + 4e$	− .45
$2I^-$	$\rightleftharpoons$	$I_2 + 2e$	− .53
$H_3AsO_3 + H_2O$	$\rightleftharpoons$	$H_3AsO_4 + 2H^+ + 2e$	− .56
H_2O_2	$\rightleftharpoons$	$O_2 + 2H^+ + 2e$	− .68
Fe^{++}	$\rightleftharpoons$	$Fe^{+++} + e$	− .77
Ag	$\rightleftharpoons$	$Ag^+ + e$	− .80
$H_2O + NO_2$	$\rightleftharpoons$	$NO_3^- + 2H^+ + e$	− .81
$NO + H_2O$	$\rightleftharpoons$	$HNO_2 + H^+ + e$	− .99
$2Br^-$	$\rightleftharpoons$	$Br_2 + 2e$	−1.06
$2H_2O + Mn^{++}$	$\rightleftharpoons$	$MnO_2 + 4H^+ + 2e$	−1.28
$2Cr^{+++} + 7H_2O$	$\rightleftharpoons$	$Cr_2O_7^{--} + 14H^+ + 6e$	−1.33
$2Cl^-$	$\rightleftharpoons$	$Cl_2 + 2e$	−1.36
$Pb^{++} + 2H_2O$	$\rightleftharpoons$	$PbO_2 + 4H^+ + 2e$	−1.46
$Cl_2 + 2H_2O$	$\rightleftharpoons$	$2HClO + 2H^+ + 2e$	−1.63
Au	$\rightleftharpoons$	$Au^+ + e$	−1.68
$MnO_2 + 2H_2O$	$\rightleftharpoons$	$MnO_4^- + 4H^+ + 3e$	−1.70
Co^{++}	$\rightleftharpoons$	$Co^{+++} + e$	−1.84
$O_2 + H_2O$	$\rightleftharpoons$	$O_3 + 2H^+ + 2e$	−2.07
$2F^-$	$\rightleftharpoons$	$F_2 + 2e$	−2.85

GLOSSARY

absolute temperature The temperature scale on which the freezing point of pure water is 273° A. and the boiling point is 373° A. at standard pressure. Absolute temperature equals centigrade temperature plus 273.

absolute zero The temperature, −273° C. or 0° A., at which all molecular motion ceases.

acid A proton donor. A substance which in aqueous solution turns blue litmus red, furnishes hydronium ions, and contains hydrogen which can be replaced by a metal.

acid anhydride The oxide of a nonmetal which reacts with water to form an acid and no other product.

acid salt A salt that contains hydrogen replaceable by a metal.

adsorption The condensation of molecules of a gas or liquid on the surface of a solid.

alcohol An organic compound containing the OH functional group; for example, CH_3OH, methyl alcohol, and C_2H_5OH, ethyl alcohol.

aldehyde An organic compound containing the CHO functional group; for example, CH_3CHO, acetaldehyde.

alkali A highly ionized water-soluble metallic hydroxide.

allotropy The property of certain elements and compounds to exist in more than one form because of the rearrangement of the atoms, molecules, or ions.

alloy A solution or mixture of two or more metals.

alpha particle A helium atom that has lost its two electrons.

alum A double sulfate salt of the general formula $M'_2SO_4 \cdot M'''_2(SO_4)_3 \cdot 24\ H_2O$, where M′ is a monovalent cation such as Na^+, K^+, Li^+, or NH_4^+ and M‴ is a trivalent cation such as Fe^{+++}, Cr^{+++}, or Al^{+++}. The above formula is sometimes condensed to $M'M'''(SO_4)_2 \cdot 12\ H_2O$. An example of an alum is $(NH_4)_2\ SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\ H_2O$ or $NH_4Cr(SO_4)_2 \cdot 12\ H_2O$, ammonium chrome alum.

amalgam An alloy containing mercury.

amorphous A term applied to a substance without apparent crystalline structure.

amphoteric substance One which may act either as an acid or a base.

amu Atomic mass unit.

angstrom A unit of linear measurement equal to 10^{-8} cm. or 10^{-10} m.

anhydrous substance One free from water.

anion A negatively charged ion which moves toward the anode during electrolysis.

anode The electrode at which oxidation occurs.

atom The smallest unit of an element that can take part in a chemical change.

atomic number The number of an atom corresponding to the net positive charge on the nucleus.

atomic weight The relative weight of an atom as compared to the weight of one atom of oxygen, which is taken as 16.00.

Avogadro's law Equal volumes of all gases under the same conditions of tem-

perature and pressure contain the same number of molecules.

Avogadro's number 6.02×10^{23}, the number of molecules in a gram-molecule.

base A proton acceptor; includes metal hydroxides.

basic anhydride Oxide of a metal.

basic salt A salt that contains replaceable hydroxyl or oxygen groups.

beta rays High-speed electrons from a nucleus.

binary compound A compound of two elements only.

binding energy As atoms are formed from their nucleons, a small amount of mass is converted to what is called *binding energy*.

boiling point The temperature at which the vapor pressure of a liquid is equal to the external pressure.

buffer solution A solution containing either a weak acid and its salt or a weak base and its salt. Such solutions are resistant to changes in acidity or basicity.

calorie The quantity of heat necessary to raise the temperature of one gram of water 1° C.

carbohydrate A compound of carbon, hydrogen, and oxygen which is either an alcohol-aldehyde or an alcohol-ketone or which yields either or both on hydrolysis. Usually the proportion of hydrogen to oxygen in the carbohydrate molecule is the same as in water, namely, 2 : 1; for example, glucose, $C_6H_{12}O_6$, and starch, $(C_6H_{10}O_5)_x$.

catalytic agent A substance which alters the speed of a chemical reaction but which itself remains unchanged chemically.

cathode The electrode at which reduction occurs.

cation A positively charged ion which moves toward the cathode during electrolysis.

centigrade temperature The temperature scale on which the freezing point of pure water is 0° and the boiling point is 100° at standard pressure.

ceramics Products manufactured from clay.

colloid A dispersion of particles consisting of aggregates of molecules.

combining volumes, law of When gases combine chemically they do so in the ratio of small whole numbers by volume.

combining weight The weight of an element which will combine with 8 grams of oxygen, or 1.008 grams of hydrogen. Same as equivalent weight.

combining weights, law of To each element may be assigned a number, its combining weight, which in itself or when multiplied by a small whole number expresses the weight of that element that combines with the combining weight of another element.

combustion A chemical change which produces both heat and light.

complex ion An ion formed by the combination of a simple ion with either another ion or a molecule.

compound A homogeneous substance composed of two or more elements, the proportions of which by weight are fixed and invariable.

concentration Weight or volume relationship between solute and solvent.

coordination number The number of ions or molecules associated with the central element of a compound.

coulomb Unit quantity of electricity; one ampere flowing for one second.

covalent molecule One in which the atoms are held together by a sharing of electrons.

cracking of petroleum A process using pressure and heat in which hydrocarbons of large molecular weight are broken down into hydrocarbons of lower molecular weight.

critical pressure Pressure necessary to liquefy a gas at its critical temperature.

critical temperature The temperature above which a gas may not be liquefied irrespective of the pressure.

crystal A solid in which the component parts (molecules, atoms, or ions) are oriented in a definite pattern or geometric configuration.

cupellation A process by which gold and silver are separated from lead.

cyclotron A device for accelerating protons, deuterons, or other charged particles of matter.

decomposition The process of changing a single substance into two or more simpler substances.

definite proportions, law of When elements combine, they do so in a fixed and invariable ratio by weight.

deliquescent substance One capable of absorbing moisture from the atmosphere to form a solution.

density Mass per unit volume.

depolarizer A substance which will remove a layer of insulating gas from an electrode.

deuterium An isotope of hydrogen of mass 2.

deuteron A nucleus of hydrogen of mass two.

dialysis A process for separating a colloid from a true solution.

diffusion Intermingling of molecular or ionic particles, one throughout the other.

dipole A molecule which is electrically unsymmetrical; that is, the centers of positive and negative charge are not located at the same point within the molecule.

distillation Vaporization of a liquid, followed by condensation.

ductility That property that allows a substance to be drawn into a wire.

Du Long and Petit, rule of The product of the atomic weight of a solid element and its specific heat is approximately equal to the constant 6.4.

effervescence Evolution of a gas from solution.

efflorescence The spontaneous loss of water from a hydrate.

effusion The property of a gas to pass through a small orifice.

electrode potential The potential difference in volts between an electrode and a solution of its ions.

electrolysis A process of bringing about a chemical change through the action of a direct electric current.

electrolyte A substance which in solution is a conductor of the electric current.

electron Negative unit charge of electricity of mass $\frac{1}{1837}$ that of hydrogen atom.

electronegative element One which tends to gain electrons.

electroplating A process by which a substance is electrolytically deposited.

electropositive element One which tends to lose electrons.

electrovalent substance A substance composed of ions.

element A substance which has not been resolved into simpler substances by chemical means.

E.M.F. Electromotive force; the electric force between two points of different potential, measured in volts.

emulsifying agent A protective colloid used to stabilize an emulsion of two liquids; for example, the addition of soap to an oil-water emulsion makes the latter more permanent.

emulsion A dispersion of one liquid in another; for example, kerosene in water.

endothermic reaction A chemical change which absorbs heat energy.

enzyme An organic compound produced from yeast cells which may act as a catalyst for certain fermentations.

equilibrium (chemical) An apparent state of rest in which two opposing chemical changes are proceeding with exactly the same speed.

equivalent weight, gram That weight of a substance which contains one gram atom of hydrogen, will combine with one gram atom of hydrogen, or will displace one gram atom of hydrogen; the weight of an element which will combine with eight grams of oxygen. *See* combining weight.

ester An organic compound of the general formula RCOOR′ produced from the interaction of an organic acid with an alcohol.

eutectic The lowest melting alloy of two or more given metals.

evaporation Conversion of a liquid to vapor.

exothermic reaction A chemical change which evolves heat energy.

Fahrenheit temperature The temperature scale on which the freezing point of pure water is 32° and the boiling point is 212° at standard pressure.

faraday Unit quantity of electricity equal to 96,500 coulombs.

Faraday's laws (1) The quantities of substances produced at the electrodes during electrolysis are directly proportional to the quantity of electricity passing through the solution. (2) The weights of substances formed at the electrodes are directly proportional to their equivalent weights.

fat Glyceryl ester of a long hydrocarbon chain organic acid.

filtrate The liquid which passes through the filter.

fission Splitting of an atomic nucleus into two parts of approximately the same size.

fixation of nitrogen A process by which free nitrogen is converted into a useful nitrogen compound.

flux A substance used to combine with impurities during a smelting process to form a slag.

formula The proper combination of symbols showing the composition of a compound substance.

fusion Melting; change of solid to liquid.

fusion, nuclear A combination of two or more nuclei to yield a heavier nucleus; it is accompanied by the release of a very large amount of energy.

gamma rays High frequency electromagnetic X rays given off by radioactive substances.

gangue Worthless rock or mineral matter associated with ores.

gas laws *Boyle's law.* The volume of a fixed mass of a given gas at constant temperature is inversely proportional to the pressure.
Charles' law. The volume of a fixed mass of a given gas at constant pressure is directly proportional to the absolute temperature.
Dalton's law. The total pressure of a gaseous mixture is the sum of the partial pressures of the component gases.
Graham's law. The rate of effusion of a gas is inversely proportional to the square root of its density.

Gay-Lussac's law Gases combine or are formed in the ratio of small whole numbers by volume.

gram-atom The atomic weight of an element expressed in grams.

gram-ion A mass in grams equal to the sum of the atomic weights of the ion.

gram-molecule The molecular weight of a substance expressed in grams; same as mole.

halogen The term means *salt former* and is applied to the salt-forming family, F, Cl, Br, I.

hard water Water that reacts with soap to form a precipitate.

heat A form of energy due to molecular motion.

heat of combustion The number of calories of heat produced by the complete combustion of a mole of a substance.

heat of formation The number of calories of heat absorbed or liberated in the formation of a mole of a compound from its constituent elements.

heat of fusion The number of calories of heat required to melt one gram of solid.

heat of vaporization The number of calories of heat required to vaporize one gram of liquid.

Henry's law The weight of a gas dissolved in a given weight of liquid at constant temperature is directly proportional to the pressure.

homogeneous Uniform; every part like every other part.

homologous series A series of compounds whose composition may be represented by a general formula; for example, methane series of hydrocarbons, C_nH_{2n+2}.

hormone Organic compound produced as a secretion of a ductless gland. In small amounts these compounds play an important role in many biological processes.

humidity, relative The ratio of the pressure of water vapor present in the atmosphere to the vapor pressure of water at the same temperature.

hydrate A compound chemically combined with water; for example, $Na_2SO_4 \cdot 10\ H_2O$.

hydrocarbon A compound containing only carbon and hydrogen.

hydrolysis A double decomposition reaction in which water is one of the reactants.

hygroscopic substance One which takes up moisture.

indicator A substance which changes color at a definite hydrogen ion concentration.

ion An atom or group of atoms possessing an electric charge.

ionic valence *See* electrovalent substance.

ionization potential A measure of the energy required to remove an electron from an atom; measured in volts.

isomers Molecules which have the same number and kinds of atoms but different molecular configurations.

isomorphous compounds Compounds which crystallize in the same geometric configuration.

isotopes Elements of the same atomic number but different mass numbers.

ketone An oxidation product of a secondary alcohol, which has the general formula RCOR'.

kindling temperature The lowest temperature at which a substance will burst into flame.

Le Chatelier's principle If a stress is placed upon a system in equilibrium that change takes place which will tend to minimize the effect of the added stress.

legumes Plants whose roots have nodules containing nitrogen-fixing bacteria.

malleability The property of a substance that allows it to be rolled or hammered into sheets.

mass defect Atomic weight mass minus the mass number.

mass number The sum of the numbers of protons and neutrons in a nucleus; or the total number of nucleons.

matter Anything that has mass and occupies space.

melting point The temperature at which a solid changes to a liquid.

meson A subatomic particle. Several kinds known.

metallurgy The science of extracting metals from their ores.

moderator A substance used in an atomic pile to slow down neutrons.

molal solution A solution containing one mole of solute in 1000 grams of solvent.

molar solution A solution containing one mole of solute in one liter of solution.

mole A mass in grams numerically equal to the molecular weight of a substance.

molecular weight Relative weight of a molecule compared to an atom of oxygen taken as 16.00.

molecule The smallest unit of an element or compound which can exist by itself in the free state.

mordant A substance used to cause a dye to adhere to cloth more firmly.

neutralization The reaction of an acid with a base to produce a salt and water.

neutrino A nuclear particle of zero charge and nearly zero mass.

neutron A fundamental particle of mass one and no charge.

normal salt One that contains no replaceable hydrogen or hydroxyl group.

normal solution A solution which contains one equivalent of solute per liter of solution.

nucleon A component of the nucleus; a proton or neutron.

nucleus of an atom The center of mass of the atom containing protons and neutrons.

nuclide A nucleus of definite mass.

ohm Unit of electrical resistance; the resistance of a column of mercury 106.3 cm. long, weighing 14.4521 grams, and of uniform cross section.

ore A natural material from which useful elements may be extracted commercially.

osmosis The diffusion of a solvent through a semipermeable membrane into a more concentrated solution.

oxidation A process involving the loss of electrons by an atom or group of atoms and the resulting gain in oxidation number.

oxidation number The apparent charge on an atom of an element in a compound which gives the compound a neutral character when oxidation numbers have been assigned to all other elements by a set of arbitrary rules.

oxidizing agent A substance containing an atom or group of atoms that gains electrons and loses in oxidation number.

packing effect The mass loss over and above the summation of atomic particle masses in the formation of atoms.

packing fraction The mass defect divided by the mass number.

periodic law The properties of the elements are periodic functions of their atomic numbers.

Permutit An artificial sodium aluminum silicate used as a water softener.

pH A notation for expressing the hydrogen ion concentration of a solution; in other words, the acidity or basicity of a solution.

photosynthesis A chemical change which utilizes light energy; for example, the production of plant tissue from CO_2 and water in sunlight.

physical change A change which does not involve a change in the chemical composition of a substance.

positive ray Positively charged particle moving away from the cathode in a cathode ray tube.

positron A subatomic particle of the same mass as the electron but of opposite charge; a positive electron.

precipitate An insoluble solid which separates from solution.

properties Qualities or characteristics by which a substance may be identified.

protein A complex organic compound composed primarily of the elements carbon, hydrogen, oxygen, and nitrogen.

proton A subatomic particle of mass one carrying a positive charge; a hydrogen ion.

quantum numbers Numbers which describe the position, shape, and energy of orbital electrons.

radical A group of atoms which function as a unit in chemical change.

radioactivity Spontaneous disintegration of atoms resulting in the emission of alpha particles, electrons, and gamma rays from the nucleus.

Raoult's law The lowering of the vapor pressure of a solvent by a nonvolatile solute is proportional to the concentration of the solute in the solution.

reaction A chemical change.

reducing agent A substance which loses one or more electrons in a chemical change and gains in oxidation number.

reduction A process involving a gain of electrons and loss in oxidation number.

roasting The heating of a sulfide ore in contact with air.

salt A substance that gives cations other than, or in addition to, hydrogen ions; and anions other than, or in addition to, hydroxide ions.

saponification The reaction of an ester with a base to form an alcohol and a salt.

saturated solution One which is in equilibrium with the undissolved solute.

slag A by-product of smelting produced by combination of flux and impurities in the ore.

sol Colloidal dispersion of a solid in a liquid.

solute Dissolved substance.

solution A homogeneous mixture of two or more substances, the relative proportions of which may be varied within certain limits.

solvent The dissolving medium or the constituent of a solution present in the larger amount.

specific gravity The ratio of the weight of a given volume of a substance (solid or liquid) to the weight of an equal volume of water.

specific heat The quantity of heat in calories necessary to raise the temperature of one gram of a substance one degree centigrade.

standard conditions 0° C. and one atmosphere (760 mm.) pressure.

standard solution A solution the composition of which is accurately known.

sublimation Change of solid to vapor or vice versa without appearance of liquid.

substance Any homogeneous matter.

supersaturated solution One which contains more solute in solution than a saturated solution would contain at the same temperature and pressure.

surface tension The force exerted on the molecules in the surface of a liquid by adjoining molecules.

synthesis The preparation of compounds.

temperature A measure of heat intensity.

ternary compound One containing three elements.

theory A plan or scheme of explaining a set of related facts by means of a set of assumptions; a hypothesis which has been subjected to experimental proof.

thermite A mixture of iron oxide and aluminum powders used for welding.

transmutation Conversion of one element to another.

tritium An isotope of hydrogen of mass 3.

Tyndall effect A luminous cone of light produced as a result of the scattering of light by particles in suspension.

valence A number which represents the combining capacity of an atom or radical referred to hydrogen as a standard.

vapor pressure The partial pressure exerted by a vapor in equilibrium with a liquid or solid.

viscosity Resistance to flow; opposite of fluidity.

vitamin A chemical compound which in small amounts appears to be necessary in the diet of man and animals.

volatile Easily vaporizable; relatively low boiling point.

volt The potential necessary to drive a current of one ampere through a resistance of one ohm.

watt A unit of electrical power; a volt ampere.

X rays High frequency light waves of short wave length.

zeolite A mineral containing sodium aluminum silicate which is used as a water softener.

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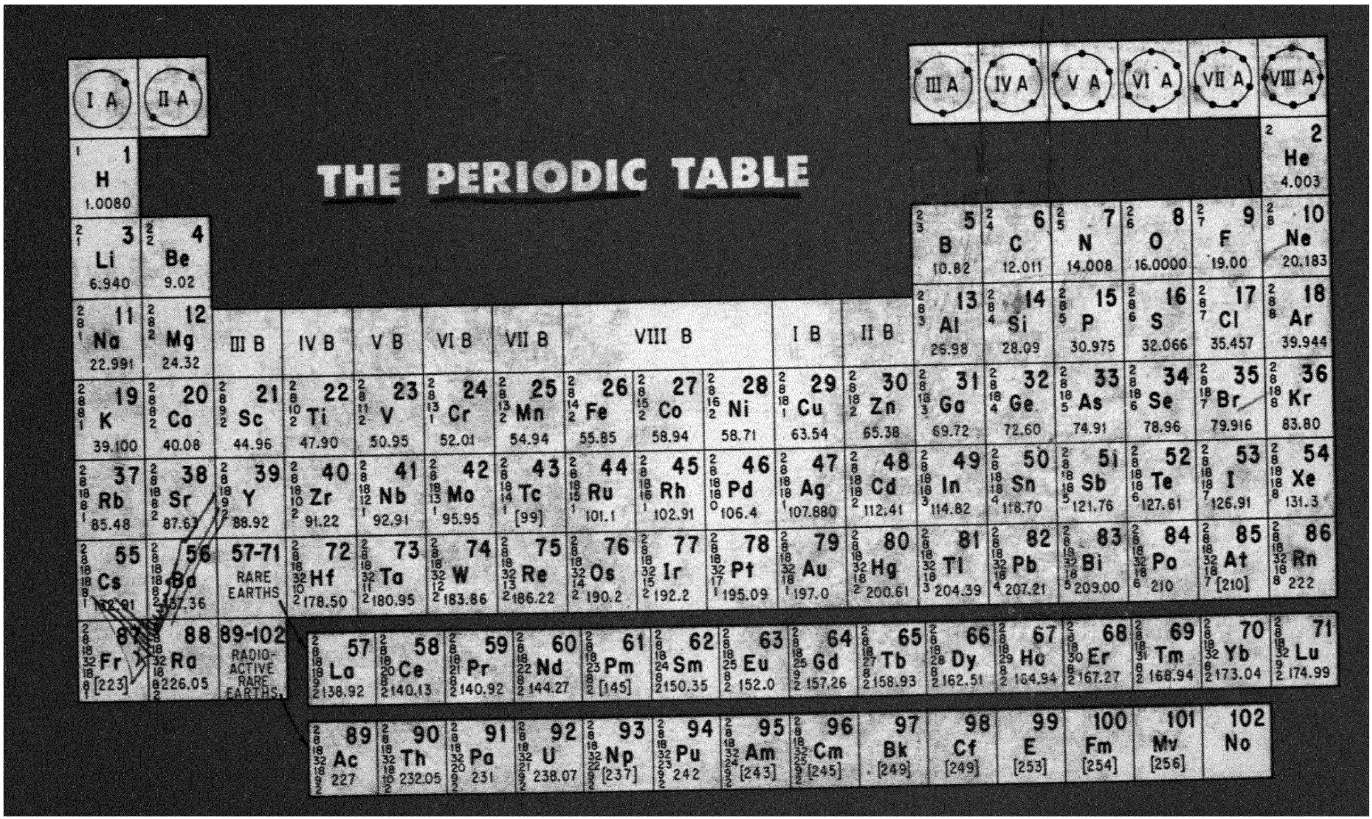
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I B
II B
1 H 1.0080
2 He 4.003
3 Li 6.940
4 Be 9.02
5 B 10.82
6 C 12.011
7 N 14.008
8 O 16.0000
9 F 19.00
10 Ne 20.183
11 Na 22.991
12 Mg 24.32
13 Al 26.98
14 Si 28.09
15 P 30.975
16 S 32.066
17 Cl 35.457
18 Ar 39.944
19 K 39.100
20 Ca 40.08
21 Sc 44.96
22 Ti 47.90
23 V 50.95
24 Cr 52.01
25 Mn 54.94
26 Fe 55.85
27 Co 58.94
28 Ni 58.71
29 Cu 63.54
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 83.80
37 Rb 85.48
38 Sr 87.63
39 Y 88.92
40 Zr 91.22
41 Nb 92.91
42 Mo 95.95
43 Tc [99]
44 Ru 101.1
45 Rh 102.91
46 Pd 106.4
47 Ag 107.880
48 Cd 112.41
49 In 114.82
50 Sn 118.70
51 Sb 121.76
52 Te 127.61
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74 W 183.86
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